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Hierarchically designed PEDOT encapsulated graphene-MnO₂ nanocomposite as supercapacitors

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A B S T R A C T
A hierarchically designed ternary nanocomposite of PEDOT:Grp-MnO₂ was synthesized as an electrode material for high performance supercapacitors. The binary composite of MnO₂ nanoparticles decorated over graphene sheets (Grp-MnO₂) were synthesized using a facile, one pot solvothermal method. Further, encapsulation of the binary composite was performed by wrapping with the conductive polymer layers of PEDOT. Structural morphology and oxidation states of Mangnese of the nanocomposite were studied using XRD, TEM, Raman spectroscopy and XPS. Supercapacitve behaviour of the nanocomposites was tested by using them as electrodes for electrochemical studies like cyclic voltammetry and charge-discharge. Highest specific capacitance value was found to be 213 Fg⁻¹ for the PEDOT:Grp-MnO₂ (with the ratio of 1:3) with improved energy and power densities. AC impedance measurement was carried out to ascertain the pseudocapacitance arising from the redox reactions over the electrical double layer capacitance (EDLC) in the composite materials.

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1. Introduction
Owing to the changing global scenario towards energy consumption, energy storage has become a primary focus in the world of scientific community. Therefore, the development of sustainable and renewable energy sources is urgently required [1,2]. For all portable electronics, batteries have been the principal choice for energy storage as they can store large amounts of energy in a lightweight and compact structure. However, Electrochemical Capacitors (ECs), also known as supercapacitors, emerged as a complementary energy and power source in the electronics market because of its high power density, fast charge-discharge rates, superior cycle lifetime, safe operation and a simple two-electrode ‘sandwich’ configuration and high reliability [3–7].

In a supercapacitor, an electrode with appreciable conductivity and a large surface area, accessible to the electrolytic dopant ions, holds the key to its high performance [8–11]. So far, carbon or carbon-based materials such as activated carbon, carbon aerogels, and carbon nanotubes (CNTs) have been extensively investigated as electrode materials for supercapacitors [12,13]. Since 2004, graphene has also immersed as potential carboneous material for supercapacitors, due to its large surface area, desirable electrical and thermal conductivities, high mechanical stiffness and low manufacturing cost [14,15]. Graphene has attracted considerable attention from the physicists and chemists worldwide not only as energy storage and conversion materials [16,17] but as electro-mechanical resonators [18], ultrastatic electronic and electromagnetic devices [19–22], in bioelectronics, drug delivery [23,24] and sensing [25–27].

The next generation ECs have evolved utilizing transition metal oxides (mainly RuO₂, Fe₂O₃, NiO, and MnO₂) as the electrode material for high performance supercapacitors. Due to high energy density, large charge transfer-reaction and pseudocapacitance, they can deliver both desirable power and energy densities. However, intense interest in MnO₂ for battery and supercapacitor has been driven by its high theoretical pseudocapacitance value (1370 Fg⁻¹), low cost, natural abundance and environmental benignity, unlike other metal oxides such as NiO, RuO₂ and Co₃O₄. At high mass loading, agglomeration and poor conductivity of MnO₂ (10⁻⁵–10⁻⁶ S cm⁻¹) [28–31] often results in limited performance and thus, hindered its wide applications. In order to overcome these limitations, hybrid nanocomposites of MnO₂ incorporated with conducting polymers (like Polyaniline, Polypyrrole, PEDOT) or carboneous materials (like CNTs, graphene)
were extensively studied, such as CNTs/MnO₂ [32–34], graphene/MnO₂ [35,36], MnO₂/Ppy [37], MnO₂/PEDOT-PSS [38] and many more [39–47].

The hybrid nanostructures not only benefit from the high conductivity of the carboneous materials or conducting polymers and the high specific capacitance of MnO₂, but from the synergistic effect between them. In order to utilize synergetic effect more effectively, the structure of a hybrid material should be coherently designed with the mass ratios of its components wisely chosen. Thus, the designing and fabrication of ternary hybrid electrode materials has emerged as an effective strategy to promote MnO₂ based high performance supercapacitors in recent research [29,45–47].

MnO₂ exhibits a very rich chemistry and can be synthesized in various crystalline and disordered shapes and sizes, with each of them exhibiting its characteristic physical and electrochemical properties [17,30,48]. Utilizing this fact about MnO₂ nanoparticle chemistry, Yan et al. [49] demonstrated a synthetic route for a ternary composite – MnO₂ nanosheet array/reduced graphene oxide/PEDOT:PSS, where K-biennisite MnO₂ nanosheet arrays were grown in between graphene sheets, followed by its coating with PEDOT:PSS. Electrochemical studies provided a specific capacitance of 169.1 F g⁻¹ at a current density of 0.2 A g⁻¹ for MnO₂-rGO/PEDOT-PSS composite material. Similarly, in another work demonstrated by Yu et al. [29], conductive wrapping of graphene/MnO₂ (GM) was performed to introduce an additional electron transport path. 3D conductive wrapping of graphene/MnO₂ nanostructures with CNFs or conducting polymers led to substantial increment in the specific capacitance with values as high as ~380 F g⁻¹.

In the present work, we have utilized a new synthetic approach for the preparation of PEDOT wrapped graphene-MnO₂ ternary nanocomposite, in order to achieve enhancing the device performance of metal oxide-based electrochemical supercapacitors. So far, MnO₂ nanoparticles were synthesized ex situ followed by formation of composite with graphene sheets or PEDOT matrix for the synthesis of nanocomposites. In the present work, we have employed a solvothermal reaction between GO and MnO₂ microspheres to obtain a binary nanocomposite of Graphene-MnO₂ where innumerable MnO₂ nanoparticles generate in-situ and decorate over graphene sheets firmly due to the spiked-shaped MnO₂ microspheres having better anchoring properties. Subsequently, this binary composite was hierarchically upgraded to a ternary composite – Grp-MnO₂/PEDOT, by wrapping it with conductive layers of PEDOT where PEDOT being a conducting polymer offers a right balance of conductivity and charge storage. This offers better specific capacitance value and appreciable power and energy densities for composite in a broadened potential window of −0.6 to +0.6 V. This 3D wrapping approach offers a promising design and direction for optimizing the electrochemical properties of hybrid electrode materials for their encouraging applications in the energy storage devices.

2. Experimental

2.1. Materials

3,4-Ethylendioxythiophene (EDOT) monomer and Graphite flakes were obtained from Sigma Aldrich. Poly-tetrafluoroethylene (PTFE) was obtained from Aldrich whereas acetylene black was obtained from Alpha Aesar. Hydrazine, KMnO₄, AgNO₃, Na₂H₂PO₄, (NH₄)₂S₂O₈ were the product of Merck.

2.2. Hierarchical synthesis of nanocomposites

2.2.1. Synthesis of Ag-nanoparticles and Ag-assisted MnO₂ microspheres

0.05 M, 40 ml NaH₂PO₄ solution was prepared in deionized water and was added to 0.5 M, 10 ml AgNO₃ solution slowly, under vigorous stirring. NaH₂PO₄ was used as a reducing agent to reduce AgNO₃ to Ag nanoparticles. The mixture was ultrasonicated in a thermostatic water bath at 50°C for an hour, before washing and collecting the yellow precipitates.

MnO₂ microspheres were synthesized by mixing a 0.1 M, 20 ml MnSO₄·H₂O solution with 0.1 M, 20 ml (NH₄)₂S₂O₈ solution. APS will oxidise MnSO₄ to MnO₂. To this added, 8 mg of dry Ag nanoparticles synthesized previously, making its concentration around 1 mM in the resultant reaction mixture. The reaction mixture was ultrasonicated in a thermostatic water bath at 50°C for an hour. The resultant brown precipitates were carefully centrifuged, repeatedly washed with water and dried at 50°C in vacuum oven.

2.2.2. Synthesis of Graphene-MnO₂ binary composite

First, graphene oxide (GO) was synthesized using improved Hummers’ method [50]. Graphite powder was treated with KMnO₄ in the presence of H₂SO₄–H₂PO₄ acid mixture under vigorous stirring for 12 h. Once the reaction is complete, the resultant mixture was cooled to room temperature and treated with cold 30% H₂O₂ solution to nullify excess KMnO₄. GO suspension was carefully washed, collected and dried to obtain GO powder.

Different Graphene-MnO₂ nanocomposites were synthesized using the solvothermal technique. To prepare 1:1 composite of graphene and MnO₂, 200 mg of GO was taken in 80 ml ethylene glycol and dissolved well under ultrasonication. 100 mg of MnO₂ microspheres were added to the GO dispersion and again kept under sonication for an hour. After the addition of 0.02 M hydrazine solution (reducing agent) to the reaction mixture, the dark brown solution was transferred to Teflon lined steel autoclave for the solvothermal reaction at 180°C for 12 h. Once the reaction was complete, the black precipitate of graphene-MnO₂ (Grp-MnO₂) was filtered and washed repeatedly with distilled water followed by drying at 60°C.

2.2.3. Synthesis of PEDOT coated Grp-MnO₂ ternary composite

Grp-MnO₂ sheets were coated with the conducting polymer film, by dispersing the monomer in an alcoholic medium. MnO₂ embedded graphene sheets (100 mg) were first dispersed in 10 ml deionized water mixed with 2 ml ethanol and ultrasonicated for an hour. For a 1:1 composite, 100 μl of EDOT monomer dissolved in deionized water with concentrated H₂SO₄ (2 ml) was added to the above solution. The reaction mixture was again sonicated for an hour. To the reaction mixture, 15 ml (0.1 M) of APS was added as an oxidant at 10°C. The reaction mixture was stirred overnight at room temperature. The resulting precipitates (PEDOT:Grp-MnO₂) were centrifuged, washed thoroughly with water and dried at 60°C in vacuum oven.

2.3. Characterization

Morphological and physical characterizations of MnO₂ microspheres and its nanocomposites were carried out using transmission electron microscope (FEI model Tecnai G2 20S with 200-kV accelerating voltage and resolution of 0.2 nm), powdered X-ray diffractometer (Philips PW 1710) with Cu Kα (λ = 1.5406 Å) radiation and Raman spectrometer (Lab Ram HR 800 (Horiba Jobin Yvon spectrometer) with the laser power of 17 mW at the operating wavelength of 632.8 nm. XPS core-level spectra were taken with an Omicron Multiprobe spectrometer (Omicron
NanoTechnology GmbH) fitted with an EA125 hemispherical analyzer. A monochromated Al Kα X-ray source operated at 150 W was used for XPS. The analyzer pass energy was kept fixed at 40 eV for all the scans.

2.4. Electrochemical measurements

In the electrochemical studies, electrodes were prepared using following procedure: ~85 wt% electroactive materials (i.e. pure MnO2 microspheres, Grp-MnO2 and PEDOT:Grp-MnO2 composites) were mixed with ~10 wt% acetylene black (AB) and ~5 wt% polytetrafluoroethylene (PTFE) to form a thick uniform pest. This pest was then compressed on a stainless steel mesh having the surface area around 1 cm². The prepared electrode meshes were dried for 6 h at 60 °C under vacuum. The total weight of the active material in the electrode is usually ~ 8 mg.

Electrochemical measurements of the samples were performed using cyclic voltammetry (CV) (AUTOLAB-30 potentiostat/galvanostat). A platinum electrode and a saturated Ag/AgCl electrode acted as counter and reference electrodes respectively in a three-electrode electrochemical cell. All CVs measurements were performed between −0.6 and 0.6 V making an operating window of 1.2 V at different scan rates. Two-electrode system, having identical electrodes of same electroactive material, was used for galvanostatic charge-discharge cycling and electrochemical impedance studies. Constant current density 1 mA cm⁻² has been employed for charging/discharging the cell in the voltage range −0.6 to 0.6 V. The discharge capacitance (C) is estimated from the slope of the linear portion of the discharge curve using the expression.

\[ C = I(dv/dt) \]  

\[ C_a = 2C/m \]

where, \( m \) is the active mass of the single electrode and \( C_a \) represents specific capacitance of the electrode. As an important parameter, power density \( (P_a) \) and energy density \( (E_d) \) have been usually used to characterize the electrochemical performance of electrochemical capacitors. To demonstrate the operational characteristics, the energy density \( (E_d) \) of the capacitor can be expressed as:

\[ E_d = 1/2 C_i V^2 \]

Hence the power density \( (P_a) \) was calculated as:

\[ P_a = E_d/t \]

where, \( t \) indicates the discharge time (s). The coulomb efficiency \( (\eta) \) was evaluated using the following relation, where \( t_c \) and \( t_d \) are the time of charge and discharge respectively:

\[ \eta = (t_d/t_c) \times 100\% \]

Electrochemical impedance spectra (EIS) were taken out at open circuit potential over the frequency range 10 kHz to 10 mHz with a potential amplitude of 5 mV. All the electrochemical experiments (i.e. CV, charge–discharge, EIS) were performed in an electrolyte containing 1 M LiClO4 in acetonitrile.

3. Results & discussions

Silver nanoparticles-assisted MnO2 microspheres were grown from MnSO4, using Ammonium peroxodisulphate (APS) as oxidant.
under sonication. TEM images (Fig. 1) indicate that MnO₂ microspheres are in agglomeration form of nanocrystals, as reported by Meng et al. [51]. Ag-nanoparticles assisted in the minute growth of MnO₂ nanowires around the large crystallite, making it look like a spiked-shaped MnO₂ spheres.

The first step of our hierarchical approach is the in-situ generation and distribution of MnO₂ nanoparticles on the graphene sheets. With a presumption that these spiked-MnO₂ microspheres would adhere to the surface of the graphene oxide sheets better than any other shape or structure, graphene oxide (GO) solution was mixed with a relevant amount of MnO₂ microspheres. Once the oxide gets anchored on the GO sheets, the GO-MnO₂ solution was transferred to the Stainless Steel coated Teflon autoclave and allowed to stand at 180 °C for 12 h in the presence of hydrazine (0.02 M), converting it to the Graphene-MnO₂ composite solvothermally. In the second step of this hierarchical route, a 3D conductive wrapping of polymer PEDOT was performed over the binary nanocomposite – Grp-MnO₂ in order to enhance the interconnectivity and electrochemical activity, (as shown in Scheme 1). Requisite amounts of binary composite was dispersed in an alcoholic solution of EDOT monomer and stirred overnight for its polymerisation in the presence of APS as the oxidant. Polymer layers of PEDOT encapsulate the graphene-MnO₂ surface, forming a 3D structure. These binary and ternary nanocomposites were further characterized to understand their physical and electrochemical behaviour.

3.1. Transmission electron microscopy

The spiked-MnO₂ microspheres were synthesized and characterized under transmission electron microscope to establish their shape and structure (Fig. 1a). When MnO₂ microspheres were incorporated with graphene sheets and exposed to high pressure and temperature in an autoclave, the microspheres burst open releasing hundreds of spiked-MnO₂ nanoparticles spreading over the graphene sheets, very clearly seen in the TEM images (Fig. 1b). Further, the TEM image of the ternary composite showed the 3D-conductive layer of PEDOT polymer encapsulating the binary Grp-MnO₂ sheets (Fig. 1c).

3.2. X-ray diffraction studies

The X-ray diffraction studies were carried out for the three samples: graphene sheets, MnO₂ nanoparticles embedded graphene sheets (Grp-MnO₂) and PEDOT coated Grp-MnO₂ composite as shown in Fig. 2.

The XRD plot for graphene sheets shows a broad hump between the 2θ values of 24–26°, representing the typical characteristic of chemically synthesized few-layered graphene [52]. In the XRD plot of Grp-MnO₂, the 2θ value of 25.16° shows the broad peak for graphene and along with that, it shows some characteristic peaks representing crystalline MnO₂ nanoparticles. The 2θ values at 24.26°, 31.36°, 37.52° and 41.42° represent the 200, 310, 211 and 301 planes of the MnO₂ crystal lattice. After the 3D conductive wrapping of PEDOT, the XRD plot of the ternary composite shows the dominance of the amorphous nature. PEDOT as well as graphene shows an overlapping broad hump at 2θ value of 25.46°. The latter part of XRD plot depicts few peaks for MnO₂ as found in the binary composite [53].

3.3. Raman studies

Raman spectroscopic studies were carried out in order to establish the characteristics of graphitic nature at each step of nanocomposite formation. The Raman spectra (Fig. 3) for all the three samples: graphene, Grp-MnO₂ and PEDOT:Grp-MnO₂ nanocomposite showed D and G peaks at 1340 cm⁻¹ and 1590 cm⁻¹ respectively, significant for the pristine graphitic nature.
The spectra do not show any major changes either in the peak positions or in their intensities for all the samples. This exhibits that graphene has not lost its graphitic characteristics at any step of the synthesis, even after incorporation of MnO₂ nanoparticles and PEDOT polymer within the graphene sheets.

3.4. XPS studies

In order to assess the exact valence states of the manganese in the nanocomposite samples which is required to determine their contribution towards the pseudo-capacitance, X-ray photoelectron spectroscopic studies were carried out with Grp-MnO₂ and PEDOT:Grp-MnO₂ (1:3) nanocomposites. The characteristic spectrum of Mn₂p₃/₂ for Mn⁴⁺ in both the nanocomposites are compared in Fig. 4. The de-convolution of the original spectrum shows the presence of two different chemical environments in both the composite materials. The lower energy peak at 640.9 eV for Grp-MnO₂ sample and 640.5 eV for PEDOT:Grp-MnO₂ sample corresponds to Manganese in 2⁺ valence state, whereas the higher energy peak at 642.5 eV for Grp-MnO₂ sample and 641.9 eV for PEDOT:Grp-MnO₂ sample corresponds to Manganese in 4⁺ valence state. The ratio of the Mn⁴⁺/Mn²⁺ in manganese oxides of the composite materials was estimated from the area under the curves which are 0.70 and 1.77 for Grp-MnO₂ and Grp-MnO₂–PEDOT respectively, which revealed the presence of Mn⁴⁺ in Grp–MnO₂ and Grp–MnO₂–PEDOT with a percentage of 41% and 64% compared to 100% in pure MnO₂ nanoparticles.

During the synthesis of binary nanocomposites, some part of manganese were reduced from 4⁺ state to 2⁺ state due to the presence of hydrazine used for the conversion of GO to RGO as evident from the XPS data. APS was used for the oxidative polymerisation of PEDOT from EDOT monomer as oxidant for the synthesis of ternary nanocomposites. During this polymerization, APS also leads to partial oxidation of manganese from 2⁺ state to 4⁺ state, resulting increase in the content of Mn⁴⁺ in the nanocomposite.

Hence, this difference in percentage ratio of Mn⁴⁺/Mn²⁺ in two composite samples can be attributed to the difference in the chemical environments (hydrazine in the binary and APS in the ternary step) present during the synthesis. Contribution towards pseudo-capacitance of the two samples would differ accordingly, on the basis of the Mn⁴⁺/Mn²⁺ ratios in the nanocomposite. As Belanger et al. suggested that Mn⁴⁺ is the most active component responsible for the pseudo-capacitive nature of MnO₂ as it exhibits Mn⁴⁺/Mn²⁺ redox behaviour [30]. XPS studies also showed (Fig. 4) that the higher concentration of Mn⁴⁺ component in the ternary nanocomposite as compared to the binary nanocomposite is responsible for higher specific capacitance value of the former. PEDOT:Grp-MnO₂ (1:3) composition was used as a typical sample for ternary nanocomposite for XPS analysis.

3.5. Electrochemical studies

3.5.1. Cyclic voltammetric studies

Typical cyclic voltammograms (CV) of all the samples, at a scan rate of 20 mVs⁻¹ over the voltage range +0.6 to –0.6 V in acetonitrile containing 1 M LiClO₄ electrolyte, are shown in Fig. 5. LiClO₄ has been used as the electrolyte, because Li⁺ ions, being the smallest ion, offers better ion movement through the non aqueous solvents. Cyclic voltammograms for all the samples are nearly semi-rectangular in shape with oblique angle, which indicates the good capacitative behaviour of the electrodes suitable for charging and discharging at a constant rate.

The current density of the CV curves for the PEDOT:Grp-MnO₂ ternary nanocomposite electrode shows larger values compared to those of the pure MnO₂ or Grp-MnO₂ binary electrode, indicating higher specific capacitance resulting from the synergistic contribution of electrochemical double-layer capacitance of graphene-PEDOT and the pseudo-capacitance of MnO₂. Moreover, the CV curves of the electrodes exhibit nearly a mirror image of current response for the oxidation-reduction half cycles indicating an excellent reversibility.

Different compositions for PEDOT:Grp-MnO₂ composites were studied to observe the effect of conductive wrapping density over the binary nanocomposite. The CV curve corresponding to the
loading of 30% PEDOT as PEDOT:Grp-MnO$_2$ (1:3) shows better capacitance than that of other two. This implies that an optimal amount of PEDOT layer wrapping over the graphene sheet is essential for getting the better performance of the electrode.

Since the scan rate makes a direct impact on the diffusion of Li$^+$ into the electrodes, the cyclic voltammograms of PEDOT:Grp-MnO$_2$ composite (1:3) was studied well at different scan rates of 5, 10 and 20 mVs$^{-1}$, as shown in Fig. 6. At high scan rate, the Li$^+$ ions will mainly approach the outer surface of the electrode while at low scan rate the cations can approach the deep pores of the electrodes and has more contribution towards total capacitance value.

3.5.2. Galvanostatic charge–discharge studies

Fig. 7 represents the galvanostatic charge–discharge curves of MnO$_2$, Grp-MnO$_2$ and PEDOT:Grp-MnO$_2$ nanocomposites. Specific capacitances of different electrode materials were compared at a constant current density of 1 mACm$^{-2}$. The specific capacitance of the electrode materials can be calculated from galvanostatic charge–discharge curve using the Eqs. (1) and (2). The galvanostatic charge–discharge curves of MnO$_2$ microspheres show the specific capacitance of 71.4 Fg$^{-1}$ at a current density of 1 mACm$^{-2}$. But after the fragmentation of the MnO$_2$ microspheres into nanoparticles, the specific capacitance for Grp-MnO$_2$ composite showed a significant increase with the value of 135 Fg$^{-1}$ due to better surface area exposure of MnO$_2$ nanoparticles over the vast graphene sheets. It can be seen that the charge–discharge profiles are quasi-symmetric and curved lines which enumerate the pseudo–capacitive behaviour of the material. The value of specific capacitance obtained by charge–discharge and CV technique were found to be comparable.

After the wrapping of conductive PEDOT layer over the Grp-MnO$_2$ nanocomposite, PEDOT polymer offered a synergistic effect through better inter-connectivity within MnO$_2$ nanoparticles and graphene, resulting in a significant increase in the value of capacitance of the electrode. In order to understand the effect of optimum coating of polymer layer required over Grp-MnO$_2$ composite, the specific capacitance value of three different compositions are measured for the PEDOT:Grp-MnO$_2$ nanocomposite, based on the composition ratio of PEDOT: (Grp-MnO$_2$) as 3:1, 1:1 and 1:3. The respective values are found to be 145 Fg$^{-1}$, 151.5 Fg$^{-1}$ and 213 Fg$^{-1}$. This suggests that 1:3 composition ratios in the ternary composite, i.e with 30% PEDOT loading over MnO$_2$ embedded graphene sheets, is found to be the optimum loading for best supercapacitor performance.

The energy density ($E_d$) and the power density ($P_d$) of the capacitor are also calculated for all the electrode materials using the relations in the Eqs. (3) and (4) respectively. The energy density of pure MnO$_2$, Grp-MnO$_2$ and PEDOT:Grp-MnO$_2$ (1:3) are 14.3 Whkg$^{-1}$, 27 Whkg$^{-1}$ and 45.6 Whkg$^{-1}$ respectively. The power densities further calculated for the three samples was found to be 115 Wkg$^{-1}$, 135.2 Wkg$^{-1}$ and 159.7 Wkg$^{-1}$ respectively.

3.5.3. Electrochemical impedance analysis

One of the principal methods examining the fundamental behaviour of electrode materials for supercapacitor is electrochemical impedance study. Nyquist impedance spectra of pure MnO$_2$ microspheres along with all the composites over a frequency range of 10 kHz–10 mHz with a potential amplitude of 5 mV are shown in Fig. 9. The total impedance of the supercapacitor comprises of electronic and ionic contributions. The electronic contribution comes from the intrinsic electronic resistance of the particles and the interfacial resistance between electrode and current collector. The ionic contribution comes from the ionic (diffusion) resistance of ions moving in small pores.

The typical EIS plot is composed of a semi-circle at high frequencies, which is related to Faradaic reactions and the linear
Fig. 8. Schematic representation of Randles equivalent circuit.

Fig. 9. Nyquist plots for the MnO₂, Grp-MnO₂ and PEDOT:Grp-MnO₂ over a frequency range of 10 kHz–10mHz with a potential amplitude of 5 mV.

Fig. 10. Cyclic stability of PEDOT:Grp-MnO₂ vs. Grp-MnO₂ for 1000 cycles.

curve at the low frequency region that can be attributed to the diffusion controlled process in the electrolyte. The high-frequency intercept of the semi-circle on the real axis represents the solution (electrolyte) resistance (Rₛ), and the diameter of the semi-circle (Z') represents the charge-transfer resistance (Rᶜ) over the interface between the electrode and electrolyte. Electrochemical impedance spectra were analyzed using semi-quantitative fittings programme supplied (AUTOLAB-30) based on the Randles equivalent circuit modelling shown in Fig. 8.

Where, the internal resistance Rₛ is in series with the electrical double layer capacitance (Cₛ) at the interface of electrode and electrolyte Cₛ is in parallel with the charge transfer resistance (Rᶜ) and Warburg impedance (W₂). The Warburg impedance is a result of the frequency dependence of ion transport in the electrolyte. The above set is in series with pseudo-capacitance (Cₚ), which is used to account for the faradaic reaction.

The smaller Warburg region for the PEDOT:Grp-MnO₂ (1:3) than that of MnO₂ or Grp-MnO₂ (in Fig. 9) clearly indicates less obstruction of the ion movement and a lower ion diffusion resistance, thus implies a better charge propagation and ion response of the composite. Also, the semicircle in the high frequency range is minimum for the PEDOT:Grp-MnO₂ (1:3) composite, which corresponds to a smaller charge transfer resistance (Rᶜ) caused by the Faradic reactions and the double-layer capacitance (Cₛ) on the electrode surface.

In brief, the MnO₂ nanoparticles embedded graphene sheets, constructed a moderate network for ions and electrons flow, where PEDOT:Grp-MnO₂ composites (especially with the composition ratio of 1:3) constructed a highly conductive 3D current collector and provided an open architecture for fast transportation of ions and electrons throughout the whole electrode matrix.

To understand the cyclic stability of the electrode material for its commercial use, the discharge capacitances were recorded at a current density of 1 mAcm⁻² for 1000 cycles. PEDOT:Grp-MnO₂ (1:3) nanocomposite showed a slight decrease in its specific capacitance value (~11%) over 1000 cycles compared to first cycle (Fig. 10).

For the better understanding of the work, Table 1 summarizes the values obtained for the specific capacitance, energy and power densities calculated for various compositions (% loadings for MnO₂ PEDOT and graphene) in the samples.

Hence, the obtained results suggest that the ternary composite would serve as a better electrode material for symmetric supercapacitor cell, in a wide operating voltage window of 1.2 V, as compare to binary Grp-MnO₂ or MnO₂ nanoparticles.

### 4. Conclusions

A hierarchically designed ternary nanocomposite – PEDOT:Grp-MnO₂ was synthesized in order to harness their synergistic properties and enhance the electrochemical behaviour. To understand the optimum loading of conducting polymer over MnO₂ embedded graphene sheets, three different compositions for PEDOT:Grp-MnO₂ (3:1, 1:1 and 1:3) were synthesized. The samples were characterized using XRD, TEM and Raman spectra, to establish their morphology and chemical environment. Cyclic voltammetric plots were nearly semi-rectangular in shape with oblique angle, depicting the good capacitative behaviour of the electrodes suitable for charging and discharging at a constant rate.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>% MnO₂</th>
<th>% Graphene</th>
<th>% PEDOT</th>
<th>Sp. Cap. (F/g)</th>
<th>Eₑ (Wh kg⁻¹)</th>
<th>Pₑ (W kg⁻¹)</th>
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<td>80</td>
<td>–</td>
<td>135</td>
<td>27</td>
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<td>70</td>
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<td>50</td>
<td>151.5</td>
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over the wider voltage window of 1.2 V.Comparative XPS studies for the Grp-MnO$_2$ and PEDOT-Grp-MnO$_2$ (1:3) sample suggested the possible mechanism for the improvement in the supercapacitive behaviour of the ternary nanocomposite. The ratio of the Mn$^{4+}$/Mn$^{2+}$ in manganese dioxide of the composite materials, estimated from the area under the curves, were found to be 0.70 and 1.77 for Grp-MnO$_2$ and PEDOT-Grp-MnO$_2$ (1:3) respectively. Charge-discharge as well as AC impedance studies performed in 1 M LiClO$_4$ electrolyte at a constant current density of 1 mA cm$^{-2}$ suggested that PEDOT:Grp-MnO$_2$ (1:3) ternary nanocomposite was the best suitable electrode material for supercapacitor having the highest value of (213 F g$^{-1}$) as compared to MnO$_2$ microspheres (71.4 F g$^{-1}$) and Grp-MnO$_2$ (135 F g$^{-1}$). Furthermore, the energy and power densities were calculated to be 45.6 Wh kg$^{-1}$ and 159.7 W kg$^{-1}$ respectively, for the best ternary nanocomposite. Also, the cyclic reversibility and stability of the ternary composite showed a very small attenuation over 1000 cycles in the widened operation window of 1.2 V, hence making the ternary composite – PEDOT:Grp-MnO$_2$ (1:3) – a promising, safe and cost-effective electrode material in the future development of supercapacitor applications.

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References

Non-enzymatic electrochemical detection of cholesterol using β-cyclodextrin functionalized graphene

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A B S T R A C T

A non-enzymatic approach towards cholesterol detection is presented here, exploiting the electrochemical non-enzymatic route of sensing which has a distinct advantage over other conventional enzymatic processes. Chemically converted Graphene modified with β-CD, being hydrophilic, electro-active and high surface area material, provides a platform for the electrochemical detection of cholesterol using Methylene Blue as redox indicator. Methylene Blue (MB) forms an inclusion complex with Grp-β-CD and emerges as a cholesterol sensing matrix. MB molecule is replaced by cholesterol molecule and moves out in the buffer solution, hence, detected electrochemically using Differential Pulse Voltammetric (DPV) technique. The sensing matrix is characterised using FT-IR and Raman spectroscopy. Transmission Electron Microscopy is carried out to study the morphology of functionalized graphene sheets.

1. Introduction

Graphene has become the most exciting nano-structured carbon allotrope over the last few years, gaining its popularity in various fields of material research including energy storage and conversion (Pumera, 2009), electromechanical resonators (Bunch et al., 2007), ultrafast electronic devices (Novoselov et al., 2004) etc. Applications of graphene have recently been extended even to biological research viz., in bioelectronics (Choi et al., 2013), drug delivery (Stoller et al., 2008; Liu et al., 2008; Ang et al., 2008), molecular resolution sensors (Schedin et al., 2007; Novoselov et al., 2006; Zhang et al., 2005) because of its large specific surface area, extraordinary electrical and thermal conductivities (Novoselov et al., 2004; Kanghyun et al., 2008), high mechanical stiffness (Lee et al., 2008), good biocompatibility (Chen et al., 2008), and lower manufacturing cost (Segal, 2009). As the high electrical and thermal conductivities of graphene originate from the extended long-range α-conjugation, it helps in enhancing its usage in electrochemical approach for biosensors (Zhu et al., 2010) which is one of the most emerging fields in recent biological science.

Cholesterol and its esters are membrane constituents widely found in biological systems which serve a unique purpose in modulating membrane fluidity, elasticity, and permeability (Ikonen, 2008). It makes the cell walls rigid and strong, protecting itself from the foreign bodies. In the human serum, 80% of cholesterol exists in the ester form. The normal level of total cholesterol in healthy human serum is ~200 mg/dl (Motonaka and Faulkner, 1993) where higher levels of cholesterol lead to life-threatening coronary heart diseases, cerebral thrombosis and atherosclerosis (Raines and Ross, 1995). Therefore, cholesterol level in the serum is one of the most important parameters in diagnostics and prevention of heart diseases. Over various analytical methodologies, the electrochemical approach for biosensing has gained momentum in past few decades, due to their high sensitivity and fast response time. The electrochemical biosensing of cholesterol has been performed by the enzymatic reaction of cholesterol with cholesterol oxidase, where the concentration of either H2O2 generated or oxygen consumed during the enzymatic reaction is being monitored (Karube et al., 1982). Detection selectivity in most of these methods relies on the use of cholesterol-selective enzymes which are expensive and prone to denaturation. As an alternative for simple and cost effective methods, the optical sensors are highly appreciable whereas an electrochemical non-enzymatic sensing process has an ample scope for better sensitivity.

It is well known that β-cyclodextrin (β-CD) is a cyclic oligosaccharide consisting of 7 β (1→4)-glucopyranose units. The internal cavity is lined with C(3)H and C(5)H hydrogen and ether-like oxygen that provide a hydrophilic environment, whereas the external faces of the cyclodextrin molecule are hydrophilic. Due to its ability to encapsulate hydrophobic compounds, this internal...
The cavity of β-CD allows hydrophobic cholesterol molecules to be soluble in aqueous solutions (Pitha et al., 1988; López et al., 2011). β-CDs have a high affinity for sterols as compared to other lipids in vitro (Irie et al., 1992; Ohtani et al., 1989), which make these compounds quite effective in modifying cholesterol metabolism. Mondal and Jana (2012) have recently carried out fluorescent detection of cholesterol using same Graphene-β-CD hybrid system, where the optical detection of cholesterol was carried out using Rhodamin 6G (R6G) dye as a fluorophore. But, to achieve higher detection sensitivity along with lower detection limit and reproducibility, electrochemical sensor delivers more authentic results than optical.

Herein, we have presented a non-enzymatic electrochemical approach for cholesterol sensing using Graphene-β-Cyclodextrin (Grp-β-CD) hybrid system as the sensing matrix. Grp-β-CD solution was synthesized in situ following the route proposed by Guo et al. where treatment of graphene oxide (GO) with β-CD in presence of ammonia and NaOH was carried out. β-CD is presumed to get covalently attached over GO sheets during the reaction forming GO-β-CD. This complex was then reduced using hydrazine, forming Grp-β-CD. Methylene Blue (MB), a redox indicator, when added into the Grp-β-CD solution, forms a host–guest complex with β-CD (Zhang et al., 2003; Zhao et al., 1999). On addition of cholesterol in the solution, the cholesterol molecule will replace the MB molecule in the cavity due to its higher affinity towards β-CD, offering better detection sensitivity range via selective host–guest interaction and graphene sheet network helps in rapid transfer of the electrochemical signal (as displayed in Scheme 1). As MB is a well known redox probe and hence can be easily detected using Differential Pulse Voltammetry (DPV) technique. Although there are ample reports in the literatures on the non enzymatic electrochemical or optical biosensing procedures for detection of different analytes, to the best of our knowledge this is for the first time, a completely non-enzymatic sensing with high sensitivity and low detection limit is being reported, using an electrochemical DPV metric method with the targeted analyte, cholesterol.

2. Materials and method

2.1. Materials

Graphite powder (20 μm), β-cyclodextrin, cholesterol, ammonia solution (25%), hydrazine monohydrate (98%), Methylene Blue (MB) and dialysis membrane (MWCO 12000) were purchased from Sigma Aldrich and used as received. Deionised water from a Millipore Milli-Q ultra puriﬁcation system having resistivity greater than 18.2 MΩ was used for synthesis. PBS Buffer with pH 7.4 was prepared using NaCl, KCl, Na2HPO4·2H2O, KH2PO4. All the chemicals were procured from Sigma Aldrich and used as received. Interference against cholesterol sensing was studied using various interfering species: NaCl, KCl, MgCl2, Glucose, Glycine, Tyrosine, Tryptophan, Ascorbic acid, Sodium Dodecyl Sulfate (SDS), few hydrophilic drugs like Lidocaine, Chloropramine, Quinine, Quindine and Piroxicam.

2.2. Synthesis of β-cyclodextrin functionalized graphene (Grp-β-CD) from graphene oxide

Grp-β-CD was synthesized following the method reported earlier (Guo et al., 2010) with some minor modiﬁcation. Aqueous solution of GO (5 mg/mL) was prepared by the modiﬁed Hummer’s method (Marcano et al., 2010). In a separate vial, 400 mg of β-cyclodextrin was dissolved in 10 mL water and mixed with 200 μL NH4OH and 1 mL GO solution. The whole solution was continuously stirred for an hour, followed by addition of 20 μL hydrazine monohydrate solutions (0.04 M). Next, the solution was heated to 80–90 °C for an hour with constant stirring. The stable black solution was then dialysed against distilled water with cellulose membrane for overnight. Finally, the solution was diluted with 0.1 M Phosphate Buffered Saline (PBS) of pH 7.4 and used as stock solution for the cholesterol sensing.

For the physical characterization of the sensing material, Transmission Electron Microscopy (TEM), FT-IR and Raman spectroscopy were carried out. The TEM images were taken using a transmission electron microscope (FEI model Tecnei G2 20 S with 200 kV accelerating voltage and resolution range of 50 nm to 1 μm). FT-IR (Perkin Elmer model Spectrum 100) was done to

![Scheme 1](image-url)
identify the nature of bonding occurring between β-CD and Graphene sheets, whereas Raman spectroscopy was performed (Horiba Raman triple spectrometer T64000 with Ar ion Laser and sample imaging using Olympus 50 × microscope) to characterise the nature of the graphene sheets, under study.

2.3. Preparation of cholesterol solution

As cholesterol has very low solubility in water, 1 mM stock solution of cholesterol was prepared by dissolving 4 mg of cholesterol in 10 mL ethanol. The prepared solution was used further for the electrochemical detection. The cholesterol solution gets solvated in PBS buffer, during its sequential additions in the electrochemical cell.

2.4. Preparation and functioning of the sensing probe

For the electrochemical studies, a Potentiostat/Galvanostat from Princeton Applied Research (Model 263A) having PS Lite software were used, connected with a single compartment cell with three electrodes (where counter as well as working electrode is Pt wire and an Ag/AgCl electrode acts as a reference electrode respectively). Initially, 3 mL Grp-β-CD solution (solvated in PBS, maintained at pH of 7.4) was taken in the electrochemical cell. 2 mL, 10 mM Methylene Blue solution was then added and kept for a while. As suggested earlier, MB molecules are expected to move inside the cavity of the β-CD molecules, forming an inclusion complex of Grp-β-CD-MB (the sensing probe). The sensing probe was then centrifuged, separated and washed thoroughly to remove the MB traces remaining on the surface. The residual probe was transferred again to the electrochemical cell with 3 mL fresh PBS solution, assuming it as a blank solution. The CV and DPV measurements were carried out before and just after mixing with sequential addition of stock cholesterol aliquots. CV plot was taken at a scan rate of 10 mV/s, within the potential window of −0.6 to 0.6 V. DPV scan was taken with pulse height of 50 mV and pulse width of 70 ms. Stock solution of cholesterol were added to it, in such a manner that its final concentration in the system would increased from 0 to 100 μM. Due to its higher binding affinity towards β-CD, cholesterol molecules are expected to replace the MB molecules, forming Grp-β-CD-cholesterol complex and the extent of MB molecule moving out of the graphene–CD system, would be detected by DPV and CV measurements after each addition. Initially the sensing probe was characterized using Cyclic Voltammetric (CV) measurements, to ensure the potential window required for the DPV.

![Image](image-url)
3. Results and discussions

During the synthesis of Grp-β-CD, initially when graphite is treated in the presence of strong oxidizing agent, KMnO₄ and mixed acid (H₂SO₄/H₃PO₄), polar oxygen functionalities developed on the graphitic sheets lead to the formation of GO. And, these oxygen functionalities (mostly epoxy, hydroxyl, carbonyl and carboxyl groups) render hydrophilic nature, thus making GO soluble in water (Zhu et al., 2010, 2008). During reduction with hydrazine, chemically converted Graphene (CCG) sheets agglomerate due to strong π–π stacking interactions with less number of hydrophilic functional groups on the GO sheets (Zhu et al., 2008). During reduction of GO in the presence of β-CD, covalent interactions occur between hydroxyl groups of β-CD and oxygen functionalities of GO, hence forming water soluble Graphene-β-CD system (Fig. 1a) (Guo et al., 2010; Xu et al., 2010; Konkena and Vasudevan, 2012).

3.1. Transmission Electron Microscopy

The images obtained for Grp-β-CD sheets under TEM, showing few agglomerations in the graphene sheet, possibly for β-CD which is covalently attached on its surface (Fig. 1b). In the TEM image, the presence of agglomerated β-CD is well established over the sheet like structure of graphene.

3.2. FT-IR studies

The characteristic FT-IR spectral signal of β-CD can be observed in the spectra of Grp-β-CD (shown in Fig. 1c), justifying the covalent interactions occurring between β-CD and CCG and no physical adsorption of β-CD over graphene sheets. The characteristic peaks of 3370 cm⁻¹ due to stretching vibration of O–H, 2925 cm⁻¹ due to C–H stretching vibration, C=O stretching vibrations gives a pick at 1720 cm⁻¹ bending stretching of C–H from CH₃ and CH₂ gives a peak at 1420 cm⁻¹, 1157 cm⁻¹ is due to coupled stretching vibrations of C=O, C–C and C–O–H, and 938 cm⁻¹ peak represents skeletal vibration involving α-1.4 linkage in Grp-β-CD. For CCG, the characteristic peaks are mainly at ~3370 cm⁻¹ due to stretching vibration of O–H (a small peak due to the presence of O–H groups in the graphene sheets after deoxygenation of GO), and 1060 cm⁻¹ is due to stretching vibrations from C–O, from the carboxyl groups remaining after hydrazine reduction. The spectrum of our sensing matrix, Grp-β-CD showed the mixed characteristic peaks of β-CD and CCG, indicating the successful covalent attachment of these two (Guo et al., 2010).

3.3. Raman spectroscopy

The Raman spectra (Fig. 1d), for the CCG and Grp-β-CD system showed D and G peaks at ~1460 and 1700 cm⁻¹ respectively, significant for the pristine graphitic nature in the CCG as well as in Grp-β-CD, even after β-CD was incorporated within the graphene sheets. The two spectra do not show any major changes in the peak positions or intensities establishing the fact that graphene didn’t lose its graphitic structure after binding with β-CD.

3.4. Electrochemical studies for the sensing matrix

Cyclic Voltammetric (CV) studies were carried out as a characterization of the sensing probe for cholesterol sensing. CV plots were taken at a scan rate of 10 mV/s, in the potential window of −0.6 to +0.6 V, for the Grp-β-CD solution in PBS, before and after dipping into MB (Fig. 2a). Cyclic Voltammograms showed that MB quite efficiently displayed changes in the peak current value between −0.1 and +0.1 V (as shown in Fig. 2b). Further addition of cholesterol in the system also exhibited significant changes in the peak current. Hence, CV results confirmed that MB is giving a peak current around −0.1 V potential (Zhang et al., 2003). Therefore, we chose the working window for DPV studies in the range of −0.4 to +0.4 V. Comprehensively, the trends in the peak position and intensity obtained in cyclic voltammograms, helped us in the better understanding of electroactivity of our sensing probe along with the selection of the potential window for further DPV measurements.

Progress of MB replacement by cholesterol is manifested in a monotonic increase of the electrochemical signal of MB in DPV with increase of target cholesterol concentration. It can be seen that initially, when the cholesterol concentration was zero, there was no MB peak in the 0 to +0.4 V regions even when the MB is present in the Grp-β-CD (Fig. 3). This indicates that the MB is bound in the cavity of the β-CD therefore, not able to give any redox signal into the electrode. Though there is some probability of MB, which is hydrophilic in nature, to get adsorbed on the graphene sheets, these will not make any difference to the CV and DPV results, as MB remains intact on the surface of graphene.
sheets in the beginning as well as at the end of the experiment. A control experiment carried out to exclude the possibility of desorption of MB from the graphene surface during cholesterol detection proved that only the MB molecule coming out from the CD cavity is responsible for the DPV signal (Fig. S4). After addition of the cholesterol, it readily moved inside the cavity of the β-CD, replacing the MB into the solution and hence, a characteristic peak was obtained at +0.05 V. Cholesterol can only go inside a hydrophobic pocket (that is of β-CD) and would replace MB molecule, as cholesterol has higher affinity towards CD as compared to MB. The measured binding constant between cholesterol and β-CD-G was ~1.6 M⁻¹ which is similar to the earlier observed value with free β-CD (Breslow and Zhang, 1996). The sensing signal of Grp-β-CD system increased periodically with increasing concentration of cholesterol, up to 100 μM, as presented in the calibration curve (Fig. 3 inset). Above 100 μM, the signal reached its saturation. Detection limit was less than 1 μM which was quite low and satisfactory with respect to other recently reported articles. Table 1 illustrates few of the recent literatures on cholesterol biosensors, establishing the edge of the present work. The detection limit and sensitivity of the present sensing matrix is comparatively better than the reported ones, with a decent sensing time. The peak sensitivity of the present sensing matrix is comparatively better than the reported ones, with a decent sensing time. The peak sensitivity of the present sensing matrix is comparatively better than the reported ones, with a decent sensing time. The peak sensitivity of the present sensing matrix is comparatively better than the reported ones, with a decent sensing time.

3.5. Interaction of the interfering species

As we know, human blood serum contains many more bio components like salts, amino acids, carbohydrates, lipids etc., those can interfere with cholesterol detection and hamper the selectivity of the biosensor. Therefore, we studied a wide range of response in DPV for the species which can interfere with the detection process of cholesterol in the blood serum. It is quite evident from Fig. 4 that salts like NaCl, KCl and MgCl₂; carbohydrates and amino acids like glucose, glycine etc. showed negligible interference even at the concentration of 2 mM, except tryptophan. Anionic surfactant like Sodium Dodecyl Sulfate (SDS) showed minute interference in the system, compared to cholesterol detected for only 30 μM against the concentration of all other substances, which is kept at 2 mM.

Table 1

<table>
<thead>
<tr>
<th>Immobilization matrix</th>
<th>Method of immobilization</th>
<th>Detection range (mM)</th>
<th>Detection Process</th>
<th>Sensitivity</th>
<th>Sensing Time (s)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetraethylorthosilicate ChOX/HRP</td>
<td>Covalent</td>
<td>2–12</td>
<td>Amperometric</td>
<td>–</td>
<td>–</td>
<td>Kumar et al. (2006)</td>
</tr>
<tr>
<td>Tetraethylorthosilicate Chβ/ChOX</td>
<td>Covalent</td>
<td>0.184–12</td>
<td>Photometric</td>
<td>8.3 × 10⁻⁷ Abs/mM</td>
<td>180</td>
<td>Singh et al. (2007)</td>
</tr>
<tr>
<td>Dithiothreitol/ChE/ChOX</td>
<td>Covalent</td>
<td>0.77–6.14</td>
<td>CV</td>
<td>1.55 μA/mM</td>
<td>13</td>
<td>Salinas et al. (2006)</td>
</tr>
<tr>
<td>GC/CM–SiO₂–MWCNTs ChOX</td>
<td>Entrapment</td>
<td>0.004–0.7</td>
<td>DPV</td>
<td>3.8 μA/mM</td>
<td>10</td>
<td>Tan et al. (2005)</td>
</tr>
<tr>
<td>ChIT–SiO₂–MWCNT/ITO ChET/ ChOX</td>
<td>Covalent</td>
<td>0.15–7.68</td>
<td>CV</td>
<td>0.059 A/mg dl⁻¹</td>
<td>10</td>
<td>Solanki et al. (2009a, 2009b)</td>
</tr>
<tr>
<td>ChOX/nano-ZnO/ITO</td>
<td>Sol-gel entrapment</td>
<td>0.278–22.2</td>
<td>CV</td>
<td>8.46 cm⁻²</td>
<td>–</td>
<td>Solanki et al. (2009a, 2009b)</td>
</tr>
<tr>
<td>Grp/β-CD/Rhodamine 6G</td>
<td>Entrapment</td>
<td>0.005–0.03</td>
<td>Fluorescence</td>
<td>Micromolar range</td>
<td>–</td>
<td>Mondal and Jana (2012)</td>
</tr>
<tr>
<td>Grp/β-CD/Methylene Blue</td>
<td>Entrapment</td>
<td>0.001–0.10</td>
<td>DPV</td>
<td>0.01 μA/mM</td>
<td>–</td>
<td>Present Work</td>
</tr>
</tbody>
</table>
4. Conclusion

In conclusion, we have developed an electrochemical method of cholesterol detection using β-CD functionalized graphene. The detection limit of cholesterol is achieved as low as 1 µM which is quite impressive compared to recent literatures. Salient features of the present study include: (1) Graphene’s increased solubility after β-CD functionalization, due to the covalent interactions occurring between the hydrophilic surfaces of the two; (2) The sensor can easily detect cholesterol using DPV technique, where cholesterol molecule is replacing MB molecule and forming the inclusion complex within the hydrophobic core of Grp-β-CD. Also, the developed detection method is important as it does not use any enzyme or antibody for detection and still, detects cholesterol efficiently in the micro molar concentration range with outstanding selectivity over the common interfering species.

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Appendix A. Supplementary Information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.bios.2014.07.037.

References

Hydrolysis of sodium borohydride using Ru–Co-PEDOT nanocomposites as catalyst

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**Highlights**

- Ru–Co nanocluster synthesis.
- Incorporation of Ru–Co in PEDOT/PSS.
- Ru–Co-PEDOT uses as catalyst in hydrolysis of NaBH₄ to get rapid hydrogen.
- PEDOT goes to solution phase and Ru–Co act as free heterogeneous nanocatalyst.
- Reuses several times with high TC% effectively.

**Article info**

**Abstract**

It is well established that sodium borohydride, (NaBH₄) is one of the most safe and attractive hydrogen-storage materials for H₂ production. In this work, we have reported a zero valent Ruthenium–Cobalt (Ru–Co) based nanocluster incorporated conducting PEDOT/PSS nanocomposite as the catalyst for rapid hydrogen production from NaBH₄. Initially, Ru–Co nanocluster was synthesized by reduction of a mixture of Ruthenium(III) chloride and Cobalt(II) chloride using sodium borohydride solution. Although the Ru–Co itself showed good synergistic catalytic effect as compared to bare Ru and Co nanoparticles, but their performance was found to be exceptionally good when incorporated into the conducting polymer (PEDOT/PSS). The obtained catalyst was characterized by TEM, EDX, XRD, four-probe conductivity measurements, etc. The hydrolysis kinetics showed that the 85 wt% NaBH₄ + 15 wt% Ru–Co PEDOT/PSS nanocomposite sample in 1 M NaOH yielded best result among all other combinations. A hydrogen generation rate of 40.1 L min⁻¹ g⁻¹ at 25 °C was achieved, which makes it a noteworthy result as compared to other catalysts reported earlier.

**1. Introduction**

One of the critical challenges of today’s world is generation of enormous amount of energy without contributing too much to the increasing global pollution. Unfortunately, the major source of energy till now is fossil fuels, which, in turn, creates a range of environmental problems. Because of this, including global warming caused by the combustion of fossil fuels, there has been a growing interest for the “hydrogen-economy” as a long-term solution toward a sustainable energy future. The development of hydrogen generation as well as hydrogen storage with the use of sustainable energy sources promises to improve numerous current problems such as air pollution, greenhouse gas production, and global security [1–7]. For real applications of H₂ energy, high gravimetric and volumetric density of hydrogen storage is required. Among various hydrogen storage systems, chemical hydrides are candidates with the greatest potential for success in terms of the low operation pressure, less cost and less energy losses [7–11]. These hydrides can evolve H₂ within few minutes in a controlled manner which is a less hazardous method, eliminating the most problematic step of carrying flammable H₂ gas. Among these chemical hydrides, hydrolysis of NaBH₄ produces hydrogen gas and water-soluble sodium metaborate, NaBO₂, in the presence of suitable catalyst [9,12–15]. By this way hydrogen can be generated safely for the fuel cell application.

\[
\text{NaBH}_4 + 2\text{H}_2\text{O} \xrightarrow{\text{Catalyst}} \text{NaBO}_2 + 4\text{H}_2 + \text{heat} \tag{1}
\]

Since the hydrolysis occurs only in the presence of a suitable catalyst, many transition metals or their derivative compounds have been tested as catalyst for this industrially important reaction.
presented in Eq. (1) [8,16–18]. The theoretical gravimetric hydrogen storage capacity of NaBH₄ is about 10.8 wt% but the effectiveness is generally reported to be below 7 wt% due to low solubility of NaBO₂ and the nature of the catalyst. In the presence of appropriate catalysts, the hydrolysis reaction of NaBH₄ can be easily initiated, controlled and even the rate of hydrogen generation can also be accelerated. Among various catalytic reagents, Ru has been widely tested as catalyst for hydrogen generation. Recently, non-toxic and non-noble metals like Ni, Co have been chosen as low cost catalyst instead of expensive Ru [19–23], although they have not yielded satisfactory results. Compared to these metal powdered catalysts, the supported catalysts are highly appreciated in the practical applications as they can prevent the aggregation of catalyst particles into larger agglomeration leading to decrease in catalytic activity and lifetime [24].

In this work, we have described the synthesis of a highly efficient heterogeneous catalyst for H₂ generation at very high rate. The catalyst was synthesized by the reduction of Ru(III) and Co(II) salts to form metallic nanoparticles followed by their incorporation into a conducting polymer blend PEDOT/PSS (poly-3,4-ethylenedioxythiophene/poly-styrenesulfonate) via in situ polymerization. Though the Ru–Co nanoparticles itself showed good synergetic effect with respect to bare Ru and Co nanoparticles, it expressed exceptionally good catalytic behavior when incorporated into the PEDOT/PSS. The conducting blend polymer of PEDOT/PSS is well known for its conducting nature, stability in long pH range and most importantly, solubility in water [25,26]. The catalytic activity of Ru and Co along with their different derivatives is well studied and reported. But, the concoction of these two metal nanoparticles showed superior performance from their expected additive values. In spite of that, the nanoparticles were mixed with the PEDOT/PSS to study the catalytic properties. In the hydrolysis process, the blend polymer easily gets solvated into the reaction medium, releasing the Ru–Co nanoparticles in free state to provide maximum surface to volume ratio for catalysis. Hydrolysis of NaBH₄ using this synthesized catalyst, not only accelerates the rate of hydrogen release, but also reduces the operation cost by recycling the used catalyst in further processes. After successful completion of 1st catalytic cycle, the remaining metal in their zero valance state can be used to regenerate the catalyst by further incorporation into the PEDOT/PSS polymer. We investigate the appropriate weight percentage of the catalyst components, molarity of the NaOH as well as the NaBH₄ loading. The effect of catalyst on the hydrogen release rate is also investigated along with its reproducibility, in order to develop a promising catalyst for hydrogen generation in real life.

2. Experimental

2.1. Materials

Sodium borohydride (NaBH₄), Cobalt chloride hexahydrate (CoCl₂, 6H₂O), and Sodium hydroxide (NaOH) were purchased from Merck-India. Ruthenium chloride (RuCl₃, xH₂O), 3,4-ethylenedioxythiophene (EDOT) monomer and poly-styrenesulfonate (PSS) were supplied from Sigma–Aldrich. Ammonium peroxysulphate (APS) was purchased from Merck. Deionized water from a Millipore’s Milli-Q ultra purification system having resistivity greater than 18.2 MΩ-cm was used in sample preparation. EDOT is distilled prior to use but except that all chemicals were of reagent grade and used as received without further purification.

2.2. Preparation of Ru–Co nanoparticles

Ru–Co nanoparticles were prepared by the reduction of their chloride salts with NaBH₄ [27]. 10 mL of 2 mM aqueous RuCl₃ solution was mixed with 10 mL of 2 mM CoCl₂ and 2 mL of 0.112 M of aqueous NaBH₄ solution was then added to this solution mixture dropwise under vigorous stirring condition. Molar ratio of NaBH₄ to (Ru + Co) must be greater than 5 times to ensure complete reduction of metal ions to its zero oxidation state. Complete reduction of the metal ions was indicated by ceasing of effervescence from the reaction mixture. The dark brown Ru–Co nanoparticles were precipitated, rinsed with acetone, filtered and dried under vacuum oven at 60 °C.

2.3. Preparation of Ru–Co-PEDOT/PSS nanocomposite

The Ru–Co nanoparticles were incorporated with the PEDOT/PSS through the oxidation of the EDOT monomer via in situ polymerization [28]. Aqueous dispersion was prepared by introducing 2 ml of PSS with 1.5 ml of distilled EDOT monomer in 1:1 mol ratio stirring in 100 ml of water. This solution was added to 100 ml colloidal dispersion containing specified quantities of Ru–Co nanoparticles and 2.28 g of APS (in 1:2.5 mol ratio w.r.t. monomer) as oxidant was added to this mixture. Polymerization reaction was allowed to continue for 20 h under vigorous stirring. Resulting dark blue colored nanocomposite samples remained in the dispersed phase. In order to isolate the samples in the solid-state, precipitation of the nanocomposites were carried out using ethanol as the non-solvent. The precipitates were washed and dried in a vacuum.

2.4. Characterization of catalyst

The morphology of prepared catalyst was identified using a JEOL-JEM, 2010, Transmission Electron Microscope (TEM) at 200 kV, whereas the elemental compositions on catalyst surface were analyzed with energy dispersive spectra (EDS). Phase identification and insertion of Ru–Co into the PEDOT was confirmed using powdered X-ray diffractometer (Philips PW 1710) with Cu Kα (λ = 1.5406 Å) radiation.

2.5. Catalyst performance test

The catalytic activity of the catalyst was measured by a self-assembled instrument where the amount of hydrogen generation was measured by using the classical water-displacement method. NaBH₄-catalyst mixture was prepared by the ‘mortar’ route as follows. NaBH₄ powder and catalyst (Ru–Co-PEDOT/PSS) were mechanically mixed together in a mortar for half an hour. In a typical measurement, 1 M NaOH solution was added in a sealed round bottom flask containing varied amount of catalyst (fitted with an outlet for collecting evolved H₂ gas) to initiate hydrolysis reaction as shown in Scheme 1. As the reaction proceeds, the water displaced by hydrogen gas in the graduated cylinder connected to the reaction flask was continually monitored. To get a clear idea about the experiment and instrumentation procedure, we have given a schematic diagram of our self assembled instrument and mechanism in Schemes 1 and 2.

In case of Ru–Co-PEDOT/PSS catalyst, once the H₂ liberation was completed, the flask was detached from the apparatus and the NaOH solution containing free Ru–Co nanoparticles was centrifuged and washed repeatedly. The residue was then dried and again used to produce the Ru–Co-PEDOT/PSS catalyst by incorporating into the PEDOT/PSS system in order to check the reproducibility of the catalyst.

3. Result and discussion

Our main objective is to improve the hydrogen generation rate through hydrolysis of NaBH₄ using the prepared catalyst in its
optimum reaction conditions (temperature, molar ratio of the NaBH₄ with catalyst). Using the mortar mixing route, different compositions varying the molar ratio of catalyst and NaBH₄ were tested to get the best result in 85:15 M ratio of NaBH₄:catalyst. Solubility of PEDOT/PSS in water promotes the release of Ru–Co nanoparticle in the reaction medium yielding effectiveness and reproducibility which are the two most important criteria to develop a H₂ storage system in practical application. The main results are reported hereafter, where we have tried to monitor the activity of the catalyst from every possible angle varying the reaction condition.

3.1. Preparation and characterization of Ru–Co-PEDOT/PSS catalyst

Water-dispersible Ru–Co-PEDOT/PSS catalyst was prepared from reduction of the metal chlorides by sodium borohydride in water and incorporated into the PEDOT/PSS polymer by in situ chemical polymerization method. Fig. 1 gives a typical TEM image of the Ru–Co nanoparticles and Ru–Co-PEDOT/PSS nanocomposites. In Fig. 1a, darker shaded part indicates the zero valent Ru nanoparticles (<15 nm) and relatively lighter shaded ones are Co nanoparticles. In order to confirm the presence of both the nanoparticles, the EDX experiments were carried out on some of the selected portions of the TEM grid. EDX results of the Ru–Co nanoparticles of Fig. 1a, which is given in the Supplementary information support the presence of the Ru and Co. In Fig. 1b, the Ru–Co PEDOT/PSS nanocomposite is shown which indicates that the modified impregnation method facilitates the formation of smaller Ru–Co particles on the PEDOT/PSS surface.

X-ray diffraction patterns of Ru–Co nanoparticles are shown in Fig. 2. The characteristic peaks of the nanoparticles as well as nanocomposites were observed at 2θ = 38 degree for the Ru(0) [29]. Another small intensity peaks correspond to the contribution of the Co(0) [30]. The contribution of Co in the nanoparticle is relatively lower than Ru which is represented in the peak intensities in XRD and EDS. In XRD, the peak position of the Ru–Co-PEDOT/PSS sample revealed the composite formation of nanoparticles into the polymer matrix. All the peaks in XRD show broad hump instead of sharp peak which reflects the nano dimensionality of the synthesized catalysts.

Four probe conductivity measurements were carried out on both the nanoparticles and the composites and it was found that the room temperature conductivity of the PEDOT and Ru–Co-PEDOT nanocomposites are 493 and 311 S/cm respectively. Detailed measurements are given in the Supplementary information section.

3.2. Catalytic activity for sodium borohydride hydrolysis

The amount of NaBH₄ in the catalyst mixture and the concentration of NaOH solution play an important role on the practical performance of hydrogen generation (HG) process. To minimize the effect of temperature changes due to the exothermic hydrolysis reaction, we checked and carefully controlled the solution temperature at 25 °C by circulating cold water over the reaction chamber. NaOH is required for stabilizing the NaBH₄ solution, but it causes HG rate loss and elongates the activation time period for hydrogen generation [24]. Taking a clue from earlier studies, we have chosen
the NaOH concentration to be 1 M for the following experiment [31–35] which was suitable for rapid preparation of the hydrogen. Maximum NaBH₄ loading was desirable for achieving good hydrogen yield. Fig. 3 shows the influence of different compositions of the catalyst prepared by the mortar route. From the catalytic phase of the graph, the HG rate was measured. It was found that the HG rate increased with the increasing composition of NaBH₄ up to 85 wt% with respect to total weight of the catalyst mixture. It was found that 100 mg of 85% NaBH₄ yielded the maximum value of HG which was 40.1 L min⁻¹ g⁻¹ (cat). However, NaBH₄ concentrations above 85 wt% resulted in a reduced HG rate. The HG rate was calculated from the slope of the graph divided per gm of catalyst used in the reaction. From Fig. 3 and Table 1, we conclude that among the different compositions of the catalyst, the selected sample showed best performance where the composition was kept constant as 85% NaBH₄ and 15% Ru–Co-PEDOT/PSS catalyst and hence chosen for further experiment.

As Ru is a very well known catalyst for H₂ generation, therefore we carried out similar hydrogen production experiments with bare Ru, CoCl₂ and Ru–Co nanoparticles mixed with NaBH₄. When we used the Ru–Co nanoparticles as catalyst, keeping constant the amount of catalyst loading, the hydrogen generation rate was found to be increased rapidly. This is attributed to the fact that the Ru and the Co showed synergistic catalytic effect in the

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**Fig. 1.** TEM image of (a) Ru–Co nanocluster and (b) Ru–Co-PEDOT/PSS catalyst.

**Fig. 2.** XRD patterns of the samples: Ru–Co nanoparticle and the Ru–Co-PEDOT/PSS nanocomposite. Peak intensities at similar position confirm the incorporation of the nanoparticle into the polymer.

**Fig. 3.** Effect of NaBH₄ wt% with the catalyst on volume of hydrogen generated as a function of time in 1 M solution of NaOH at 25 °C.
catalysis reaction which increased the HG rate in comparison to the individual metal nanoparticles (Ru, Co). Achieving high rate and yield of hydrogen after incorporating the Ru–Co nanoparticles into the PEDOT/PSS polymer could be attributed to the in situ generation of catalyst surface taking place by the solubility of the PEDOT/PSS polymer. Hence, the Ru–Co nanoparticles are available for reaction with NaBH4 readily which makes the H2 generation process faster. Besides this, the BO2⁻ anion, formed as a side product of the hydrolysis process can bind with the cationic backbone of the PEDOT polymeric surface which increases the solubility of the NaBO2. Possibility of removal of the BO2⁻ anion from hydrolysis reaction mentioned in Eq. (1), increases the rate of forward reaction significantly, resulting in faster hydrogen generation. Though the bare nanoparticles also showed efficient catalytic behavior, the nanocomposite formation increased the H2 production rate with more rapid process and higher TC (Fig. 5). For easy understanding, a pictorial view of the hydrogen liberation from our proposed catalyst is given as Scheme 2.

The total conversion (TC) is the percentage ratio of evolved hydrogen volume to the maximum possible hydrogen volume calculated from the Eq. (1). The TC for all the six sets of experiments was calculated to be very high percentage value (Table 1). The hydrogen production from all the prepared NaBH4-Ru–Co-PEDOT/PSS samples was initially very slow in its 25 s activation phase as well as in the final phase. The rate of HG was calculated only from the slope of the catalytic phase (Fig. 3). The TC was around 88% which is quite satisfactory with respect to recent similar studies [10,24,32,36].

### 3.3. Activation energy determination with temperature variation

The NaBH4 hydrolysis reaction kinetics was investigated within a temperature range of 25–50 °C. Considering observed influence of the catalyst on the hydrogen generation rates, further experiments were carried out using sample having weight ratio of NaBH4 and catalyst as 85:15 (see Table 2). The NaOH solution concentration was always kept at 1 M. The obtained kinetic curves for the temperature variation are presented in Fig. 4a. It was observed that the rate of HG increased with increasing reaction temperature as expected. In the present study, the HG rates at varied solution temperature were used to determine the activation energy. The rate equation can be written as follows:

\[ r = \frac{k_o}{T} \exp\left(-\frac{E_a}{RT}\right) \]

where \( r \) is the reaction rate (ml min⁻¹ g⁻¹), \( k_o \) – the reaction constant (ml min⁻¹ g⁻¹), \( E_a \) – the activation energy for the reaction (kJ mol⁻¹), \( R \) – the gas constant (8.314 kJ mol⁻¹ K⁻¹) and \( T \) – the reaction temperature in Kelvin.

For activation energy calculation, an Arrhenius plot, in which ln \( r \) is plotted against the reciprocal of absolute temperature (1/T), is shown in Fig. 4b. From the slope of the straight line, the activation energy is calculated to be 37.42 kJ mol⁻¹ for the catalyzed hydrolysis of sodium borohydride. Although this value is higher than the previously reported values of 28.51 kJ mol⁻¹ for Ru(0) nanoparticles [32], but it is much less with respect to the activation energy reported by Amendola [9,12], and Kaufman and Sen [37] for the same hydrolysis but with different metal catalysts (75 kJ mol⁻¹ for Cobalt, 71 kJ mol⁻¹ for nickel, and 63 kJ mol⁻¹ for Raney nickel). Considering these results it can be concluded that, Ru–Co-PEDOT/PSS nanocomposites have shown better performance as a catalyst in H2 generation as compared to the other low cost metals except Ru.

### Table 1

Hydrogen generation rate and TC% determination with respect to catalyst composition in the reaction mixture in 1 M NaOH solution. 85:15 wt. ratio (Bold) refers to the composition for the highest hydrogen generation rate.

<table>
<thead>
<tr>
<th>Sample (wt. ratio)</th>
<th>Total wt. of NaBH4 mixture taken in the flask</th>
<th>wt. of Ru-Co-PEDOT catalyst</th>
<th>Hydrogen generation rate (ml min⁻¹ g⁻¹)</th>
<th>%TC</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaBH4: Ru–Co-PEDOT</td>
<td>10 mg</td>
<td>3 mg</td>
<td>7.1 L min⁻¹ g⁻¹</td>
<td>82</td>
</tr>
<tr>
<td>75:25</td>
<td>2.5 mg</td>
<td>19.2 L min⁻¹ g⁻¹</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>80:20</td>
<td>2 mg</td>
<td>32.25 L min⁻¹ g⁻¹</td>
<td>85.5</td>
<td></td>
</tr>
<tr>
<td>85:15</td>
<td>1.5 mg</td>
<td>40.1 L min⁻¹ g⁻¹</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>90:10</td>
<td>1 mg</td>
<td>38.1 L min⁻¹ g⁻¹</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>100:0</td>
<td>0</td>
<td>Very low</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2

Comparison of Ru–Co-PEDOT/PSS catalyst with some recent catalyst in NaBH4 hydrolysis for H2 generation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>HG rate (ml min⁻¹ g⁻¹)</th>
<th>Activation energy (kJ mol⁻¹)</th>
<th>Ref. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtRu/LiCoO2</td>
<td>10.24</td>
<td>28.51</td>
<td>[38]</td>
</tr>
<tr>
<td>RAH</td>
<td>13.62</td>
<td>29.24</td>
<td>[36]</td>
</tr>
<tr>
<td>Ni–Ru</td>
<td>0.41</td>
<td>32.17</td>
<td>[32]</td>
</tr>
<tr>
<td>Ru(acac)₃</td>
<td>0.12</td>
<td>38.12</td>
<td>[31]</td>
</tr>
<tr>
<td>Ru(0)</td>
<td>0.51</td>
<td>28.51</td>
<td>[33]</td>
</tr>
<tr>
<td>Zeolite-confined ruthenium(0)</td>
<td>0.81</td>
<td>49.2</td>
<td>[4]</td>
</tr>
<tr>
<td>Ru/graphite</td>
<td>32.3</td>
<td>61.1</td>
<td>[24]</td>
</tr>
<tr>
<td>CoCl₂</td>
<td>1.4 L min⁻¹ g⁻¹</td>
<td>42.28</td>
<td>[40]</td>
</tr>
<tr>
<td>RuO₂(p-AMS)</td>
<td>8.2 L min⁻¹ g⁻¹</td>
<td>28.51</td>
<td>[39]</td>
</tr>
<tr>
<td>Ni-p(AMS)</td>
<td>0.23</td>
<td>42.28</td>
<td>[40]</td>
</tr>
<tr>
<td>Co(PCS)</td>
<td>10.4 L min⁻¹ g⁻¹</td>
<td>24.04</td>
<td>[41]</td>
</tr>
<tr>
<td>[C₆(mpy)₂][NiCl₄]²⁻</td>
<td>0.23</td>
<td>56.36</td>
<td>[42]</td>
</tr>
<tr>
<td>Ru–Co-PEDOT/PSS</td>
<td>40.1 L min⁻¹ g⁻¹</td>
<td>37.42</td>
<td>Current work</td>
</tr>
</tbody>
</table>
and the Ru(0), which were already well known for their HG catalytic action, also showed lower values of HG compared to the present nanocomposite system which is clearly indicated in Fig. 5. Ru and Co being well established for their catalytic activity in Hydrogen generation, newly synthesized nanocomposite is comparatively studied against them. However, the Ru–Co catalyst is when blended with PEDOT/PSS polymer, the catalytic activity exhibited by the nanocomposite is surprisingly high. Obtained results and its economic advantage make this nanocomposite quite attractive since noble Ru is much more expensive than non-noble Co and the PEDOT polymer. Furthermore, it is confirmed from the above experiments that the HG rate with higher TC of nanocomposites of the Ru–Co/PEDOT/PSS catalyst can replace existing Ru or Pt catalyst in the hydrolysis of NaBH₄. Until now, the utilization of Co in this type of process has been mainly defended only by virtue of its low cost but now the Ru–Co/PEDOT/PSS nanocomposites may be replaceable with Ru or Pt for its reactivity. A comparison table is given to establish the excellent catalytic behavior of the nanocomposites over some recently used catalyst, illustrated in recent journals.

3.5. Reproducibility of the catalyst

Reproducibility of a catalyst is a crucial parameter which determines its role in the practical HG application. In this study, reproducibility of the catalyst was checked after the 1st catalytic hydrolysis reaction by separating the Ru–Co nanoparticles from the by-product solution by the vacuum lyophilization and incorporating it further into PEDOT/PSS blend system. As shown in Fig. 6, the catalyst performed well in the next cycle without any significant loss in its activity (three sets of same catalyst mixture were tested for reproducibility and the average value is given in Fig. 6 with error bar). Even after five times of usage, the exhibited catalytic activity is only slightly lower to that in the first cycle.

4. Conclusion

Ru–Co nanoparticles have been prepared by the reduction of Ruthenium chloride and Cobalt chloride using sodium borohydride as a reducing agent. The nanoparticle was incorporated into the PEDOT/PSS conducting polymer blend via in situ polymerization of EDOT monomer to prepare the desired catalyst. The Ru–Co/PEDOT/PSS catalyst gave a good HG rate of 40.1 L min⁻¹ g⁻¹ with low activation energy of 37.42 kJ mol⁻¹ though the nanoparticles itself show excellent catalytic effect. After introducing the catalyst in the aqueous reaction medium, the PEDOT/PSS gets dissolved in water to generate the free nanostructured Ru–Co as the working catalyst for hydrogen generation. The catalyst showed excellent catalytic activity and reproducibility up to five times without compromising much its activity, making it a promising catalyst for hydrogen generation in practical application.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2014.11.108.

References


Highly efficient electromagnetic interference shielding using graphite nanoplatelet/poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) composites with enhanced thermal conductivity†

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Graphite nanoplatelet (GNP)/conducting polymer (poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS) composites were synthesized to evaluate their electromagnetic interference (EMI) shielding effectiveness (SE) in the X-band frequency region. The use of a conducting polymer, instead of a conventional polymer, as the base matrix for the composite negates the primary requirement of achieving the percolation threshold to get an appreciable SE. We show that an addition of 0.5 wt% GNP to PEDOT:PSS takes the EMI SE to ~30 dB. For 10 and 25 wt% GNP loadings the SE, with dominant absorption, reaches the value of ~47 and 70 dB, respectively, for a thickness of 0.8 mm. The SE remains nearly constant for the whole frequency range and is the highest achieved so far for non-porous, non-foamy carbon composites of comparable thickness. Owing to their low density, GNP/PEDOT:PSS composites give a high specific EMI SE of up to 67.3 dB cm3 g−1, which is higher compared to even foam structures particularly designed for making low density EMI shields. The drawbacks of foam structures like brittleness and crack formation could also be avoided. Addition of GNPs to PEDOT:PSS results in a several times increase in its pristine thermal conductivity, making it capable of long term use by reducing the chances of chemical degradation through the formation of hot-spots.

Introduction

The rapid penetration of modern electronics into every sphere of our lives has come with the cost of increased electromagnetic interference (EMI). EMI, consisting of spurious radiation signals of electrical origin, causes serious degradation of the performance and reliability of electrical instruments. Shielding plays the crucial role of protecting equipment otherwise susceptible to EMI. Therefore, great effort has been devoted to developing effective EMI shielding materials.

EMI shielding effectiveness (EMI SE), defined as the logarithmic ratio of transmitted power to incident power, depends on a number of physical properties of the shielding material, like the electrical conductivity (σ) (i.e. on mobile charge carriers) and the dielectric constant (εr). The principal mechanisms of shielding are reflection and absorption. In the case of reflection of radiation, mobile charges like electrons interact with the incident electromagnetic field.1 Metals typically show this type of shielding. Whereas, when the electrical (or magnetic) dipoles of a highly dielectric material (or a material with a high magnetic permeability) interact with the incident radiation significant absorption takes place.2 Another mechanism of shielding relies on multiple reflections at the various surfaces or interfaces in the shielding material and this is how composites containing polymers and electrically conducting fillers work.

Unlike metals, which are usually rigid, prone to corrosion and impose a severe weight penalty, electrically conducting polymer composites (CPC) offer several distinct advantages like light weight, flexibility, resistance to corrosion, tunable conductivity and comparatively lower cost than metals.3–4 These advantages make them particularly suitable for aerospace and mobile applications.

Recent trends to explore the shielding properties of polymer/non-metallic composites have led to the use of different types of combinations of the same by researchers. For example, Yong Li et al. studied multiwalled carbon nanotube (MWCNT) filled polyacrylate composite films,5 whereas Kim et al. explored MWCNT/poly(methylmethacrylate) (PMMA).6 MWCNTs have also been used with other polymers like polystyrene,7 fluorocarbon foam etc.7 Other forms of carbon that have been used as a conductive filler for making composite materials for EMI shielding include carbon black8, carbon fibers,9 graphene and graphite nanoplatelets (GNPs).2–4,10–15
shielding include single walled carbon nanotubes (SWCNT),\textsuperscript{8} carbon fibers,\textsuperscript{9} carbon nanofibers,\textsuperscript{10} and graphene.\textsuperscript{11,12}

In the case of composites, the polymers used are mostly of low conductivity and the conductivity depends strongly on the percolating network formed by the filler particles. According to the percolation theory, conductive fillers with high aspect ratios lower the percolation threshold (i.e., the minimum percentage of filler required for appreciable conductivity) and, thereby, the critical concentration to achieve the desired EMI SE also comes down.\textsuperscript{2} In this context, carbon nanotubes, nanofibers and graphene, all having a large aspect ratio, allow low loading of the filler without compromising the other inherent properties of the polymer.\textsuperscript{13} In addition, because of their superior mechanical properties, carbon nanotubes and graphene also provide physical strength to the composite. When the EMI shield is designed to work at high frequencies, the depth of penetration of the electromagnetic radiation is very small and the skin depth (δ), defined as the depth at which the field drops to 1/e times the value of the incident radiation, is given by \( \delta = (2\pi f\mu)\) where \( f \) and \( \mu \) denote frequency, permeability and electrical conductivity, respectively.\textsuperscript{2} Both CNTs and graphene (along with related graphene based materials like few- and multi-layered graphene, graphite nanoplatelets (GNP) or nanoflakes (GNF), graphene nanoribbons \textit{etc.}) with their large conductivity and very small dimensions can, therefore, play the key role as efficient fillers in CPC EMI shielding materials. The available data from the literature show that about 8 wt% MWCNTs,\textsuperscript{5} or 15 wt% SWCNTs\textsuperscript{13} or graphene\textsuperscript{14} is needed to obtain an EMI SE of about 20 dB. This is good enough for everyday FCC Class B commercial applications. But for defense purposes a more efficient shielding (>70 dB) is required. However, the additional loading of carbon based fillers beyond a certain percentage is untenable because of processibility problems arising out of poor filler-matrix bonding and severe agglomeration.\textsuperscript{3}

In order to reduce the density of the carbon containing polymer composites, foam structures of the same have been made.\textsuperscript{2,4,12} However, as mentioned by several groups, during the foaming process the conducting network in the composite becomes impaired.\textsuperscript{3,12} Furthermore, the large pores present in the foams make them brittle and often cracks start to evolve. In addition, porous structures are prone to attracting moisture and are susceptible to environmental changes. This causes a serious reliability problem, particularly for outdoor applications in countries with large rainfall or snowfall. It is, therefore, of tremendous technological importance to make a CPC that will have the advantages of high conductivity and lightweight, and yet get rid of the problems resulting from the porosity of the foam structures. The aim of this paper is to address this open issue.

The objective of our present investigation is, therefore, to find a non-foamy CPC with low density and a very high EMI SE. Herein, we report the electromagnetic shielding performances of graphite nanoplatelet (GNP)/conducting polymer composites in the X-band frequency region (8.2–12.4 GHz) to demonstrate that they satisfy both the desired criteria. GNP\textit{s} are stacks of multilayered graphene sheets with platelet morphology. They are cheaper and easier to produce on a large scale compared to graphene and carbon nanotubes, and because of their very high surface energy form strong interfacial bonds with the host matrix.\textsuperscript{14} In addition, composites with GNP\textit{s} have shown higher thermal conductivity enhancement than with SWCNTs.\textsuperscript{13} On the other hand, the use of a conducting polymer, instead of a conventional polymer, as the host matrix of the composite offers a unique advantage that, as it is already in a conducting state, the preliminary requirement to achieve the minimum conductivity (i.e., in other words, the percolation threshold) to get an appreciable SE is negated. The addition of any amount of conducting filler like GNP\textit{s} would increase the conductivity and thereby a much improved SE with a low filler loading is expected. We have chosen poly(3,4-ethylenedioxythiophene) (PEDOT), with poly(styrenesulfonate) (PSS) as the dopant anion, as the conducting polymer for preparing composites with GNP\textit{s}. Henceforth it will be referred as PEDOT:PSS. The choice of PEDOT:PSS is justified by its several outstanding properties like high conductivity, ability to spin coat, optical transparency and stability.\textsuperscript{15,17} Here we show that the GNP/PEDOT:PSS composite not only exhibits much enhanced SE at a lower thickness and filler percentage, but that its specific shielding effectiveness (i.e. SE/density) is far better than any known solid, non-foamy material of comparable thickness.

**Experimental**

The GNP/PEDOT:PSS samples were prepared using GNP\textit{s} (lateral dimension \( \sim \) 400–800 nm, thickness \( \sim \) 15–25 nm, carbon content > 99.5\%) and PEDOT:PSS \textit{via} a chemical synthesis route, the details of which are given below.

**Materials**

Graphite nanoplatelets (code KNG-150), obtained from Xiamen Knano Graphite Technology Co. Ltd. China, were subjected to ultracentrifugation in water–alcohol (isopropyl) medium (10 000 rpm for about an hour) in order to discard the heavier and larger GNPs and to obtain lighter and smaller ones. The quality and reproducibility of the obtained GNPs were checked by Raman spectroscopy, TEM, SEM, and density measurements. It has been found that the GNPs have a lateral dimension of \( \sim \)400–800 nm, thickness of \( \sim \)15 nm, carbon content > 99.5\% and density of \( \sim \)2.1 g cm\textsuperscript{-3}. The 3,4-ethylenedioxythiophene (EDOT) monomer and PSS were supplied by Sigma-Aldrich. Ammonium peroxysulphate (APS) was purchased from Merck. Deionised water from a Millipore Milli-Q ultra-purification system, having a resistivity of 18.2 MΩ cm at 25 °C, was used in sample preparation. EDOT was distilled prior to use. Apart from that, all the chemicals were reagent grade and used as received without further purification.

**Synthesis of the GNP/PEDOT:PSS composite**

The GNP/PEDOT:PSS composites were prepared by \textit{in situ} polymerization of EDOT monomers in the presence of an appropriate amount of GNPs. An aqueous micellar dispersion was prepared with 1 g PSS in 80 ml of deionized water under constant stirring. To this solution, a corresponding amount of
GNPs (for 0.5, 1, 5, 10 and 25 wt% loadings) and 0.71 g of distilled EDOT monomer (in 1:1 mole ratio with respect to PSS) were added and solubilized under constant stirring for 1 h. 1.14 g of APS, in a 1:1 mole ratio with the monomer, was added to this mixture as an oxidant. The polymerization reaction was allowed to continue for 20 h under vigorous stirring. The resulting dark blue colored sample remained in the dispersed phase. In order to isolate the sample in the solid state, precipitation was carried out using ethanol as a non-solvent. The precipitate was washed with a copious amount of alcohol–water mixture and dried under vacuum for 24 h at 60 °C. Finally the composite was mold pressed in a specially designed rectangular mold corresponding to the dimensions of the wave guide (1.03 cm × 2.31 cm) sample holder. Another sample containing pristine PEDOT:PSS (i.e. without any GNPs) was also prepared to serve as a reference. The resulting samples were 0.8 mm thick [i.e. the dimensions of each sample used in this investigation are 10.3 mm × 23.1 mm × 0.8 mm].

Characterization

The morphology of the GNP/PEDOT:PSS composite was investigated using scanning electron microscopy (FEI, Quanta 200) and transmission electron microscopy (FEI Tecnai S-Twin). The room temperature electrical conductivities of the samples were measured by a four probe method using Keithley 2400 as the current source and Keithley 2182A as the voltmeter. The samples used here are homogeneous in nature and the mass that contributes to the increase in density (which is in close vicinity also increases the tunnelling probability of the charge carriers). However, it is worth noting here from Fig. 1a and b that with the increase in GNPs the density as well as the electrical conductivity of the samples are given in Table 1. The morphology of the GNP/PEDOT:PSS composite was shown in Fig. 1a. The most prominent peaks in the Raman spectrum of the GNPs are the G-band at ~1580 cm⁻¹, the 2D band at ~2680 cm⁻¹, and the small disorder induced D band at ~1350 cm⁻¹. The most prominent peaks in the Raman spectrum of the GNP/PEDOT:PSS composite are shown in Fig. 1e. The measured scattering parameters were $S_{11}$ (the forward reflection co-efficient), $S_{12}$ (the forward transmission co-efficient), $S_{21}$ (the reverse transmission co-efficient) and $S_{22}$ (the reverse reflection co-efficient). The unit for the $S$ parameters is decibels (dB).

Results and discussion

Fig. 1a and b show the morphology of the GNPs and GNP/PEDOT:PSS composite, respectively, as found by scanning electron microscopy. High resolution transmission electron micrographs (Fig. 1c and d) reveal that the GNPs (with lateral dimension ~800 nm and thickness ~15 nm) are well dispersed in the polymer matrix and no large agglomerations can be observed. Furthermore, the PEDOT:PSS chains are uniformly segmented between the GNPs.

The morphology of the GNP/PEDOT:PSS composite was investigated using scanning electron microscopy (FEI, Quanta 200) and transmission electron microscopy (FEI Tecnai S-Twin). The room temperature electrical conductivities of the samples were measured by a four probe method using Keithley 2400 as the current source and Keithley 2182A as the voltmeter. The samples used here are homogeneous in nature and the mass that contributes to the increase in density (which is in close vicinity also increases the tunnelling probability of the charge carriers). However, it is worth noting here from Fig. 1a and b that with the increase in GNPs the density as well as the electrical conductivity of the samples are given in Table 1.

The density of the GNP/PEDOT:PSS composite can be attributed to the presence of interlayer voids and cavities between the polymer coated GNPs and segmented polymer chains. However, it is worth noting here from Fig. 1a and b that these voids or cavities are much smaller than the regular and dense microcellular cells seen in nanocomposite foams that are reported to have diameters from ~3 μm (ref. 12) up to ~100 μm. Also it is evident from Table 1 that with the increase in GNP content the density as well as the electrical conductivity increase. The samples used here are homogeneous in nature (with less than 0.75% density variation among the various parts of the sample (Table S1†)), so we can infer that the majority of the mass that contributes to the increase in density (which is also a conductor) is well distributed throughout the sample, rather than concentrated at a small portion within it. Again, since the filler GNPs are of a high aspect ratio, the presence of more GNPs will contribute to the larger number of backbone structures for charge transport (because of a similar reason, the high aspect ratio fillers lower the percolation threshold in the conductor–insulator matrix). The presence of conducting fillers in close vicinity also increases the tunnelling probability of the charge carriers. Based on the above argument we can conclude that in this particular set of experiments the enhancement of conductivity with the increase in the GNP filler amount is due to the increase in the number of paths available for charge transport. The synergetic effect is the enhancement in electrical conductivity measured by a four probe method using Keithley 2400 as the current source and Keithley 2182A as the voltmeter.
conductivity and, as a consequence of this, improved SE as discussed in the following sections.

The EMI SE reported in this paper is equivalent to the attenuation in forward transmission of the radiation and is given by $|S_{21}|$. The low (~1%) discrepancies between the forward and reverse measurements confirm the same SE on both sides. Fig. 2 shows the variation of the EMI SE over the frequency range of 8.2–12.4 GHz for GNP/PEDOT:PSS composites with various GNP loadings. The same plot for the pristine PEDOT:PSS sample is also shown.

The pristine PEDOT:PSS without any GNP gives an EMI SE of about 21 dB. This is obviously quite high compared to the conventional polymer matrices used for carbon based composites, viz. polystyrene (<1 dB), poly(dimethylsiloxane) (PDMS) (~1 dB), etc., and comparable to conducting polymers like a polypyrrole impregnated polyurethane membrane (~20 dB). An addition of 0.5 wt% GNPs to PEDOT:PSS increases the EMI SE to ~30 dB. For 10 and 25 wt% GNP loadings the SE reaches a value of about 47 and 70 dB, respectively. It is worth noting here that this is much better than previously reported values of X-band SE and, to the best of our knowledge, the highest value obtained for carbon based composites of comparable thickness. For example, a 7 wt% CNT/polystyrene foam showed a SE of ~19 dB for a thickness of 1.2 mm, for 0.8 wt% graphene/PDMS (1 mm thick foam) the SE is 30 dB, and 1.8 vol% graphene/poly(methylmethacrylate) (2.4 mm thick foam) gives a SE of 19 dB. Even the SE of other combinations, viz. 15 wt% graphene/epoxy (21 dB), 30 wt% graphene/polystyrene (29 dB, 2.5 mm), 40 vol% carbon fiber/polyethersulphone (PES) (30–38 dB, 2.87 mm), remains lower than the values reported here. A comparative survey of the SE of various carbon (CNTs/graphene/fibers) containing composites, along with the present results, is given in Table 2.

Yang and co-workers pointed out that for application of EMI shielding in aerospace technology it would be more appropriate to compare different shielding materials in terms of their specific EMI shielding effectiveness (i.e. EMI SE/density). For example, nickel has a specific EMI SE of 9.2 dB cm$^3$ g$^{-1}$ and for copper the same is 10 dB cm$^3$ g$^{-1}$. In the present work, the specific EMI SE for the sample with a 0.5 wt% GNP loading is 29.44 dB cm$^3$ g$^{-1}$. Whereas, for the samples with 10 and 25 wt% GNP loadings the specific EMI SE is 45.58 and 67.3 dB cm$^3$ g$^{-1}$, respectively. Clearly the EMI SE values of the GNP/PEDOT:PSS composites are much higher than those of typical metal shields. They are even better than a CNT/polystyrene composite foam (33.1 dB cm$^3$ g$^{-1}$, 1.2 mm thick), 1.8 vol% graphene/PMMA foam (17–25 dB cm$^3$ g$^{-1}$, 2.4 mm thick), and 30 wt% graphene/polystyrene composite in porous form (64.4 dB cm$^3$ g$^{-1}$, 2.5 mm thick) in the same frequency band. Notably this was achieved avoiding the drawbacks of the porous foams like brittleness and proneness to cracking.

Here we would like to point out that the comparison of different shielding materials in terms of specific EMI SE without the mention of thickness bears no meaning. For example, it has been found that EMI SE is enhanced with increasing thickness

Table 1 Physical properties of the prepared GNP/PEDOT:PSS composites. Numbers in parentheses show the standard deviation of EMI SE.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>GNP content (wt%/vol%)</th>
<th>Density (g cm$^{-3}$)</th>
<th>Electrical conductivity (S cm$^{-1}$)</th>
<th>EMI SE (dB)</th>
<th>Thermal conductivity (W m$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0/0</td>
<td>1.011 ± 0.03</td>
<td>1.45 ± 0.04</td>
<td>21 (1.4)</td>
<td>0.19 ± 0.03</td>
</tr>
<tr>
<td>2</td>
<td>0.5/0.25</td>
<td>1.019 ± 0.04</td>
<td>1.49 ± 0.05</td>
<td>30 (1.6)</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>1.0/0.52</td>
<td>1.023 ± 0.05</td>
<td>1.73 ± 0.05</td>
<td>36 (2.0)</td>
<td>—</td>
</tr>
<tr>
<td>4</td>
<td>5.0/2.6</td>
<td>1.026 ± 0.04</td>
<td>2.50 ± 0.04</td>
<td>43 (2.6)</td>
<td>—</td>
</tr>
<tr>
<td>5</td>
<td>10.0/4.9</td>
<td>1.031 ± 0.05</td>
<td>3.15 ± 0.05</td>
<td>47 (3.1)</td>
<td>0.60 ± 0.04</td>
</tr>
<tr>
<td>6</td>
<td>25.0/12.9</td>
<td>1.041 ± 0.03</td>
<td>6.84 ± 0.06</td>
<td>70 (4.2)</td>
<td>0.83 ± 0.05</td>
</tr>
</tbody>
</table>

Fig. 1 Scanning electron micrographs of the GNPs (a) and GNP/PEDOT:PSS composite (b). (c and d) Transmission electron micrographs of a GNP/PEDOT:PSS composite with 10% GNPs. (d) reveals that the thickness of the GNPs is ~15 nm. (e) Raman spectra of the GNPs, PEDOT:PSS and the GNP/PEDOT:PSS composite with 10 wt% GNPs.

Fig. 2 EMI shielding effectiveness as a function of frequency for the GNP/PEDOT:PSS composites with various GNP loadings.
of the shielding material. Therefore, the same material with uniform density and composition will give a higher SE, and consequently a better specific EMI SE, when a thicker sample is used for shielding measurements instead of a thinner one. We, therefore propose to compare the efficiency of different shielding materials by specific EMI SE per unit thickness. 1 mm is a good scale for specific EMI SE comparison. Assuming a linear relationship between SE and thickness for a single piece of homogeneous and isotropic material, the specific SE/thickness for 0.5 wt% graphene/PEDOT:PSS was found to be 41.25 dB cm$^3$ g$^{-1}$ and for 25 wt% GNP/PEDOT:PSS it is 92.95 dB cm$^3$ g$^{-1}$, when both have a thickness of 1 mm.

To elucidate the shielding mechanism of the GNP/PEDOT:PSS composite we have also studied the part of the incident radiation that has been reflected and absorbed. When an electromagnetic wave falls on a material the incidental power is divided into reflected power, absorbed power and transmitted power. The corresponding reflectivity ($R$), absorptivity ($A$) and transmittivity ($T$) are related as $R + A + T = 1$. Total shielding effectiveness ($SE_{\text{tot}}$) is the summation of the effectiveness of all the attenuation mechanisms, viz. absorption ($SE_A$), reflection ($SE_R$) and multiple reflections ($SE_{\text{ra}}$). Thus, $SE_{\text{tot}} = -10 \log_{10}(P_i/P_o) = SE_A + SE_R + SE_{\text{ra}}$, where $P_i$ and $P_o$ denote transmitted and incoming power, respectively, $SE_{\text{tot}} = S_{11} = -10 \log_{10} R$, $SE_R = -10 \log_{10}(1 - R)$, and $SE_{\text{ra}} = -10 \log_{10}[T/(1 - R)]$. $R$ is related to the forward reflection co-efficient ($S_{11}$) by $S_{11} = 10 \log_{10} R$. The contribution from multiple reflections is assumed to be negligible when $SE_{\text{tot}} \geq 15$ dB. Fig. 3a shows the plots of $SE_{\text{tot}}$, $SE_A$ and $SE_R$ of the sample with a 10 wt% GNP loading for the whole frequency range. It is quite clear that the main contribution to shielding comes from the absorbance of the incident electromagnetic waves. The same trend is valid for all the samples with different filler percentages (Fig. 3b, with values at 10 GHz). Absorption dominates even for the shielding behavior of the sample without GNPs (i.e. pristine PEDOT:PSS) (Fig. S2 in the ESI†). It is worthwhile to mention here that for composites with other forms of carbon, viz. SWCNTs and MWCNTs, the dominant shielding mechanism was found to be reflection. However, our results show that for GNP composites the microwave (X-band) reflection is negligibly small compared to that of absorption for the whole frequency range. The contribution due to reflection in the GNP/PEDOT:PSS composite is <5 dB, like other graphene containing composites, and remains almost constant for all GNP concentrations (Fig. 3b). Fig. 3b also shows that $SE_{\text{tot}}$ and $SE_A$ both increase with increasing GNP percentage. Therefore, it can be concluded that a major part of the contribution due to reflection comes from the base PEDOT:PSS and when GNP filler is added to it the absorption part increases rapidly. The presence of many GNPs, in the form of large face to face two dimensional structures separated by polymer chains, facilitates multiple reflections of the incident microwave radiation inside the composite and, because of its longer stay, the chance for it to get absorbed through lattice heating increases. This leads to absorption-dominant EMI shielding.

The absorption-dominant shielding offers several advantages over a shielding mechanism where reflection is the major contributor. In spite of the ability to prevent the penetration of radiation beyond the shields, reflection dominated EMI shielding may lead to spurious damage to the components of an electric circuit due to reflection coming either from the shield of the neighboring components or from the electronic housing of the circuits with such an EMI shielding cover. As pointed out

### Table 2

EMI shielding effectiveness of different carbon containing composites. Values for copper are also given for comparison.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Filler %</th>
<th>SE (dB)</th>
<th>Specific EMI SE (dB cm$^3$ g$^{-1}$)</th>
<th>Thickness (mm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene/PEDOT:PSS</td>
<td>0.5 wt%</td>
<td>30</td>
<td>29.4</td>
<td>0.8</td>
<td>Present work</td>
</tr>
<tr>
<td></td>
<td>10 wt%</td>
<td>46</td>
<td>45.6</td>
<td>0.8</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>25 wt%</td>
<td>70</td>
<td>67.3</td>
<td>0.8</td>
<td>49</td>
</tr>
<tr>
<td>MWCNT/polyacrylate</td>
<td>10 wt%</td>
<td>20</td>
<td>—</td>
<td>1.5</td>
<td>5</td>
</tr>
<tr>
<td>MWCNT/fluorocarbon foam</td>
<td>12 wt%</td>
<td>42–48</td>
<td>—</td>
<td>3.8</td>
<td>7</td>
</tr>
<tr>
<td>SWCNT/PS foam</td>
<td>7 wt%</td>
<td>19</td>
<td>33</td>
<td>1.2</td>
<td>2</td>
</tr>
<tr>
<td>SWCNT/epoxy</td>
<td>15 wt%</td>
<td>15–49</td>
<td>—</td>
<td>1.5</td>
<td>15</td>
</tr>
<tr>
<td>Carbon fiber/PES</td>
<td>40 vol%</td>
<td>30–38</td>
<td>—</td>
<td>2.9</td>
<td>9</td>
</tr>
<tr>
<td>CDG/PMMMA foam</td>
<td>5 wt%</td>
<td>19</td>
<td>17–25</td>
<td>2.4</td>
<td>12</td>
</tr>
<tr>
<td>Graphene/PVDF foam</td>
<td>7 wt%</td>
<td>28</td>
<td>—</td>
<td>—</td>
<td>23</td>
</tr>
<tr>
<td>Porous graphene/poly styrene</td>
<td>30 wt%</td>
<td>29</td>
<td>64.4</td>
<td>2.5</td>
<td>4</td>
</tr>
<tr>
<td>Graphene/PDMS foam</td>
<td>0.8 wt%</td>
<td>30</td>
<td>333</td>
<td>1.0</td>
<td>3</td>
</tr>
<tr>
<td>Copper</td>
<td>90</td>
<td>10</td>
<td>10</td>
<td>3.1</td>
<td>22</td>
</tr>
</tbody>
</table>

*Fig. 3* (a) The comparison between $SE_{\text{tot}}$, $SE_R$ and $SE_A$ for the graphene/PEDOT:PSS sample with 10% graphene loading, and (b) the same for samples with different graphene loadings at 10 GHz.
by Chen et al.\(^4\) this type of problem is most perennial when a circuit component, that needs EMI shielding, itself generates EMI radiation. Shielding materials like GNP/PEDOT:PSS, where absorption is the principal shielding mechanism, can get rid of such a problem.

In the case of microwave absorption the material gets heated. Therefore, the thermal behavior of the absorbing material merits special attention. This is particularly important when the absorbing layer is using a polymer as the base material. It is well known that the conventional polymers are poor conductors of heat. As a result, the absorbed energy is often localized and leads to the formation of ‘hot-spots’ causing irreversible structure degradation.\(^24\) Several groups have studied the thermal degradation of PEDOT:PSS and found that prolonged exposure to high temperature decreases the electrical conductivity of PEDOT:PSS.\(^25,26\) Since EMI SE depends directly on conductivity, it is also expected to decrease. Thus there exists a close relation between the EMI SE and thermal conductivity of the shielding material. However, there is a dearth in EMI literature where the thermal conductivity has been reported for the shielding material. With the advent of graphene and EMI shielding, where absorption is the dominant mechanism, this can no longer be ignored. The room temperature thermal conductivity of pristine PEDOT:PSS was measured and was found to be \(-0.19\) W m\(^{-1}\) K\(^{-1}\), close to the values reported.\(^27\) When GNPs (thermal conductivity \(-3000\) W m\(^{-1}\) K\(^{-1}\)) are mixed with a polymer, its thermal conductivity is expected to increase. According to a parallel thermal resistor model\(^27\) the thermal conductivity of the composite (\(k\)) is given by \(k = k_m V_m + k_f V_f\), where \(k_m\) and \(k_f\) denote the thermal conductivities of the matrix and the filler, respectively, and \(V_m\) and \(V_f\) are the volume fractions (i.e. volume of the indexed material/total volume) of the matrix and the filler. Taking \(k_m = 0.2\) W m\(^{-1}\) K\(^{-1}\), \(k_f = 3000\) W m\(^{-1}\) K\(^{-1}\) and the densities of the GNPs and polymer as 2.25 and 1 g cm\(^{-3}\), respectively, for 25 wt% graphene loading the theory predicts a thermal conductivity of \(~250\) W m\(^{-1}\) K\(^{-1}\).

However, it has been found that for 10 wt% GNP/PEDOT:PSS the room temperature thermal conductivity is 0.6 W m\(^{-1}\) K\(^{-1}\), whereas when the GNP loading is 25 wt% it becomes 0.83 W m\(^{-1}\) K\(^{-1}\). This discrepancy arises due to the fact that nano-inclusions and nanointerfaces act as scattering centers for phonons and thereby reduce the value of thermal conductivity.\(^28,29\) Many of the GNP–GNP junctions are capped by thin layers of PEDOT:PSS and this hinders the phonon (i.e. thermal energy) transport through GNP–PEDOT:PSS–GNP interfaces. The thermal conductivity values of the GNP/PEDOT:PSS composites reported here are, however, similar to or better than graphite/epoxy (\(-0.25\) W m\(^{-1}\) K\(^{-1}\)),\(^30\) MWCNT/epoxy (\(-0.45\) W m\(^{-1}\) K\(^{-1}\))\(^30\) or SWCNT/PANI (\(-1.0\) W m\(^{-1}\) K\(^{-1}\))\(^30\) with similar filler loadings. The high thermal conductivity is very important in tandem with the high EMI SE of the graphene based polymer composites, because now the heat can be well distributed throughout the sample. Consequently the energy can be transferred to the environment more efficiently and the chance of hot-spot formation is reduced significantly.

To estimate the thermal degradation behavior of the composites, two samples, one with 25 wt% GNP loading and the reference pristine sample (i.e. without any GNPs), were subjected to repeated microwave exposure, 500 times at 40 W power (each exposure time being 180 s). It was found that the resistance of the reference pristine sample showed \(-3\)% decrease from the initial value, whereas for the sample with 25 wt% graphene there was no significant resistance drop (Fig. 4).

Consequently, there has been \(-5\) dB decline in the SE of the pristine sample. In case of other samples it is, however, less than \(-1\) dB. Therefore, it can be concluded that due to the high thermal conductivity of the GNP/PEDOT:PSS sample it can withstand the thermal degradation and/or the thermal fatigue much better than the pristine PEDOT:PSS sample. Thus the higher thermal conductivity of GNP/PEDOT:PSS than pristine PEDOT:PSS makes it particularly suitable for long term applications as EMI shielding material.

**Conclusions**

This paper addresses the ongoing quest for high efficiency, lightweight and thermally conducting EMI shields. GNP/PEDOT:PSS composites with different amounts of graphene loading have been prepared. The composites provide a high X-band SE from 30 dB (with 0.5 wt% GNP loading) up to 70 dB (with 25 wt% GNP loading) for a thickness of only 0.8 mm, which surpasses the best reported values of EMI SE for materials with a comparable thickness. The use of a conducting polymer, instead of a conventional polymer, to make the composite eliminates the primary requirement of achieving the percolation threshold and pushes the SE to a higher value with low filler content. Owing to their low density, GNP/PEDOT:PSS composites give high specific EMI SE values, up to a value of 67.3 dB cm\(^{-2}\) g\(^{-1}\). The values are higher compared to even foam structures particularly designed for making low density EMI shields. The negative aspects of foam structures like brittleness and crack formation could also be avoided. The addition of 25 wt% GNPs has increased the thermal conductivity of PEDOT/
PEDOT:PSS composites promise efficient shielding for use in mobile, aerospace, defense and electronic industries.

Acknowledgements

Authors thank Nazir Khan, Ajoy Kumar Bhattacharya, Ankan Dutta Chowdhury and Dr Deep Talukdar for helpful discussion. This work is supported by BARD Project, SINP.

References

Response to the Reviewer’s comments

CONTENT

Some of the chapter titles are a little terse and should be extended to increase their meaning (required). This is the first area visited by the reader and some of the acronyms need a little expansion even for the examiner (meanings become clear after the reading the abbreviations list). Thus it should be required that, as a minimum, β-CD be named in full and EMI be spelled out in full (the latter in an extended Chapter title).

The thesis, received, electronically seems to lack an initial brief abstract.

Response –
The names of the titles and all the abbreviations have been extended wherever needed in the content list. Abstract has been written and added in the beginning of the Thesis.

CHAPTER 1

This is a good introduction to a wide-ranging experimental study of several potential applications. There is an issue with the way units are used – this is often inconsistent in the thesis, and units are often run into each other rather than appropriately spaced (the general rule is that IUPAC and SI recommendations should be followed). It is required that attention be given to this matter throughout the thesis; for instance in Chapter 3 where $S \text{ cm}^{-1}$, $S/cm$ and $\Omega^{-1} \text{ cm}^{-1}$ are variously used for what should be $S \text{ cm}^{-1}$. Similarly (elsewhere) $W \text{ h kg}^{-1}$ should be $W \text{ h kg}^{-1}$. The text is nonetheless fully comprehensible – the point is that the notation is not fully consistent.

Figure 1.5 requires a reference.

Figure 1.7 is not a Figure and needs to be redesignated.

In the general discussion of graphenes (plural):

(1) I am unsure of the meaning of “graphene has two oxidation states” (page 14), not least because compounds do not have oxidation states (elements do).

(2) In Figure 1.14 I am not clear what the pyramidal nitrogen species is. Does this need reconsideration?

(3) Fig 1.15(b) is incorrect in that there exclusively cations in the electrolyte and some of these are shown as migrating towards the anode.

(4) Is there a reference for Figure 1.16?

The initial discussion of graphene could suggest that “graphenes” are always single layers. The candidate knows this is not the case, and indeed uses XRD data to assign the number of graphene sheets in a graphene packet. It is required that a single paragraph be added at an
appropriate point to introduce multi-layer graphenes and also to discuss commercial “graphenes” such as few layer graphenes (FLGs) and graphene nanoplatelets (GNPs).

Response –

All the units have been checked thoroughly in this chapter and a standard notation has been followed.

Figure 1.5 – is now provided with an appropriate reference.

Figure 1.7 is now renamed as Table 1.1 and subsequent changes have been made in the numbering accordingly, in the text.

On page 14 – phrase ‘graphene has two oxidation states’ has been changed to ‘Graphene shows two oxidized states’. Also, few lines have been added to justify the next statement given by the reviewer about the importance of few-layer graphenes over single layer graphene, with proper referencing.

In figure 1.14, now figure 1.13, all the details about the reactant species have been introduced in the caption.

Figure 1.15b, now figure 1.14 b, has been corrected according to the comment given by the reviewer.

Figure 1.16, which is now Figure 1.15 after modifications in numbering, does not need any referencing from my end as it is taken from one of the random powerpoint presentations.

CHAPTER 2

Is the font correct on page 44?

This Chapter is a reasonable summary, if brief. There are some problems with unit notation – thus KV should be kV and hr should be h (the latter is used in later chapters). Necessary corrections should be required.

Figure 2.1(b) requires a little more discussion (this area has been mentioned above in my report).

The caption for figure 2.3(b) needs the (TEM) removed – that adds nothing and invites confusion with use of the same acronym for another technique elsewhere in the thesis.

What is X in the first paragraph on page 51?

In 2.3.2 line 1 the relevant subscripts should be used (required correction).

The formula for hydrazine hydrate is incomplete on page 52.

Response –

Font is correct on page 44.

All the corrections in the units have been made throughout the script, according to SI notations.
Figure 2.1b has been elaborately discussed, in pretext of single layer to few layers and many layers graphene using Raman spectra.

Figure 2.3 is corrected and TEM term has been removed to avoid further confusion.

On page 51 – term ‘X’ is for the X- band we worked with, in the range of 8.2 to 12.4 GHz of EM spectrum. Frequency ranges are mentioned in the chapter as well.

On page 52, formula of Hydrazine hydrate has been completed.

CHAPTER 3

Generally very good work. In this Chapter faradic (small f is correct) should be faradaic (after Professor Faraday) throughout. Correction required.

On page 59, °A should be Å

On page 64, valance (part of a bedding set….) should be valence.

I am unclear why the state Mn3+ has not been considered as a reason for their being 3 component peaks underlying the XPS spectra. That oxidation state is well known to occur in the solid state chemistry of manganese oxides. This requires discussion and possible correction. The author even refers to Mn3+ on page 65.

Response –

Spelling of ‘faradic’ has been changed to ‘faradaic’ throughout the chapter and Thesis.

On page 59, angstrom unit has been corrected to Å, wherever needed.

On page 64, spelling changes for ‘VALENCE’ has been made at appropriate places.

A brief discussion regarding the XPS spectrum of Mn3+ and its peak, has been done in order to clear the doubts raised by the reviewer.

CHAPTER 4

A sound study. I am not sure of the meaning of “highly appreciable” in the penultimate line of the full paragraph on page 75.

In figure 4.4 the horizontal axes must be changed to read “wavenumber” (required). Do check other vibrational spectra also.

Include (MB) after methylene blue in line 6 of 4.2.3, for clarity.

Response –

On page 75, the phrase ‘highly appreciable’ has been changed to ‘proved to be beneficial and already present in the literature’.
Figure 4.4 has been corrected accordingly and the word ‘wavelength’ has been changed to ‘wavenumber’.

In 4.2.3, line 6, page 78 – MB has been included in brackets, as per the suggestions.

CHAPTER 5

Again, this is very good work. This chapter is away from the main thrust of the thesis (around nanocarbons and their applications primarily) and the author may have wondered how to include it. Nonetheless, I strongly support its inclusion.

In the kinetics discussion, section 5.3.5, it should be made clearer whether the analysis applies to the whole kinetic curves, or whether the activation energies are calculated from the initial rates [requires discussion]. This area could also be discussed at the oral examination.

In table 5.1, I assume Sigma should be the Greek small symbol or s.d.?

The inclusion of the Ru/Co ratio determinations is good practice. I do believe a comment on the toxicity of Co is warranted.

Response -

In section 5.3.5, kinetics, activation energies as well as its calculations from the graph has been well explained, best to my knowledge.

Table 5.1 has been corrected as per suggestions.

CHAPTER 6

This all looks satisfactory to me, subject to the general comment on the standardisation of units used.

Response -

Again, the standardisation of units has been done in the chapter, wherever needed.

CHAPTER 7

This is an almost redundant summary. It could be improved perhaps by the inclusions of a number of suggestions for further work and optimisations of the promising behaviours observed. A comment on pathways to implementation by industry could also be due.

Response –

Relevant modifications have been made in the concluding section, discussing briefly the promising future of these materials and their implementations at industrial scale.