

Biomimetic synthesis and characterization of semiconducting hybrid organic–inorganic composite materials based on polyaniline–polyethylene glycol–CdS system

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Abstract. Triple hybrid materials based on polyaniline–polyethylene glycol and cadmium sulphide have been prepared by the diffusion–limited biomimetic route and characterized by a number of spectroscopic, XRD, SEM, thermal and electrical measurements. These hybrid materials have been prepared by controlled precipitation of cadmium sulphide by passing H₂S gas and mixing the resultant colloid with the acidic solution of aniline. *In situ* polymerization of adsorbed anilinium ions on anionic surface of CdS resulted in hybrids. Water–soluble polyethylene glycol led to diffusion–limited growth of polyaniline and CdS resulting in a nano-sized hybrid material as indicated by UV-visible spectra, X-ray diffraction (XRD) and scanning electron microscopy (SEM). AC impedance spectroscopic studies on binary and ternary nanocomposites of polyaniline with polyethylene glycol and cadmium sulphide separately and triple hybrid system have been reported. Equivalent circuits were determined and discussed in the light of contributions made from different sources such as grain, grain boundary and electrode.

Keywords. Polymers; chemical synthesis; differential scanning calorimetry; electrical properties.

1. Introduction

Conducting hybrid organic–inorganic nanomaterials have caught the attention of a number of research groups worldwide due to their unique electrical, optical, mechanical, thermal and magnetic properties (Nalwa 2001, 2002). The integration of organic semiconductors based on conducting polymers and conventional semiconductors such as metal sulphides and oxides on nanoscale has been envisaged as a useful process for developing novel optoelectronic devices that combine the best features of these two types of materials (Yang *et al* 2006). Such materials may play a crucial role not only in light-harvesting from UV to visible range due to absorptions from the two components but also facile transfer of photo-generated charge carriers through conjugated network of conducting polymers. These materials provide large interface for the dissociation of excitons and the transport of charge. Biomimetic approach (Castelvetto and Vita 2004) to materials chemistry has led to new avenues for the synthesis of nanomaterials. It offers the possibility of controlling size, shape, crystal structure, orientation and organization of

nanomaterials (Klem *et al* 2005). Biomimetic synthesis of CdS nanocrystals in aqueous solution of pepsin at room temperature was reported recently (Mann 1997). Highly efficient resonant coupling of optical excitations have been found in the *J*-aggregates of cyanine dyes and crystalline semiconductor quantum dots grown by layer-by-layer self assembly (Zang *et al* 2007). Polyaniline–CdS system has been one of the best studied semiconducting polyaniline–metal sulphide system due to the commercial potential of both the components. CdS is a direct band gap semiconductor with band gap of 2.42 eV. It is used in photovoltaic and photosensitive devices such as photoresistors because its electrical resistance changes with the intensity of incident light. Mixed with ZnS, it acts as a phosphor with a long-after-glow. Polyaniline is one of the most studied conducting polymers due to ease of synthesis, tunable electrical and optical properties dependent on various degrees of oxidation/reduction and proton doping of the polymer. One of the first reports on these composites appeared in 1991 not for the purpose of electronic properties but for the removal of cadmium ions with the help of sulfonated polyaniline (Dallas *et al* 1991). Although it was mentioned in the same paper that the controlled deposition of CdS on conducting polymers such as polyaniline may lead to the development of new photovoltaic elements, no attention was paid to these observations. The same authors had reported earlier the

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overgrowth of CdS on sulfonated polyaniline which yielded high conductivity and induced nucleation of CdS (Kallitsis *et al* 1989). Composite films of polyaniline and CdS were prepared by electrochemical polymerization of aniline in acidic solution containing suspended CdS particles (Yonema *et al* 1994). These films exhibited photo-induced electrochromism by illumination at open-circuit potential in presence of EDTA as electron donor. Electrochemical deposition of CdS nanoparticle-polyaniline composite films yielded a particle size of 30 Å (Pethakar *et al* 1999). Films with good optoelectronic properties were prepared by controlling deposition parameters. Nanocomposites of polyaniline with CdS and Cu₂S of 1–2 nm sizes were prepared from their trifluoromethane sulfonates, co-dissolved in N-methyl pyrrolidone (NMP) (Godovsky *et al* 2001). Appreciable photovoltaic effect was observed in multilayer devices. CdS and Cu₂S were incorporated in polyaniline host matrix in which CdS was a *n*-type semiconductor and Cu₂S a *p*-type semiconductor (Chandrankanthi and Careem 2002). Photoluminescence studies on CdS quantum dots self-assembled in alternate layers with sulphonated polyaniline have been reported (Ma *et al* 2002). The intensity of luminescence increased with number of layers and heat treatment. Photovoltaic devices having varying concentrations of CdS and Cu₂S were fabricated and tested in dark and under illumination of 100 mW/cm². It was found that both short-circuit current (I_{sc}) and open-circuit potential (V_{oc}) increased with the CdS concentration. CdS coated with polyaniline was prepared by reverse micro-emulsion polymerization technique (Khiew *et al* 2004). Blue-shift in the UV-visible spectra of the composite was attributed to the quantum-confinement effect in the composite of average particle size of 17.8 ± 2.7 nm. Surfactant-stabilized nanoreactors provided cage-like effect that inhibited the excessive growth of coated nanoparticles. Dimethyl cadmium was used as an organometallic precursor in DMF (dimethyl formamide) to prepare polyaniline–CdS nanocomposites (Khanna *et al* 2004). A blue shift from 515 nm to 440 nm for CdS nanoparticles was reported. However, the proposed mechanism of interaction between zero-valent cadmium in cadmium dimethyl and nitrogen of polyaniline seems improbable for uniform distribution of CdS in polyaniline. Yellow and orange light emission from CdS nanoparticles embedded in polyvinyl alcohol was reported (Khanna *et al* 2005). Multi-modal particle size distribution of CdS nanoparticles led to broad patterns in the photoluminescence studies. Poly vinyl alcohol (PVA) was a particle growth protector for CdS in the composite synthesis of HCl-doped polyaniline–CdS nanocomposites by use of organometallic precursor to prepare polyaniline blended with CdS (Khanna *et al* 2006). It was found that physical blending yielded composites with better electrical conductivities than ones prepared by *in situ* blending. It was also dependent on the CdS content and morphological changes produced by the inorganic component.

Optoelectronic properties of hybrid solar cells based on CdS nanorods and conjugated polymer were studied (Kang and Kim 2006). Improved efficiencies of solar cells were reported due to the organic–inorganic interface where bound electron–hole pairs could dissociate more effectively.

Recently, optical and electrical properties of self-assembled CdS nanorods–polyaniline composites were reported (Dutta *et al* 2007). Significant changes in electronic absorption spectra of CdS nanorods and polyaniline indicated strong interaction between them. Blue-shift in CdS from 530 nm to 475–432 nm in different samples was explained on the basis of quantum size effect. It was shown that synergistic effects between nanocrystalline CdS and polyaniline led to correlated barrier type conduction in these composites. CdS–polyaniline composites with improved thermal stability were reported. It was found that the electronic band of nanosized CdS found at 420 nm was blue-shifted due to quantum size effects but it overlapped with polyaniline.

It is evident from the above reports that polyaniline–CdS system is an interesting hybrid material which has commercial potential. However, these composites are neither processable nor mechanically strong. Adding a third insulating polymer component will not only enhance the processability of the composites but will also work as a growth protector for nanomaterials. The present work reports the biomimetic synthesis of mono-, bi- and tri- component systems based on polyaniline–polyethylene glycol–CdS on which detailed a.c. impedance spectroscopic studies have been made. The samples have been characterized by FTIR, UV-visible spectroscopy, XRD, differential scanning calorimetry (DSC) and SEM. Grain, grain-boundary and electrode contributions to the total a.c. impedance have been separated using complex non-linear least square (CNLS) software. Temperature dependence of electrical properties has been studied to learn about the transport mechanism in these hybrid materials. It is expected that these data will help in designing optoelectronic devices based on a new class of semi conducting organic–inorganic hybrid materials.

2. Experimental

2.1 Material and methods

Aniline (Merck, A.R. grade) was distilled twice at normal pressure before use. Polyethylene glycol 6000 (Average molecular weight 7000–9000) (LOBA chemicals, A.R. grade), cadmium nitrate (Qualigen) and ammonium per disulphate (Merck) were used as received. Triple distilled water, obtained from a quartz double distillation unit, was used for the synthesis.

2.2 Synthesis

Due to toxicity of cadmium, utmost care was taken while handling it. Polyaniline was prepared by using standard procedures (Trivedi 1997). The composites with polyethylene glycol were prepared by the same procedure using 1 g polyethylene glycol dissolved in water.

2.3 Polyaniline and cadmium sulphide composite

Aniline, 3 g (0.03 mol) was dissolved in 60 ml 2 N HCl and kept in ice bath. 6 g (0.025 mol) cadmium nitrate was dissolved in 50 ml 2 N HCl into which H_2S was passed for 10 min. A yellow coloured colloidal cadmium sulphide was obtained which was cooled to a temperature $< 5^\circ C$. A pre-cooled solution of 9 g (0.04 mol) of ammonium per disulphate dissolved in 60 ml water was added slowly by burette into the aniline hydrochloride and cadmium sulphide mixture with continuous stirring. A green coloured precipitate formed indicating the formation of polyaniline. The reaction was allowed to proceed for 50 min, and then the mixture was kept in freezer overnight. After polymerization, a bluish green colour precipitate was obtained. The precipitate was filtered and washed with 2 N HCl and thrice by triple distilled water in order to remove unreacted reagents. The precipitate was dried in an oven at $60-70^\circ C$ and then kept over anhydrous $CaCl_2$ in a desiccator. The yield was 98% (w/w ratio). The efforts to prepare CdS–polyaniline composite from a mixture of cadmium nitrate and aniline hydrochloride and passing H_2S and adding ammonium per disulphate simultaneously yielded a very small amount of composite due to formation of yellow elemental sulfur on reduction of hydrogen sulphide by ammonium per disulphate. It was tested by passing H_2S in ammonium per disulphate solution.

2.4 Polyaniline–polyethylene glycol–cadmium sulphide composite

Aniline, 3 g (0.03 mol) was dissolved in 60 ml 2 N HCl and kept in ice bath, and then mixed thoroughly with 1 g polyethylene glycol dissolved in 25 ml water. 6 g (0.025 mol) cadmium nitrate was dissolved in 50 ml 2N HCl and H_2S passed into it for 10 min. A yellow coloured colloidal cadmium sulphide was obtained, which was mixed thoroughly in aniline–HCl and polyethylene glycol mixture and cooled below $5^\circ C$ in an ice bath. Ammonium per disulphate 9 g (0.04 mol) dissolved in 60 ml water was added slowly in an hour along with continuous stirring. The green colour precipitate was kept in freezer overnight, filtered, washed and dried. The yield was 84 % (w/w).

3. Measurements

FT–IR spectra of the samples were recorded using Varian 3100 FT–IR Excalibur series in the range $400-4000\text{ cm}^{-1}$ in KBr medium. UV-visible spectra was obtained by UV-1700 Pharma Spec. Simadzu corp. in the range 300–1100 nm in nujol medium. Differential scanning calorimetry measurements were made using a TC 15 TA Controller Mettler Tole Do. instrument. The powder X-ray diffraction of the polyaniline, polyethylene glycol and CdS composites were obtained from a Rigaku (Model-RINT-2000; Japan) X-ray diffractometer using $CuK\alpha$ radiation (1.542 \AA) in the 2θ range $5-60^\circ C$. Scanning electron microscopic studies were conducted using Leica Cambridge 440 microscope. AC impedance/conductance in the frequency range of 40 Hz–100 KHz and temperature range of 308–348 K were made using a LCZ meter (Keithley 3330) and data were simulated using EG&G PARC USA CNLS software to determine equivalent circuits. The basic accuracy of the LCZ meter used for measurement was 0.1% for the impedances in the range of $0.1\text{ m}\Omega$ to $19.999\text{ M}\Omega$; capacitances in the range of 0.001 pF to 199.99 mF and for conductance in the range of $0.001\text{ }\mu\text{S}$ to 199.99 S . The relaxation times were evaluated from the products of R and C obtained from the equivalent circuit analysis. The thermal energy of activation was determined from the Arrhenius plots between logarithm of specific conductivity ($\log\sigma$) vs inverse temperature (T^{-1}).

4. Results and discussion

4.1 Synthesis

The mechanism of formation of polyaniline–polyethylene glycol–cadmium sulphide hybrid: The formation of nano-sized triple hybrid materials based on polyaniline–polyethylene glycol–CdS is illustrated in figure 1. Polyethylene glycol sheets act as a biomimetic synthesis aid by separating anilinium hydrochloride molecules which remain isolated after the reaction with ammonium per disulphate leading to smaller (nano-sized) particles of polyaniline (figure 1a). On addition of CdS anilinium ions are adsorbed on it and these particles remain isolated in the polyethylene glycol matrix. On addition of the oxidant, polymerization of aniline occurs on the CdS templates forming a core-shell nanostructure as supported by the uniform bluish-green colour and absence of any yellow CdS and also by SEM studies discussed below (figure 1b).

4.2 FTIR spectra

The FT–IR spectra of the hybrids and pure samples are shown in figure 2. A very good agreement between these

spectra and those reported by Khiew (Khiew *et al* 2004) for polyaniline–cadmium sulphide nanomaterials prepared in emulsion has been found indicating that biomimetic synthesis leads to hybrid nano-materials based on these systems. The addition of water soluble third component i.e. poly ethylene glycol as a biomimetic synthesis agent not only controls the particle size but also enhances the processability of hybrid materials. For example, characteristic bands for the conducting polyaniline form were observed at 3444, 3226, 2924, 2856, 1566, 1482, 1300, 1243, 800 and 703 cm^{-1} according to literature (Kang *et al* 1998; Khanna *et al* 2006). The bands at 1482 cm^{-1} were found to undergo a red-shift to 1466 cm^{-1} in presence of CdS along with similar shifts from 1144 to 1118 cm^{-1} and 703 to 672 cm^{-1} . Nitrogen is associated with these bands and red shifts indicate weakening of bonds by interaction with metal ion centre. Similar interactions between polyaniline and CdS have been proposed earlier as well, but the nature of these interactions seems to be particulate rather than at the molecular level as proposed for CdS–SPAN system (Ma *et al* 2002). The interaction of cationic anilinium ions with anionic CdS colloidal particle may be responsible for bringing CdS particles close to the nitrogen sites which lead to weak interactions between the conducting polyaniline shell with

non-conducting CdS core. Such molecular interactions have been proposed for the formation of rod-like CdS–polyaniline nanostructure (Dutta *et al* 2007).

4.3 UV-Visible spectra

UV-Visible spectra are helpful not only to identify the nanomaterials but also the extent of conjugation in conducting polymers (Nalwa 2001). The spectra for various samples prepared by biomimetic route are given figure 3. Pure polyaniline bands at 868 nm indicate high degree of conjugation and a high conductivity of 0.44 Scm^{-1} at room temperature. The UV-Visible spectra of polyaniline–polyethylene glycol–CdS system exhibit exactly similar behaviour as polyaniline– SiO_2 core–shell nanostructure reported recently (Jang *et al* 2006). Thus a formation of core–shell nanostructured material based on polyaniline and CdS could be described by the mechanism proposed by these authors. An additional proof of the existence of CdS nanoparticles came from the blue–shift of particulate CdS visible band at ~ 500 nm to around 430 nm due to size quantization effects

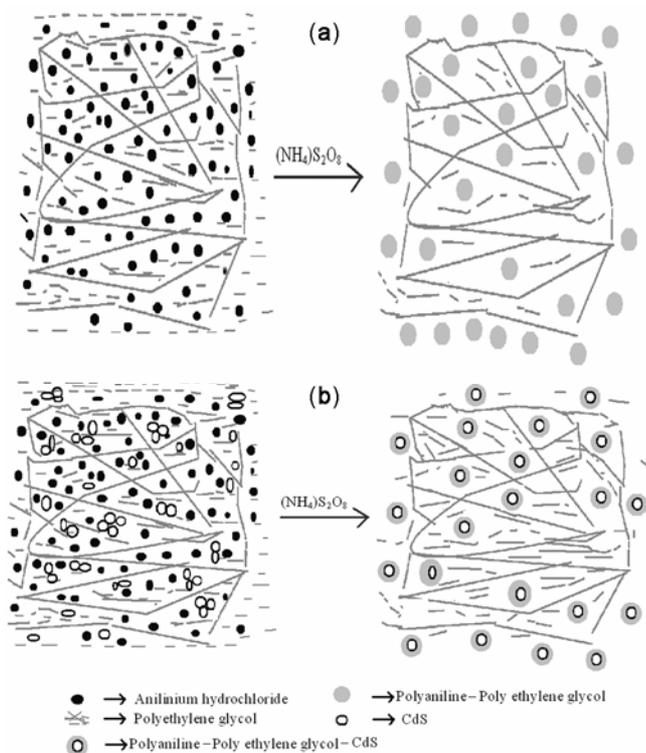


Figure 1. Proposed mechanism for formation of polyaniline, polyethylene glycol and cadmium sulphide particle. **a.** Polyaniline–polyethylene glycol and **b.** polyaniline–polyethylene glycol–cadmium sulphide.

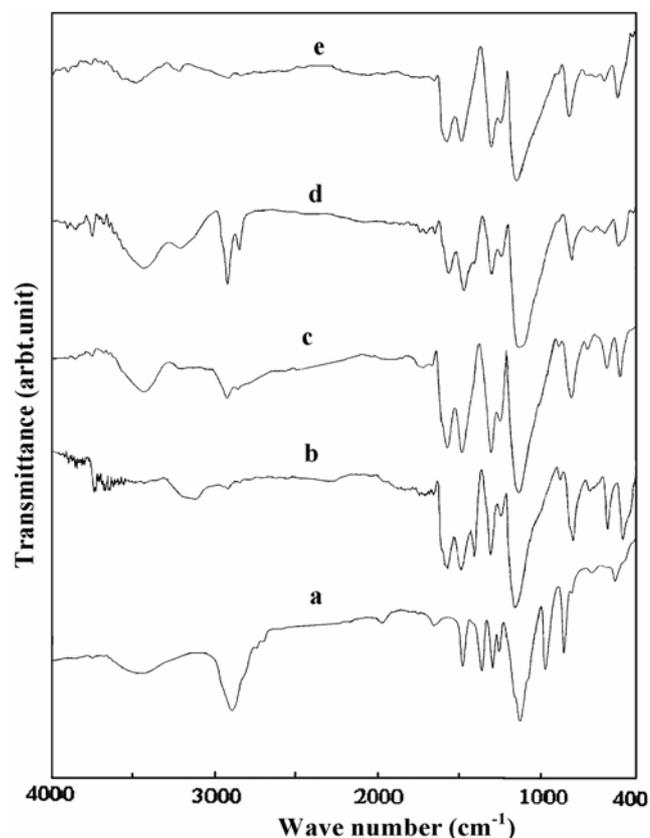


Figure 2. Infra-red spectra of (a) polyethylene glycol, (b) polyaniline, (c) polyaniline–polyethylene glycol, (d) polyaniline–cadmium sulphide and (e) polyaniline–polyethylene glycol–cadmium sulphide.

(Singh *et al* 2007). It may be pointed out that the band due to nano-sized CdS at 430 nm overlapped with the excitonic transition of polyaniline around 420 nm and the band around 500 nm in particulate CdS was absent in the composite. There were no yellow coloured particles of CdS present in the preparations containing polyaniline

and CdS indicating good coating of CdS nanoparticles by polyaniline. The colour of the composite material was similar to pure polyaniline and one-to-one matching in UV-Visible peaks were observed. The broadbands between 700 and 1100 nm indicate extensive conjugation which in turn yielded highly conducting composites.

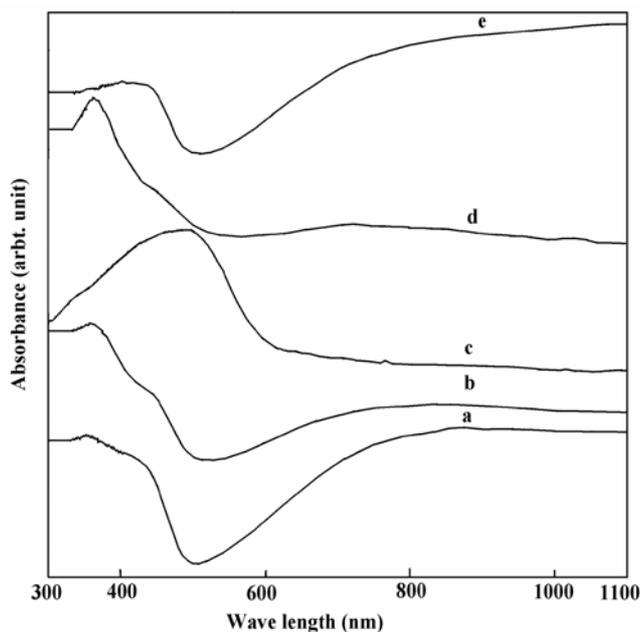


Figure 3. UV-Visible spectra of (a) polyaniline, (b) polyaniline-polyethylene glycol, (c) cadmium sulphide, (d) polyaniline-cadmium sulphide and (e) polyaniline-polyethylene glycol-cadmium sulphide.

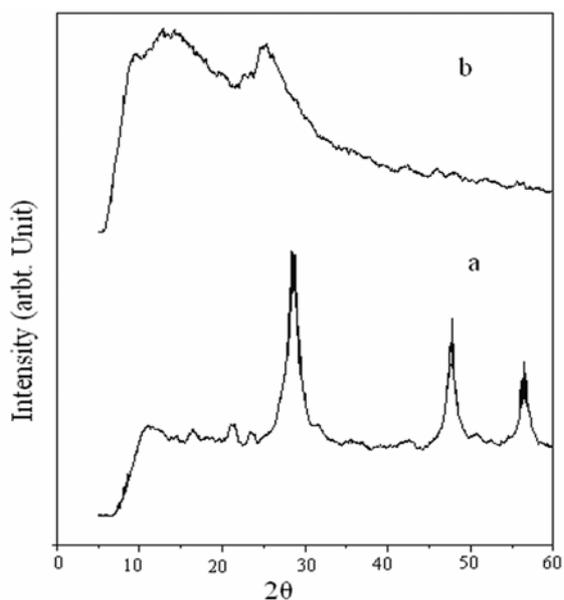


Figure 4. XRD spectra of (a) cadmium sulphide and (b) polyaniline-polyethylene glycol-cadmium sulphide.

4.4 X-ray diffraction

X-ray diffraction (XRD) patterns of different samples are given in figure 4. It is evident from the figure that pure CdS had sharp peaks indicating its crystalline nature but the composite had broad diffuse peaks due to its amorphous behaviour. In cadmium sulphide, three sharp peaks at d -values of 3.1403, 1.9013 and 3.8504 Å with respective diffraction angles of 2θ at 28°C, 48°C and 56°C were obtained. These values are quite different from the crystal structure data of this compound reported in XRD data files indicating a different form of the material prepared by our method probably due to its nanocryst-

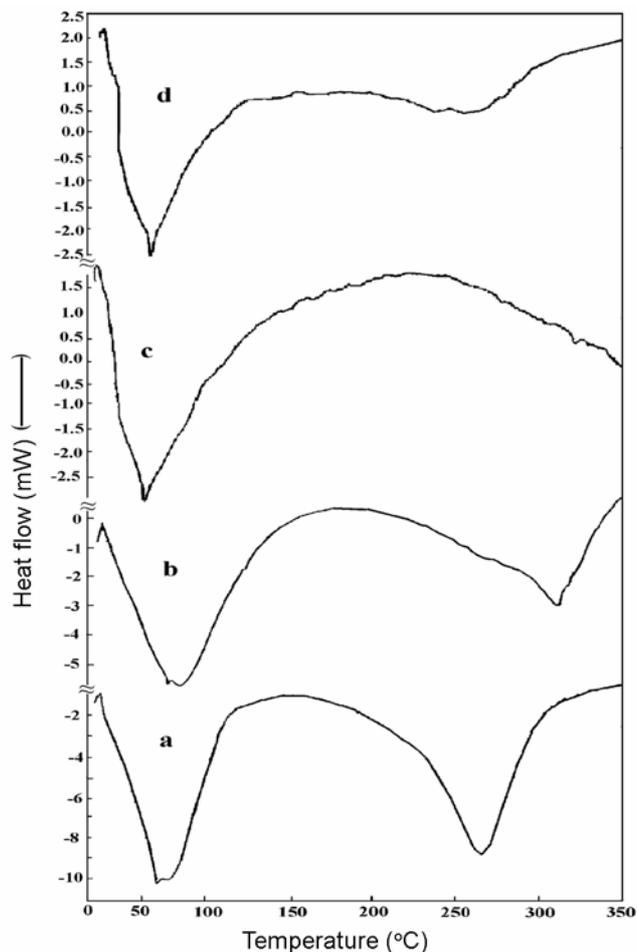


Figure 5. DSC thermograms of (a) polyaniline, (b) polyaniline-polyethylene glycol, (c) polyaniline-cadmium sulphide and (d) polyaniline-polyethylene glycol-cadmium sulphide.

talline nature. X-ray diffraction of polyaniline–polyethylene glycol–CdS composite showed broad peaks at 7.2051 Å and 3.8504 Å interplanar spacing with corresponding 2θ values of 13°C and ca 24°C. These data are analogous to those reported recently for polyaniline–CdS polymer nanocomposites (Chandrakanthi and Careem 2002). The crystalline domain size, L , was estimated using the Scherrer formula (Pouget *et al* 1991).

$$L = \frac{0.9\lambda}{\Delta(2\theta)\cos\theta}$$

where L is the size of the particle, λ = X-ray wave length, $\Delta(2\theta)$ = full width at half-maximum (fwhm).

The average particle size (L) of polyaniline–polyethylene glycol–CdS was 40 nm and for CdS it was 22 nm. These data not only confirm the formation of nanocomposites but also the increase in particle size supported the intimate coating mechanism proposed in figure 1.

4.5 Differential scanning calorimetry measurements

Differential scanning calorimetry (DSC) of some composite samples as shown in figure 5. These figures also match with the recent measurements on polyaniline system indicating the formation of similar materials (Gangopadhyay *et al* 2001). Two endothermic peaks were observed for pure polyaniline; one having a peak temperature at 70.7°C and integral heat of 4528 mJ and normalized heat of 427 Jg⁻¹ and the other with a peak at 264.3°C with integral heat of 4277 mJ and normalized heat of 404 Jg⁻¹. When polyaniline was prepared in presence of polyethylene glycol, the first endothermic peak at 71.1°C showed a decrease in the heat from 4528 to 3304 mJ. Similarly, the second peak showed a decrease from 4277 to 2618 mJ, indicating the presence of another component facilitated the melting of the polyaniline. A drastic decrease in the first integral heat from 4528 to 248 mJ was seen for polyaniline–CdS system and to 222 mJ for polyaniline–polyethylene glycol–CdS systems, respectively. The second endothermic peak was eliminated in the hybrid system. These thermal data indicate the softening of polyaniline on addition of polyethylene glycol and CdS thus enhancing their thermoplasticity and hence the thermoprocessing.

4.6 Scanning electron microscopy studies

Scanning electron microscopic image of the triple hybrid is given in figure 6. It was proposed in figure 1 that the colloidal CdS particles had a nucleation effect on the polymerization of aniline leading to homogeneous coating of CdS with polyaniline. It was further pointed out that CdS had strong effect on morphology of polyaniline from fibrous to particulate depending on the polyaniline con-

centration. The SEM images not only support these propositions but also the particle size estimates from XRD. These microstructures also support our equivalent circuit analysis discussed below in terms of RC circuit from grain contribution with single time constants. The average diameters for the polyaniline–CdS nanocomposite particles were estimated to be ca 17.8 nm with a standard deviation of 2.7 nm using TEM (Khiew *et al* 2004). These values are approximately double for the triple hybrid prepared by the biomimetic route.

4.7 AC impedance studies

Electrical properties of composites are highly dependent on synthetic conditions. AC measurements not only avoid the polarization effects but also lead to separation of various contributions to total impedance or conductance. Highly conducting polyaniline–CdS, were prepared, having room temperature conductivities in the range of 1.85×10^{-2} to 2.53×10^{-1} Scm⁻¹ depending on the amount of aniline taken from 1.5–5 g (keeping the amount of Cd(NO₃)₂ fixed at 6 g). Addition of

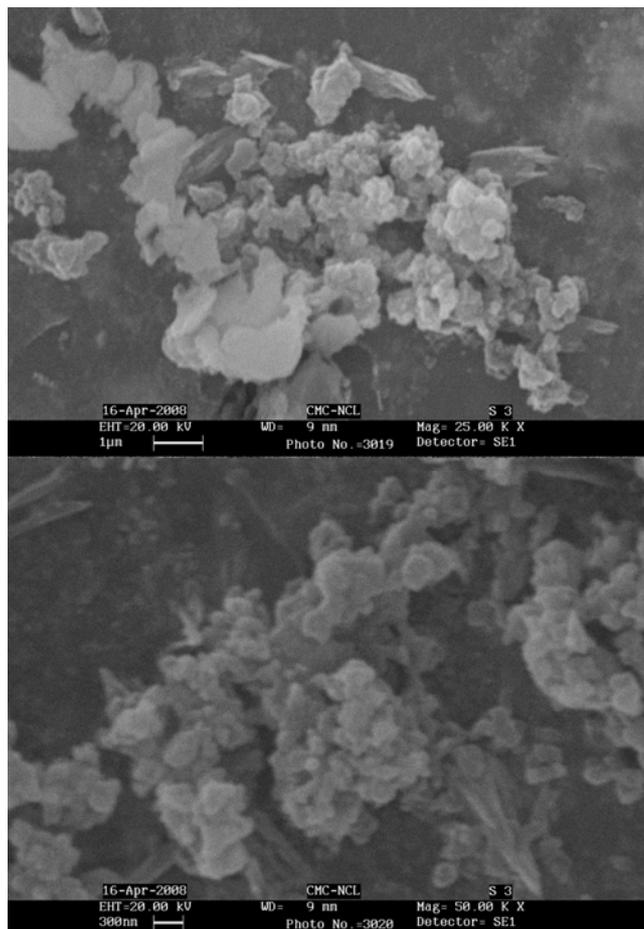


Figure 6. SEM micrographs of polyaniline–polyethylene glycol–cadmium sulphide.

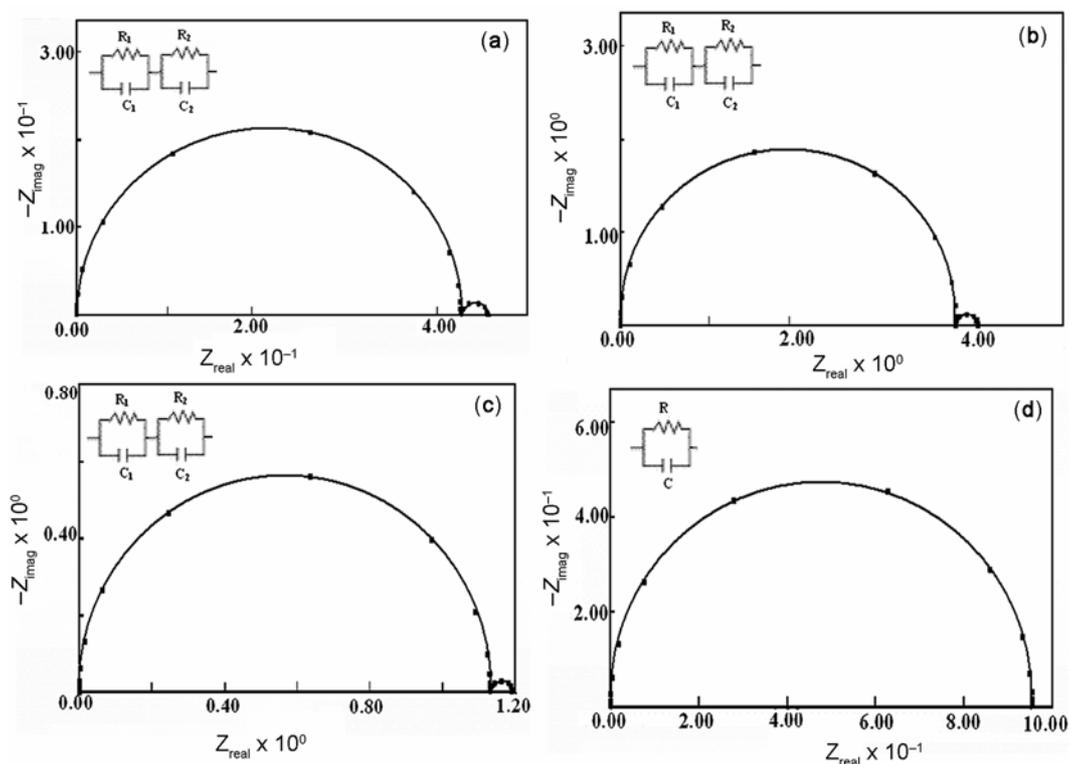


Figure 7. Complex impedance plots (a) polyaniline, (b) polyaniline–polyethylene glycol, (c) polyaniline–cadmium sulphide and (d) polyaniline–polyethylene glycol–cadmium sulphide.

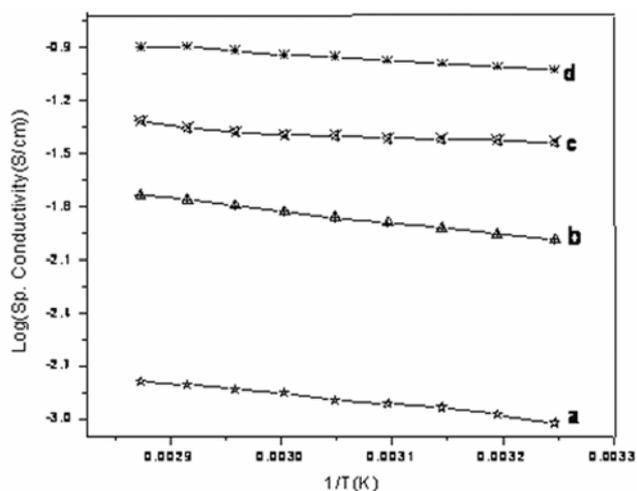


Figure 8. Arrhenius plots for (a) polyaniline–cadmium sulphide, (b) polyaniline, (c) polyaniline–polyethylene glycol and (d) polyaniline–polyethylene glycol–cadmium sulphide.

polyethylene glycol in the range 0.5–1.6 g changes the conductivity from 1.34×10^{-2} to $2.06 \times 10^{-1} \text{ Scm}^{-1}$. Addition of CdS prepared from aqueous solution to polyaniline gives slightly higher value of conductivity from 2.50×10^{-1} to $3.17 \times 10^{-1} \text{ Scm}^{-1}$ indicating no

effect of presence of acidic solution (2N) on the formation and stability of CdS colloids. Similarly a composite with CdS plus ZnS yielded a conductivity of $3.32 \times 10^{-1} \text{ Scm}^{-1}$. These results indicate that highly conducting, reproducible hybrid materials can be prepared by biomimetic route. The AC impedance measurements for a representative sample; polyaniline–CdS, made at various frequencies are given in table 1 and its simulated values for the determination of equivalent circuits in table 2. These data are a representative set given with the purpose of illustrating the analysis of equivalent circuits. Impedance plots for different samples given in figure 7 show distinct changes in the nature of arcs. Pure polyaniline and its composite with polyethylene glycol have two similar arcs and circuit elements indicating good match between these samples. However, pure cadmium sulphide had three arcs indicating significant contributions from grain, grain–boundary and electrode. It is interesting to note that the triple hybrid of polyaniline–polyethylene glycol–CdS had only one arc indicating some sort of synergistic effect reported earlier (Dutta *et al* 2007). The circuit elements for the various samples are reported in table 3. Grain and electrode contributions could easily be separated but grain–boundary contributions could not be obtained from both the impedance and modulus plots except for CdS–polyethylene glycol system. The

Table 1. Measured a.c. impedance data of polyaniline–cadmium sulphide composite* using ammonium per disulphate as oxidizing agent.

ν (frequency, Hz)	$C_p \times 10^{-8}$ (capacitance, Farad)	$Z_{ }$ (impedance, Ohm)	Q (quality factor)	D (dissipation factor)	$\sigma \times 10^{-2}$ (conductivity, S/cm)	X (reactance, Ohm)	θ (phase angle)
4.00×10^1	20.00	1.2421	0.0000	OF	5.554	0.0000	0.00
6.00×10^1	20.00	1.2370	0.0000	OF	5.672	0.0000	0.00
8.00×10^1	20.00	1.2142	0.0000	OF	5.716	0.0000	0.00
1.00×10^2	20.00	1.2118	0.0000	OF	5.783	0.0000	0.00
2.00×10^2	10.00	1.1797	0.0001	15543	5.896	0.0001	0.00
3.00×10^2	10.00	1.1664	0.0001	10255	5.966	0.0001	0.01
4.00×10^2	10.00	1.1650	0.0002	6828	5.998	0.0002	0.01
5.00×10^2	10.00	1.1561	0.0002	5495	6.021	0.0002	0.01
6.00×10^2	10.00	1.1552	0.0002	4112	6.047	0.0003	0.01
7.00×10^2	6.00	1.1468	0.0003	3644	6.066	0.0003	0.02
8.00×10^2	6.00	1.1462	0.0003	3470	6.096	0.0004	0.02
1.00×10^3	5.00	1.1390	0.0004	2679	6.115	0.0004	0.02
2.00×10^3	5.00	1.1380	0.0007	1422	6.136	0.0008	0.04
3.00×10^3	5.00	1.1320	0.001	970	6.151	0.0012	0.06
5.00×10^3	5.00	1.1317	0.0017	600	6.168	0.0019	0.1
7.00×10^3	5.00	1.1264	0.0022	450	6.182	0.0025	0.13
9.00×10^3	4.40	1.1260	0.0028	360	6.200	0.0031	0.16
1.00×10^4	4.40	1.1209	0.0031	324	6.211	0.0035	0.18
2.00×10^4	4.00	1.1212	0.0056	178	6.228	0.0063	0.32
4.00×10^4	3.30	1.1166	0.0095	103	6.234	0.0105	0.54
6.00×10^4	3.10	1.1169	0.0129	77	6.246	0.0145	0.75
8.00×10^4	2.91	1.1125	0.0161	62	6.259	0.0179	0.92
1.00×10^5	2.74	1.1120	0.0191	53	6.272	0.0212	1.09

*Weight of aniline = 3.0 g, weight of cadmium sulphide = 2.70 g, weight of ammonium per disulphate = 9.0 g. OF → overflow.

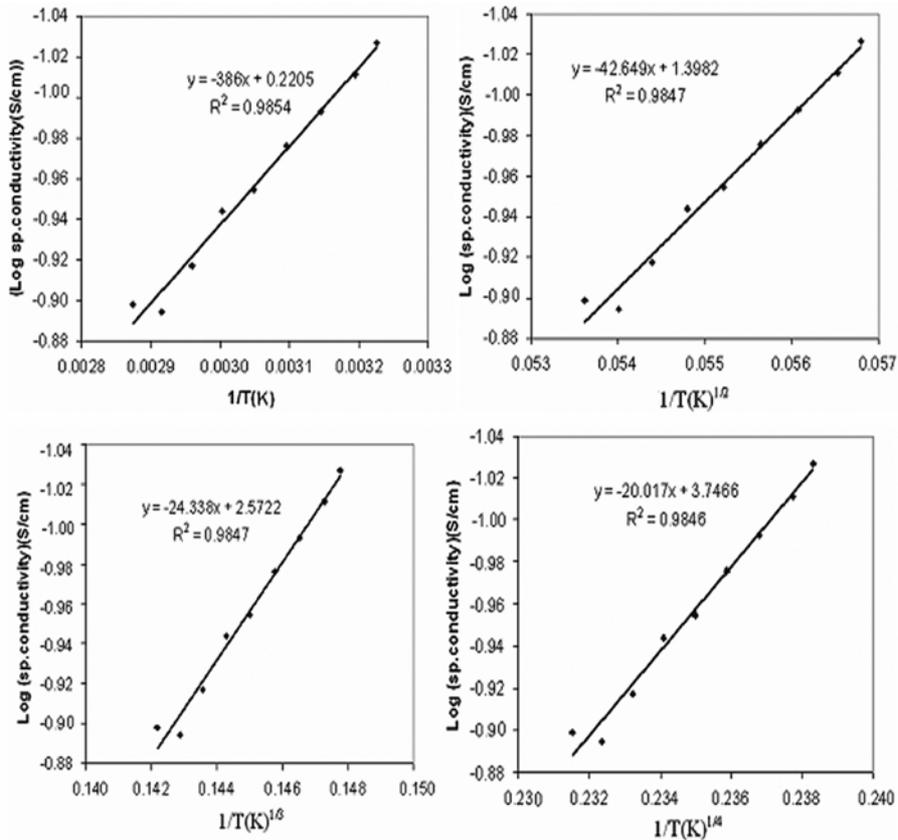


Figure 9. Regression analysis graph of polyaniline–polyethylene glycol–cadmium sulphide.

Table 2. Simulated AC impedance data of polyaniline-cadmium sulfide composite using ammonium per disulphate as oxidizing agent.

ν (frequency, Hz)	C (capacitance, Farad)	$Z_{ }$ (impedance, Ohm)	D (dissipation, factor)	$\sigma \times 10^{-2}$ (conductivity, S/cm)	Permittivity	θ (phase angle)
1.00×10^{-3}	1.363×10^{-5}	1.191×10^0	9.811×10^6	5.851	1.073×10^7	5.84×10^{-6}
4.64×10^{-3}	1.363×10^{-5}	1.191×10^0	2.113×10^6	5.851	1.073×10^7	2.71×10^{-5}
2.15×10^{-2}	1.363×10^{-5}	1.191×10^0	4.553×10^5	5.851	1.073×10^7	1.26×10^{-4}
1.00×10^{-1}	1.363×10^{-5}	1.191×10^0	9.811×10^4	5.851	1.073×10^7	5.84×10^{-4}
4.64×10^{-1}	1.363×10^{-5}	1.191×10^0	2.113×10^4	5.851	1.073×10^7	2.71×10^{-3}
2.15×10^0	1.363×10^{-5}	1.191×10^0	4.553×10^3	5.851	1.073×10^7	1.26×10^{-2}
1.00×10^1	1.363×10^{-5}	1.191×10^0	9.811×10^2	5.851	1.073×10^7	5.84×10^{-2}
4.64×10^1	1.351×10^{-5}	1.191×10^0	2.132×10^2	5.851	1.063×10^7	2.69×10^{-1}
2.15×10^2	1.159×10^{-5}	1.182×10^0	5.395×10^1	5.894	9.122×10^6	1.06×10^0
1.00×10^3	2.870×10^{-6}	1.143×10^0	4.851×10^1	6.095	2.259×10^6	1.18×10^0
4.64×10^3	1.913×10^{-7}	1.133×10^0	1.582×10^2	6.151	1.506×10^5	3.62×10^{-1}
2.15×10^4	3.445×10^{-8}	1.132×10^0	1.896×10^2	6.157	2.711×10^4	3.02×10^{-1}
1.00×10^5	2.704×10^{-8}	1.132×10^0	5.200×10^1	6.154	2.129×10^4	1.10×10^0
4.64×10^5	2.673×10^{-8}	1.127×10^0	1.134×10^1	6.158	2.104×10^4	5.04×10^0
2.15×10^6	2.671×10^{-8}	1.048×10^0	2.445×10^0	6.156	2.102×10^4	2.23×10^1
1.00×10^7	2.670×10^{-8}	5.276×10^{-1}	5.268×10^{-1}	6.157	2.102×10^4	6.22×10^1
4.64×10^7	2.671×10^{-8}	1.276×10^{-1}	1.136×10^{-1}	6.162	2.102×10^4	8.35×10^1
2.15×10^8	2.671×10^{-8}	2.767×10^{-2}	2.445×10^{-2}	6.158	2.102×10^4	8.86×10^1
1.00×10^9	2.670×10^{-8}	5.963×10^{-3}	5.267×10^{-3}	6.156	2.102×10^4	8.97×10^1
4.64×10^9	2.670×10^{-8}	1.285×10^{-3}	1.135×10^{-3}	6.154	2.101×10^4	8.99×10^1
2.15×10^{10}	2.671×10^{-8}	2.770×10^{-4}	2.450×10^{-4}	6.156	2.102×10^4	9.00×10^1
1.00×10^{11}	2.670×10^{-8}	5.968×10^{-5}	5.268×10^{-5}	6.157	2.102×10^4	9.00×10^1

Table 3. AC components along with its values of polyaniline and its composite using ammonium per sulphate as oxidant in HCl medium.

Sample	Electrical properties				Energy of act. (eV)	Conductivity at room temperature (S/cm)
	Grain		Electrode			
	R (Ohms)	C (Farad)	R (Ohms)	C (Farad)		
olyaniline	4.26×10^{-1}	3.00×10^{-7}	2.93×10^{-2}	1.82×10^{-2}	0.058	4.40×10^{-1}
CdS	7.06×10^2	8.15×10^{-10}	2.70×10^3	4.19×10^{-7}	–	8.75×10^{-5}
olyaniline–olyethylene glycol	3.79×10^0	1.11×10^{-9}	2.45×10^{-1}	1.45×10^{-3}	0.064	4.28×10^{-2}
olyaniline–CdS	1.13×10^0	2.67×10^{-8}	5.92×10^{-2}	5.50×10^{-3}	0.021	8.75×10^{-5}
olyaniline–olyethylene glycol–CdS	9.55×10^{-1}	2.59×10^{-7}	–	–	0.033	6.12×10^{-2}

conductivities calculated from the grain resistances match very well with the values for different samples. The relaxation times determined from respective R&C values lie in the range of 1.28×10^{-7} to 1.30×10^{-8} s for grain and 5.32 – 2.51×10^{-4} s for electrode processes. In all the systems, conductivity increased with temperature indicating the semiconductor behaviour of materials. Some Arrhenius plots are shown in figure 8. The thermal energy of activation determined from the temperature dependence of electrical conductivity is included in table 3. The values lie in the range of 0.021–0.064 eV which are typical values for organic semiconductors. The regression analysis graph of PANi–PEG–CdS is shown in figure 9. The regression analysis of conductance data as a function of temperature showed three-dimensional variable range hopping charge transport in these materials

except for PANi–CdS system in which two dimensional variable–ranges hopping was observed.

5. Conclusions

A simple and elegant method for the preparation of conducting hybrid organic–inorganic nanomaterials has been reported. A mechanism has been suggested for the formation of a core–shell nanostructure in the triple hybrid system. The role of water soluble organic polymer; polyethylene glycol as biomimetic synthetic aid has been outlined. The proof of formation of nanosized hybrids have been given from spectral measurements. These materials may be useful for light–harvesting by organic–inorganic semiconductors for solar cell applications because of good absorption both in UV and visible region as well as

good conductivity for facile charge transfer of photo-generated charge carriers. These aspects are under investigation.

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