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Polyaniline–polyelectrolyte–gold(0) ternary nanocomposites: Synthesis and electrochemical properties

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ABSTRACT

Ternary composites based on polyaniline (PAni), a polyelectrolyte—namely poly(diallyldimethylammoniumchloride) (PDDMAC) and gold (Au(0)) nanoparticles have been formulated and synthesized where the high concentration of PDDMAC acted as medium of reaction. The nanocomposites are characterized by FT-IR, UV–vis, XRD, XPS, SEM, AFM and TEM techniques. XRD showed the presence of all three viz., polyaniline, PDDMAC and Au(0) components in the ternary system. The composites exhibited higher conductivities in the range 26×10^{-6} to 217×10^{-6} S/cm compared with the binary composite of PAni–PDDMAC. The ternary composites were adsorbed on a GC electrode and used for sensing dopamine. The composites are useful in sensing as low as 0.05 mM concentration of dopamine at lower potential values compared to some binary PAni–Au nanocomposites.

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1. Introduction

In recent times polyaniline has been extensively studied because of its stability and tunable electrical properties [1]. Nanostructured polyaniline, for example, nanofibers, are more responsive than bulk polyaniline to external stimulation due to their large surface area and hence they are identified as promising materials in sensing and catalytic applications [2–4]. Polyaniline–metal composites exhibit broadened applications such as sensing and electrocatalysis, compared to pure polyaniline [5–8]. As conducting polyaniline is intractable and not processable, synthesis and fabrication of nanoscaled conducting polyaniline in the form of colloids or fibers have gained importance [9–12]. In general polyaniline colloids (PAni colloids) are synthesized using polymeric templates such as poly(acrylic acid) (PAA), poly(styrenesulphonate) (PSS), poly(vinylpyridine) [13–16]. These colloids are useful in constructing multilayer thin films with alternating polycations such as polyethylenimine (PEI), poly(diallyldimethylammoniumchloride) (PDDMAC) and poly(allylamine hydrochloride) (PAH) by using the spin-assembly method. Spin assembled colloids with alternating cationic binders can result in the increase of film growth and also optical properties. Construction of such multilayer thin films comprised of polyelectrolytes and organic/inorganic [17,18], and metallic colloids [19,20], which lead to thin films with novel optical [21], electrical [22] and magnetic [23] properties.

Nanometallic particles such as Ag(0), Au(0), Pd(0) and Cu(0) can be easily incorporated into polyaniline or polypyrrole matrices by one step oxidation–reduction mechanism as these metal ions have suitable oxidation potentials to polymerize the monomer unit [24–29]. Wang et al. showed that metal nanoparticles of Ag, Au and Pt with reasonable size dispersity can be obtained by using conducting polymer colloids as reducing agents [30]. Dong et al. showed that multilayers of Au–mercaptoethanesulphonate(MES)–PAni or Fe₃O₄–PDDMAC can be fabricated using ion–dipole/electrostatic interactions [31,32]. Multilayers of Au–PDDMAC were obtained by thermally reducing AuCl₄[−]–PDDMAC⁺ complex [33].

We recently demonstrated that the polyelectrolyte PDDMAC and PAni can be blended in an in situ polymerization mechanism to give electrochemically active, processable conducting polyaniline films [34]. Thinking further, we have planned to use PDDMAC as mother matrix to keep and carry colloidal polyaniline and gold nanoparticles to form a homogeneous ternary composite. Presence of PDDMAC in the composite acts as stabilizer for the conducting polyaniline, gold nanoparticles and also restricts the conducting polyaniline to grow only to the nanodimensions. In the present communication, we describe an effective and novel one step method for the formation of ternary composite. We used the anion–cation pair [AuCl₄][−]–[PDDMAC]⁺ as an oxidizing agent from which [AuCl₄][−] oxidatively polymerizes aniline and concomitantly deposits on/in the polyaniline and PDDMAC as a nanosized Au(0) metal particles. Different ternary composites with gold and polyaniline concentrations were synthesized, characterized and used for dopamine sensing.

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2. Experimental

2.1. Methods and materials

PDDMAC (35 wt% in water, average Mw <100,000) is purchased from Aldrich chemical company. All other chemicals (C.D.H. Chemicals, India) are analytical grade and used as received. X-ray diffraction patterns (XRD) were obtained with PANalytical MPD diffractometer using Cu K α radiation. FT-IR spectra of KBr powder pressed pellets were recorded on model no. nexus-670 spectrometer from Thermo Nicolet. Cyclic voltammetry was performed on AUTOLAB 302 electrochemical system using three electrode assembly consisting of a glassy carbon (2 mm diameter) working electrode, a glassy carbon rod (8 cm long, 2 mm dia) auxiliary electrode and a SCE as reference electrode. Dopamine sensing was carried on GC electrode adsorbed with binary (B1) (PAni–Au) and ternary composites (T1–T6) (PAni–PDDMAC–Au) using cyclic voltammetric method in buffer of pH 7.4.

TEM experiments were conducted on FEI make Tecnai-20-G² machine with tungsten filament at 200 kV. X-ray photoelectron spectroscopic (XPS) analyses were carried out on ThermoFisher

Scientific (model no. multilab 2000) X-ray photoelectron spectrometer. The stability and the amount of Au within the composite was determined by thermogravimetric analysis (TGA) on TA instruments Inc., on model SDT Q600 from room temperature to 900 °C at a heating rate of 20 °C/min in an air atmosphere. The conductivity was measured by a four-probe meter connected to a KEITHLEY nanovoltmeter and a source meter at room temperature using cast films on glass slides.

2.2. Synthesis of binary composite PAni–Au (B1)

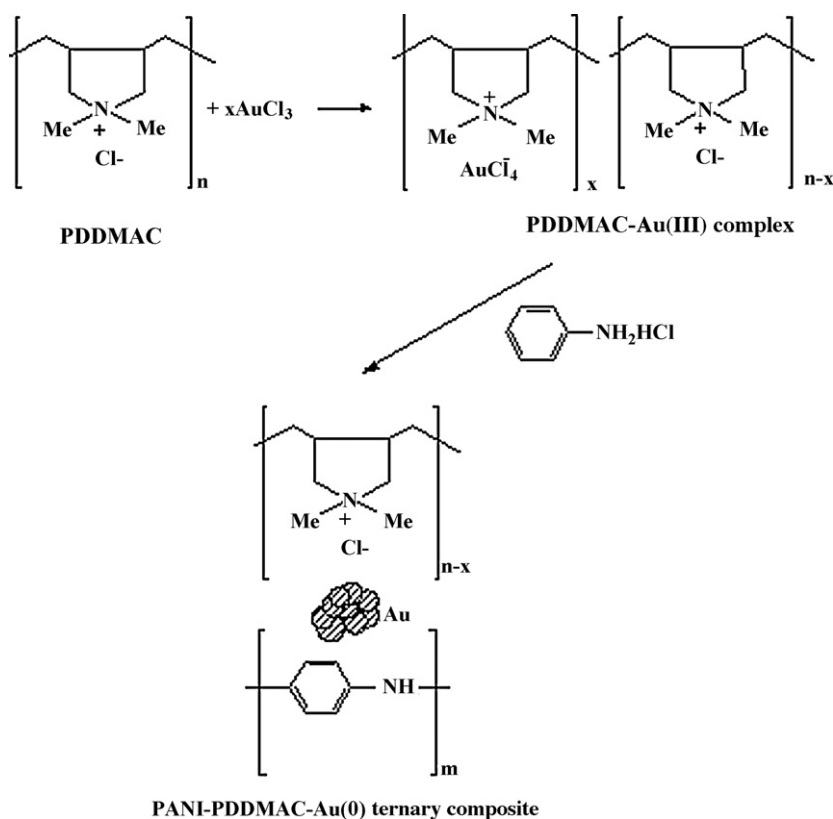
Gold(III) chloride (0.25 mM) was dissolved in 50 ml water and anilinium hydrochloride (2 mM) in 20 ml of water was added dropwise. The mixture was stirred for 12 h at RT and the PAni–Au composite was centrifuged and washed 3 times with water. The product was finally dispersed in 50 ml of methanol.

2.3. Synthesis of ternary composites (T1–T6)

In typical experiment, 5 ml of PDDMAC was dissolved in 45 ml water with 0.5 mM of AuCl₃ (in 15 ml water). The yellowish float-

Table 1
Initial compositions of reactants for synthesis of binary and ternary composites and the conductivities of the resulting composites.

Composite	Composition			Conductivity of the cast film (S/cm)
	Au(III)Cl ₃	Aniline	PDDMAC	
B1	0.25 mM	2.0 mM	–	
B2 ³⁴	–	10.0 mM	5 g	4.5 × 10 ^{–6}
T1	0.25 mM	2.0 mM	5 g	148 × 10 ^{–6}
T2	0.25 mM	10.0 mM	5 g	26 × 10 ^{–6}
T3	0.50 mM	2.0 mM	5 g	217 × 10 ^{–6}
T4	0.50 mM	5.0 mM	5 g	101 × 10 ^{–6}
T5	0.50 mM	10.0 mM	5 g	60 × 10 ^{–6}
T6	0.50 mM	50.0 mM	5 g	–



Scheme 1. Scheme showing the synthetic strategy of the ternary composite.

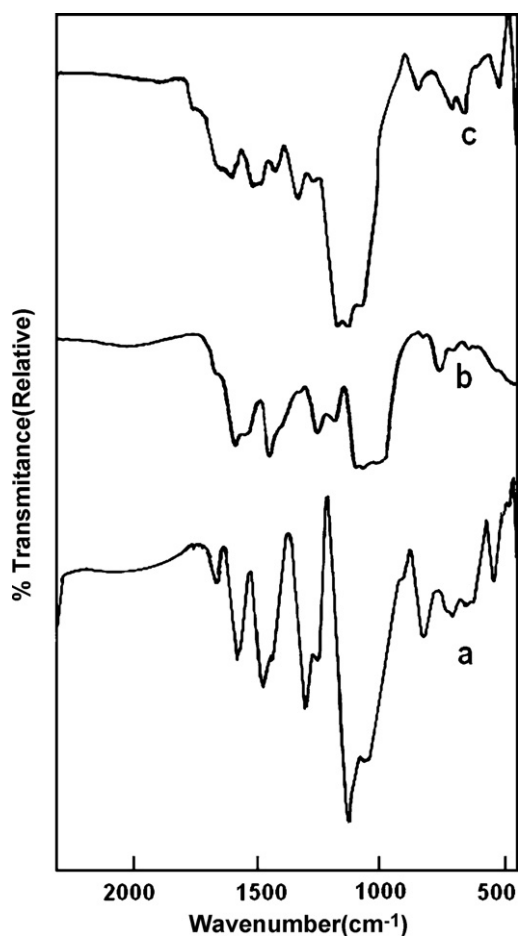


Fig. 1. FT-IR spectra of (a) PANi-HCl, (b) PANi-Au (B1) and (c) PANi-Au-PDDMAC ternary composite (T1).

ing precipitate was subjected for sonication for 20 min to disperse homogeneously. Anilinium hydrochloride (0.2 g; in 10 ml water) was added to the above solution and stirred for 12 h at room temperature by which time the entire solution became green colour. The material was collected by centrifuge and washed couple of times with 10–15 ml of water. The purified sample was dispersed in 50 ml of methanol and used for characterization and dopamine sensing. Table 1 lists of the preparative conditions used in synthesis of various binary and ternary composites.

3. Results and discussion

3.1. Mechanism of formation and characterization of the composites

The ternary composite containing PDDMAC, polyaniline and gold nanoparticles is conveniently synthesized according to the strategy shown in Scheme 1. The concentrations of gold chloride and aniline are varied, keeping PDDMAC concentration constant and the synthesized ternary composites are listed in Table 1 along

Table 2

FT-IR spectral data for the composites and its constituents.

Polymer/composite	Wavenumbers (cm ⁻¹)									
	C-H _{op}	C-N _(ar)	N-B-N	N-Q-N	CH _(ar)	N-H	C-H _(alk)	C-N _(alk)	C-H _n	O-H _(st)
PAni/HCl	794.7	1294	1474	1116,1574	2923	3438	–	–	–	–
B1	826	1303	1494	1150,1583	2924	3430	–	–	–	–
T1	794.1	1306	1493	1150,1579	2923	3415	1473	1118	3000–2857	3446

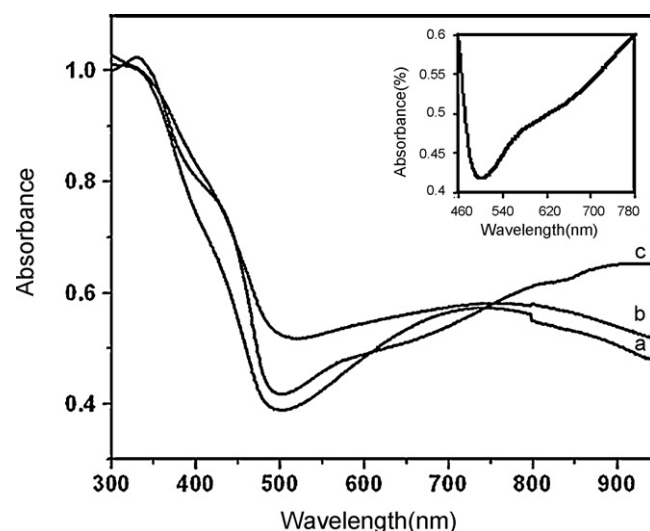


Fig. 2. UV-vis spectra of the composites (a) T2, (b) T5 and (c) T3. Inset in the figure shows surface plasmon band at 550–570 nm due to gold nanoparticles.

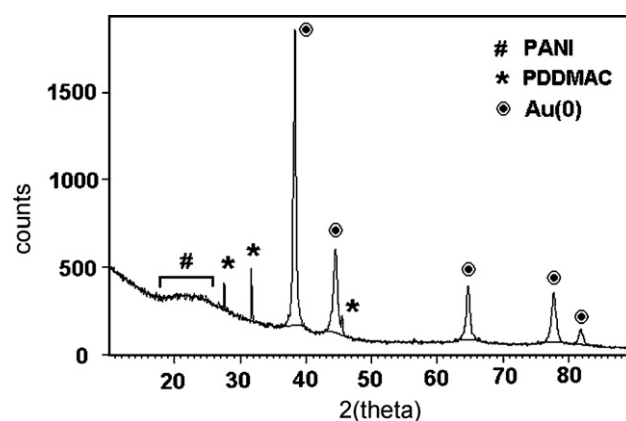
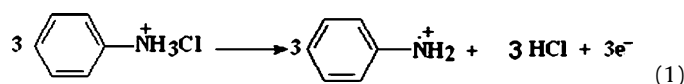
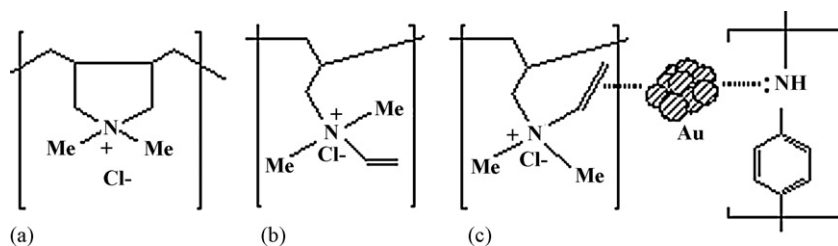


Fig. 3. XRD profile for the representative composite T4.

with their surface conductivity data. Upon mixing AuCl₃ with PDDMAC, which contain free Cl⁻ ions, a yellow anionic complex AuCl₄⁻ is formed and is homogeneously dispersed by sonication. When stoichiometric aniline is added to this complex solution, polyaniline is formed due to the oxidation of aniline by AuCl₄⁻ complex. The reaction proceeds with concomitant incorporation of Au(0) nanoparticles on/in to the polyaniline and PDDMAC. The following reaction sequence would take place during polymerization of aniline monomer units. Three free electrons are produced upon the oxidation of three monomer units of aniline (step 1) and are consumed by one unit of Au³⁺ to get reduced to Au(0) (step 3). The anilinium radical cations formed in step 1, after 1,4 coupling, yield doped polyaniline (step 2).





Scheme 2. Scheme showing the structure of (a) pure PDDMAC, (b) its major contaminant and (c) stabilization of gold particles by PANI and PDDMAC.

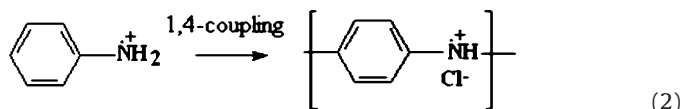


Fig. 1 shows the FT-IR spectrum (the data are collected in Table 2) of (a) PANi-HCl, (b) PANi-Au (B1) and (c) T1. The binary composite B1 showed the characteristic peaks at 1583 and 1494 cm^{-1} corresponding to the C=C stretching of quinonoid and benzenoid rings [35]. The above quinonoid band showed tendency to split into another peak at 1629 cm^{-1} suggesting interaction with Au(0) particles. Peaks at 1303 and 1243 cm^{-1} are related to the C-N and C-N⁺ stretching modes [36], the peak at 1150 cm^{-1} is assigned to the in-plane bending of C-H [37] and the peak at 826 cm^{-1} is attributable to the out-of-plane bending of C-H [38].

For ternary composites, e.g., T1, the broad band at 3415 cm^{-1} is due to N-H stretching of polyaniline, which is also mixed with O-H stretching vibration of water arising due to moisture absorption of the composite. Bands at 1578 and 1493 are C=C stretching of quinonoid and benzenoid segments of polyaniline chain, respectively. Further, these two bands showed tendency to split into another two peaks at 1637, 1473 cm^{-1} due to $\nu_{\text{C}=\text{C}}$ of PDDMAC [39,40]. More over, the intensity of these two bands is greatly reduced in the composite suggesting possible π electrons interaction with gold clusters, akin to π - π interactions of PDDMAC-CNTs [40]. It was earlier [40] shown that PDDMAC-CNT composite is mainly stabilized by allylic π electrons from the PDDMAC's main contaminant, structure (b) (Scheme 2). The C-H stretching of polyaniline which appear as doublet type peaks at 1140 and 1000 cm^{-1} appear as triplet at 1150, 1105, 1041 cm^{-1} due to PDDMAC. Overall, the FT-IR spectrum of the composite showed the formation of polyaniline in presence of PDDMAC and the gold clusters in the composite are stabilized by (PDDMAC) π ...Au...N(PANI) and π (PANI) interactions, as shown in structure (c), Scheme 2. The conductivity (Table 1) exhibited by the composites are relatively high compared to pure PANi-PDDMAC binary composite (B2) studied in our earlier communication [34]. Pure PANi-PDDMAC (1 ml:5 ml) binary composite (B2) film showed 4.5×10^{-6} S/cm whereas the present ternary composites with gold concentrations 0.25, 0.50 mM (T2 and T5) showed 26×10^{-6} and 60×10^{-6} S/cm, respectively which is attributed to the presence of gold clusters on the surface of the polymers. It is also observed that when gold concentration is fixed, the conductivity of the ternary composites decreases as the concentration of aniline increases. This is so because, the gold nanoparticles are distributed on to higher amounts of polyaniline formed when the concentration of aniline is increased and the connectivity of the surface by gold nanoparticles is decreased. Similarly when the concentration of aniline is kept constant and concentration of gold chloride is increased, we observe similar trend of increase in surface conductivity due to increase in overall gold concentration. The following order is observed for the surface conductivities exhibited by the ternary

composites:

$$\sigma(\text{T5}) < \sigma(\text{T4}) < \sigma(\text{T3}) \quad (\text{when } C_{\text{AuCl}_3} \text{ is constant})$$

and

$$\sigma(\text{T1}) < \sigma(\text{T3}) \quad (\text{when } C_{\text{aniline}} \text{ is constant})$$

The UV-vis spectrum of PANi-Au (B1) composite showed surface plasmon band at 556 nm due to gold nanoparticles with moderate intensity. The spectrum (Fig. 2) for T3 nanocomposite primarily has shown two categories of bands; one set due to polyaniline system and another weak band due to the presence of gold nanoparticles. This weak shoulder centered between 550 and 570 nm is due to surface plasmon absorption of gold nanoparticles, which in many composites is masked by high intensity PANI bands and hence is seldom seen. It is also known that the surface plasmon resonance

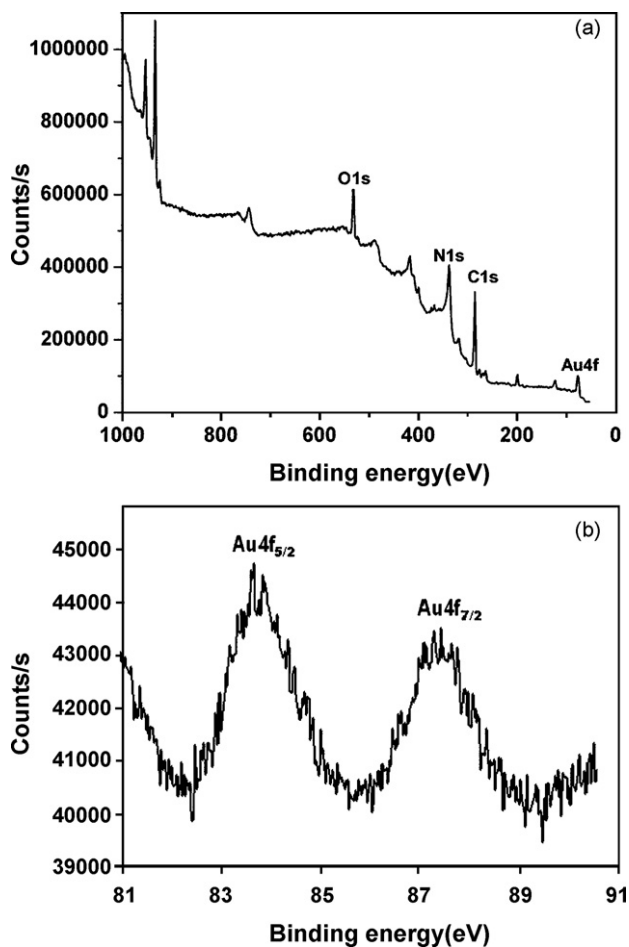


Fig. 4. XPS spectrum for the composite T1 (a) survey spectrum and (b) zoomed spectrum showing bands due to Au(0) particles.

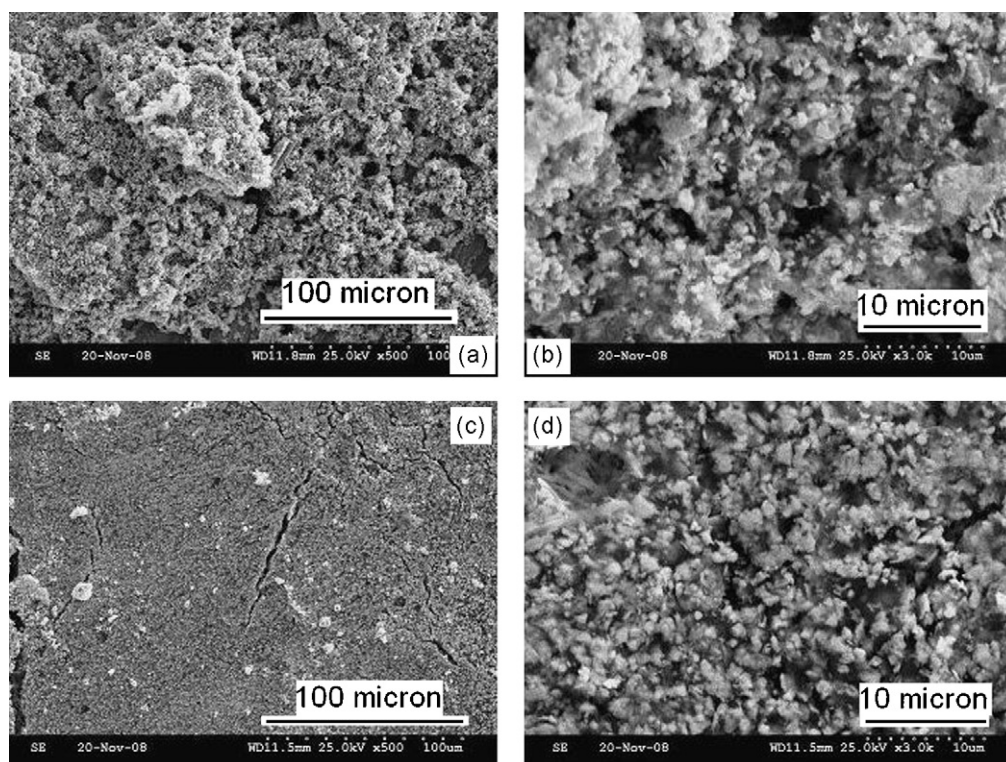


Fig. 5. SEM pictures of the binary composite B1 at magnification (a) 500 \times (b) 3000 \times and ternary composite T1 at magnification (c) 500 \times and (d) 3000 \times .

bands of metal NPs are sensitive to their surrounding environment [41]. The absorption peak position and its intensity can be changed if the dielectric constant of the medium is changed. Moreover, the strong absorption of conducting polyaniline can also lead to the lack of observation of a peak in the same region. The characteristic peaks of PANi in the composite appear at 357, 430, and around 800 nm, which are attributed to π - π^* , polaron- π^* , and π -polaron transitions, respectively [42,43].

The XRD spectra of the composites confirmed the presence of the gold in the nanocomposite. A representative XRD profile is shown for composite T4 (Fig. 3) with peaks at $2\theta = 38.21^\circ$, 44.42° , 64.58° , 77.61° and 81.77° due to the Bragg reflections corresponding to the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) sets of lattice planes which may be indexed based on the fcc structure of gold. Further, a broad absorption between $2\theta = 10$ – 25° (shown as #), is also seen due to amorphous polyaniline material. Peaks at $2\theta = 27.50^\circ$, 31.70° are due

to crystalline regions of PDDMAC (shown as *) matrix, all indicating the presence of three components in the system. XPS was also used to characterize the composites. The survey and zoomed XPS spectrum for representative sample T1 is shown in Fig. 4. The zoomed spectrum showed two distinct bands at binding energy of 83.7 and 87.6 eV for Au_{5/2} and Au_{7/2} shells, respectively, which are typical value for Au(0) state [42,44,45].

3.2. Morphology, composition and stability

The morphology of the composites was examined by SEM, AFM and TEM techniques. Scanning electron micrographs (Fig. 5) showed that the binary composite B1 is a micrometer sized material in the form of flakes and powder (a), the powder being evenly distributed on the flakes giving a porous structure to the composite (b). In contrast the ternary composite T1 is composed of bigger

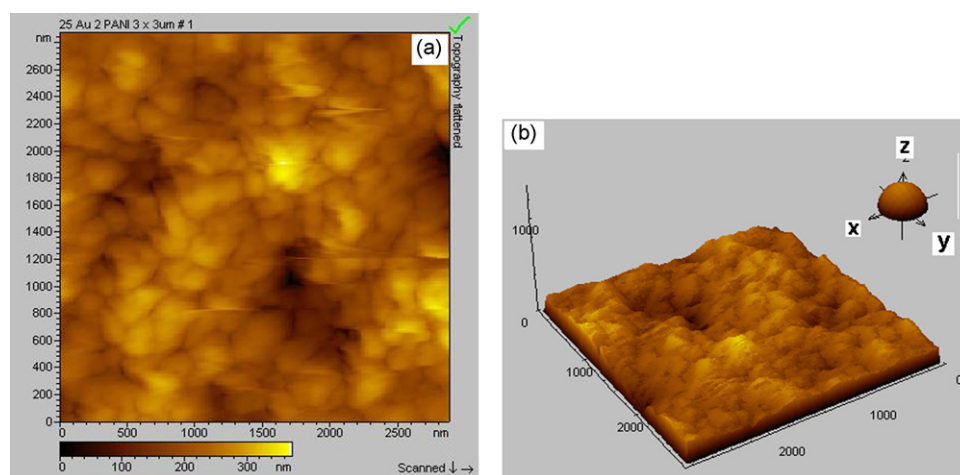


Fig. 6. Atomic force micrographs of composite T1 self assembled on GC electrode: (a) flattened image and (b) topography.

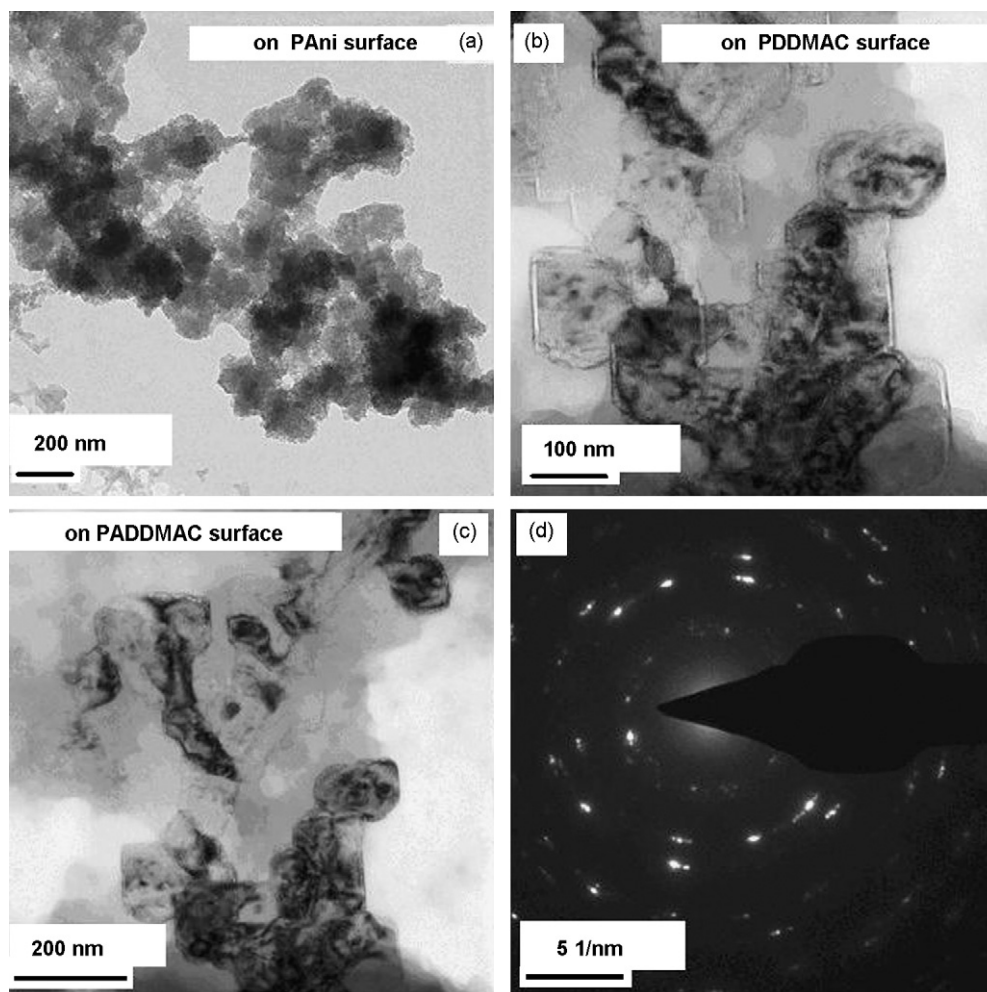


Fig. 7. TEM pictures of the ternary composite T1: (a) gold particles on PANi surface (b) and (c) gold particles on PDDMAC surface (d) SAED picture of the above composite.

flakes (c) which appear like a thick film. There is also deposition of micro-islands (c) which on magnification show particle type morphology (d). Overall, the study showed that in presence of PDDMAC, the composite formed more aggregated structures.

Fig. 6 shows the atomic force micrograph of the self assembled layer of the composite T1 on the GC electrode. The flattened image (a) shows that the oval type particles are distributed evenly on the electrode with their diameters in the range 100–200 nm. The topography (b) shows that the surface is not very smooth but is composed with few voids.

The TEM analysis (Fig. 7) on the sample T1 showed that the gold particles are aggregated and do not occur as small size particles. They spread over few hundred nanometers on both polyaniline (a) and PDDMAC (b, c). The thick and bright spots due to electron diffraction of gold particles (d) also suggest that the particles are considerably big. In contrast, the distribution of gold particles on PANi in B1 is even and individual particles are seen (Fig. 8(a, b)) which are less than 50 nm. Thus the presence of PDDMAC in ternary systems leads to more aggregation of the gold nanoparticles. This is due to localization (or the less mobilization) of oxidizing species AuCl_4^- in PDDMAC⁺ matrix due to ion-pair formation and their interaction. In case of B1, the oxidizing species AuCl_3 is evenly distributed in water reaction medium (no ion-pair formation) and deposited on PANi evenly. Hence the deposits are seen as individual particles. The SAED picture taken on this sample shows circular rings from gold particles are seen and are identified as (1 1 1) and (2 0 0) planes of Au(0) in fcc arrangement.

All the composites are hygroscopic and are best stored as aqueous or methanol dispersions, which are stable up to few months. TGA studies showed that the moisture and doped HCl are lost up to 240 °C. There is a continuous degradation of the composite up to 500 °C. The composite T5 leaves polymeric and gold residues of 24.4 wt% at 550 °C. The standard PANi–HCl and PDDMAC polymers together leave about 17 wt% residues at this temperature. Thus the final residual of about 7.4 wt% is due to gold incorporation in the composite.

3.3. Electrochemical sensing of dopamine

Dopamine (DA) is an important neurotransmitter in mammalian central nervous systems and the loss of DA-containing neurons may lead to serious disease known as Parkinson's disease. The detection of DA has therefore been a subject of considerable interest in recent times in electro-analytical chemistry. It is well known that conducting polymers such as polyaniline and polypyrrole exhibits good electrochemical behavior and have been applied to the field of chemically modified electrodes for detection of biomolecules [46,47]. In the present investigation, a GCE has been modified by the synthesized composite by way of dipping the GCE for 60 s in methanol solution of the composites.

First the immobilization of the ternary composite on the GC electrode was established by scanning the potential of the electrode between –0.2 and 1 V vs SCE in 1 M sulphuric acid electrolyte. Fig. 9 shows the typical cyclic voltammogram of the composite T5,

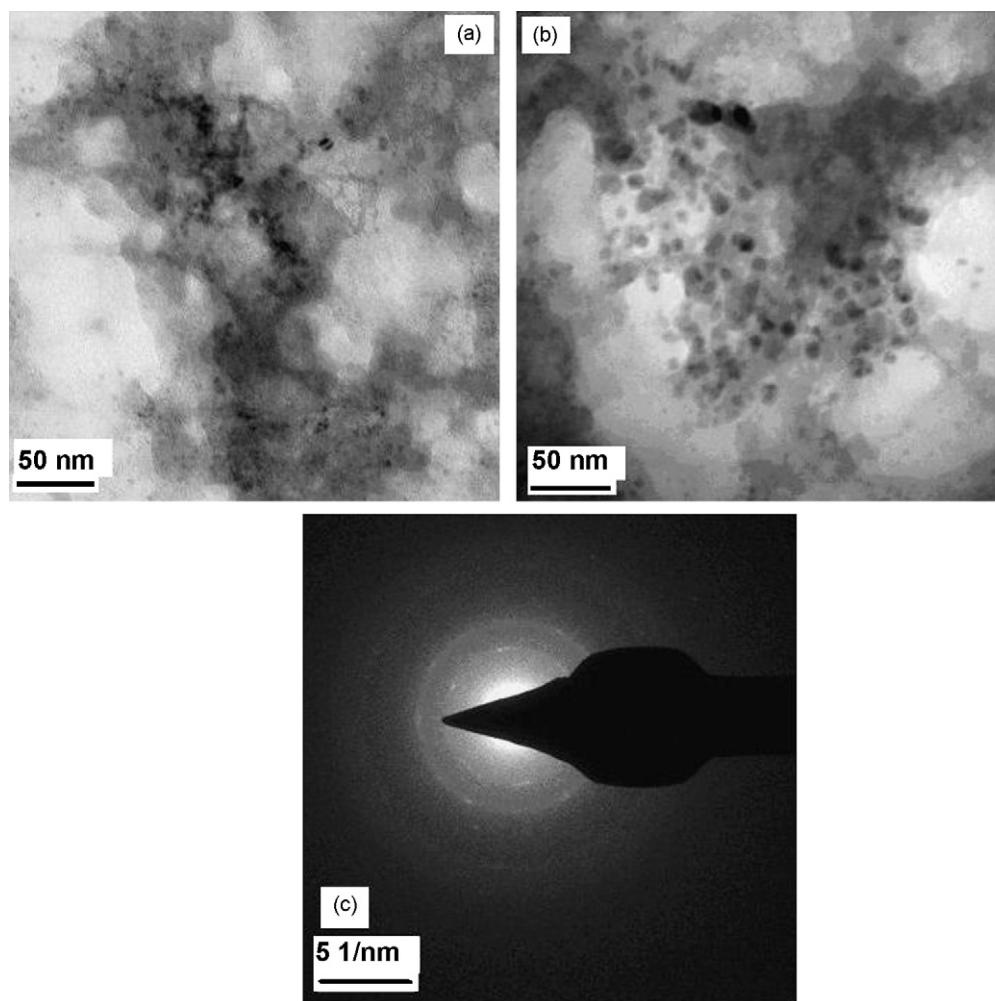


Fig. 8. TEM images of the binary composites B1 (a) and (b) distribution of gold particles on PANi and (c) SAED picture of the above composite.

which is similar to the literature [48], i.e., it exhibited two separate redox peaks in 1 M sulphuric acid solution. The first oxidation wave around $E_{SCE} = 0.248$ V is assigned to the transition of leucoemeraldine to emeraldine salt, and the second oxidation wave around $E_{SCE} = 0.672$ V is due to the transition from emeraldine salt to the pernigraniline state. The middle peak at $E_{SCE} = 0.490$ V is due to

degradation product quinone/hydroquinone. It is to be noted that the formation of the middle peak is observed only in the composites where higher concentrations of aniline (T2 and T5) is used suggesting formation of more impurities/degradation products.

Cyclic voltammetric profile (Fig. 10) shows the oxidation of various concentrations of dopaminehydrochloride using the modified

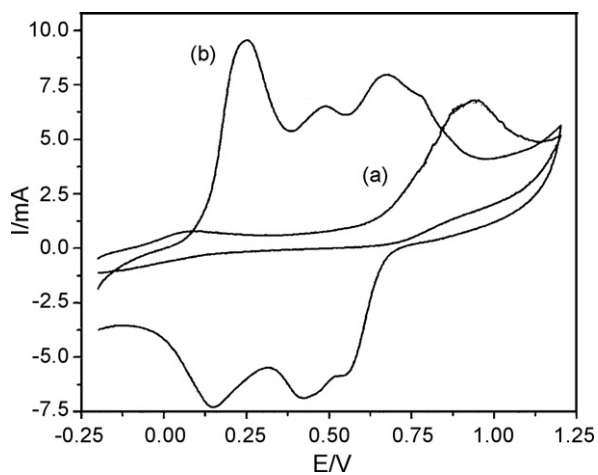


Fig. 9. CV profile of the T5-GC electrode at pH 7.4 (a) and pH 1 (b) at a scan rate of 50 mV/s.

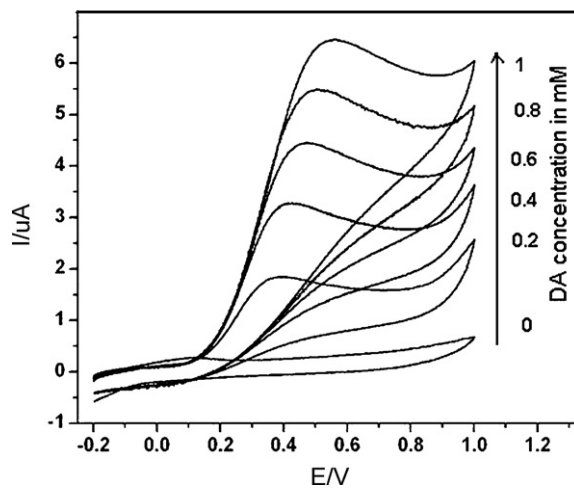


Fig. 10. The CV profiles of oxidation of dopamine by the composite T1 on GC electrode at pH 7.4 at a scan rate of 50 mV/s.

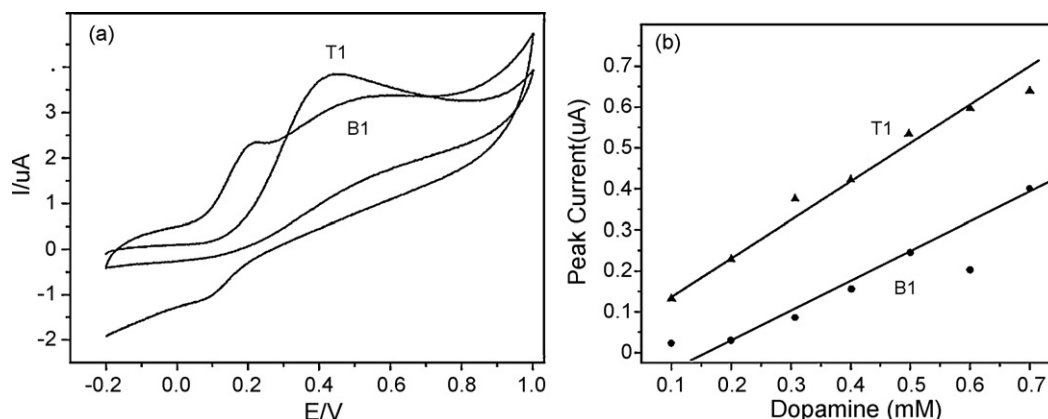


Fig. 11. Electrochemical comparison of the ternary system (T1) with binary system (B1): (a) oxidation of dopamine on GC electrode at pH 7.4 at a scan rate 50 mV/s and (b) calibration plot for dopamine sensed by T1 and B1.

electrode in pH 7.4 for the representative composite T1. The oxidation peak in the presence of DA appears at 0.361 V and is attributed to the oxidation of DA to dopaminequinone [49]. Important observation here is that the anodic current of the our modified GCE (with T1) is observed at a less positive potential compared with that polyaniline-modified GCE in literature [42], implying that the ternary composites is catalytically effective in the oxidation of DA. However, it is to be noted that though oxidation peak current is increased with the gradual addition of DA, there is a positive shift in the potentials. This is because there is only a low level of loading of the composite is possible by the adsorption process which leads to ratio-mismatch between the concentration of the composite and dopamine at higher concentrations of DA. Fouling of the modified electrode due to the adsorption of polymeric product [49] may also be another reason. In the absence of protonic acid in the electrolytic medium, dopamine is oxidized to melanin-type polymeric material and inhibit electron transfer [49]. The efficiency of the ternary system in sensing DA is compared with binary system B1. Fig. 11(a) shows that the currents observed by B1 are less compared to T1 and also occur at less positive potentials for ternary system T1 (Fig. 11(b)). Thus the catalytic efficiency improved is due to the presence of PDDMAC in the ternary systems.

The present modified ternary electrodes are useful in sensing DA as low as 50 μM . Fig. 12 shows calibration plots for DA sensed by composites T2, T3 and T5. The plots are found to be linear with correlation coefficients (R^2) 0.98, 0.99, 0.95 with decreasing order of

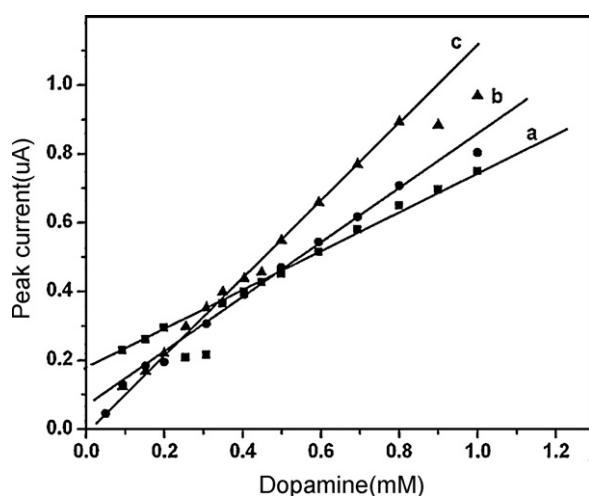


Fig. 12. Calibration plot for dopamine sensed by composites (a) T5, (b) T3 and (c) T2.

their slopes 0.98, 0.80 and 0.62 $\mu\text{A}/\text{mM}$, respectively. The optimum dipping time is selected at 60 s and the sensing properties are not influenced by increasing the time. The influence of gold: polyaniline ratio in the composite on the performance of dopamine sensing is also tested by using the composite T6. The results showed that the oxidation potential of dopamine is shifted too positive (above 0.7–0.8 V) and the sensing is improper for lower dopamine concentrations which is possibly attributed to lowering of gold particles concentration on increased polyaniline amounts derived from higher (50 mM) aniline concentration used. Thus composites T1 to T6 are good sensing materials for dopamine.

4. Conclusions

We demonstrated that a stabilized ternary composite can be formulated using a conducting polymer polyaniline, a polyelectrolyte PDDMAC and gold nanoparticles. The polymer PDDMAC acts not only as the component of the ternary system, but also as stabilizer and carrier of polyaniline and gold particles. It is shown that gold nanoparticles are distributed and stabilized by both the polymers evenly. The conductivities of the ternary composites are higher than binary composite involving PANi and PDDMAC, which is attributed to the presence of gold clusters. The composites can be self assembled on to a glassy carbon electrode and are useful in sensing dopamine as low as 50 μM concentration at physiological pH conditions at lower potential values. The ternary composites are also more catalytically active in sensing dopamine compared to the binary composite (B1) without PDDMAC.

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