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In situ synthesis of gold–polyaniline composite in nanopores of polycarbonate membrane

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Abstract In situ one-step chemical synthesis route for the preparation of a gold–polyaniline composite in nanopores of polycarbonate (PC) membrane is reported. PC membrane, which was placed in a specially designed two-compartment cell, separated the aqueous solution of aniline from $HAuCl_4$ solution. Concentration gradient across the membrane caused movement of $AuCl_4^-$ and anilinium ions in the pores of polycarbonate membrane. Nanopores in PC membrane acted as reaction vessels where aniline and $HAuCl_4$ were allowed to mix together, and the redox reaction between aniline and $HAuCl_4$ led to the formation of gold–polyaniline composite. The gold–polyaniline composite in PC membrane was characterised by EDXRF, XRD, UV–Vis spectroscopy, FTIR and TEM. Peak broadening in XRD suggests that Au particles formed in the membrane are nanocrystallites and average crystallite size is (24 ± 4) nm. TEM studies show that gold nanoparticles are randomly dispersed in polyaniline clusters formed in the nanopores of PC membrane. Characterisation results show that the surfaces of the PC membrane exposed to $HAuCl_4$ and aniline have significantly higher concentrations of Au nanoparticles and polyaniline, respectively.

Introduction

Composites of electrically conducting polymers and metal nanoparticles are finding great interest not only because of scientific curiosity, but also for their potential applications in molecular electronic devices, gas sensors, biosensors, capacitors and catalysts [1–6].

Amongst the conducting polymers, polyaniline is of much interest because of its great environmental stability, controllable electrical conductivity and interesting electrochromic properties associated with different redox states [7–11]. Polyaniline nanowire has better electronic properties than polyaniline and thus has better gas sensing capability (higher sensitivity). The incorporation of metal nanoparticles in the polymer matrix produces composites with improved physical and chemical properties and performance superior to polymer and metal nanoparticles alone [6]. Therefore, polymer/metal composites find more widespread applications in catalysis, sensing, electronics, etc. than either polymer or metal nanoparticles alone. Gold nanoparticles of different shapes and sizes have been extensively studied due to their unique electronic, optical, sensing and catalytic properties [12–24]. Gold nanoparticles are very stable and their surface can easily be functionalised by self-assembling of organic molecules through sulphur atom. Gold–polyaniline composite, prepared by incorporation of gold nanoparticles into polyaniline matrix, has good stability, high conductivity and the unique optical properties. Many reports show that incorporation of gold nanoparticles in polyaniline matrix significantly enhances its electrocatalytic and sensing properties [25–30].

Many chemical and electrochemical methods have been developed for synthesis of gold–polyaniline composite. Preformed polyaniline has been used for the preparation of gold–polyaniline composite by exploiting multiple-oxidative states of polyaniline [31]. Completely reduced state of polyaniline (viz. leucoemeraldine) acts as a reductant for $AuCl_4^-$ reduction to Au. Polyaniline is prepared by either chemical or electrochemical oxidation of aniline [32, 33]. Chemical synthesis of polyaniline is carried out by

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oxidising aniline using ammonium persulphate as the oxidising agent. Polyaniline and gold–polyaniline composite are prepared as powder or precipitate in solution. Electrochemical oxidation of aniline is carried out by using any of the three methods viz. galvanostatic, potentiostatic or potentiodynamic. In electrochemical synthesis, polyaniline and gold–polyaniline composite are prepared as film of varying thickness on various conducting substrate—gold, platinum, indium tin oxide, and various carbonaceous electrodes. For putting these polymer/metal composites in real world applications, it is desirable to immobilize them on some support/substrate. Therefore, electrochemical synthesis is more favored than chemical synthesis for sensors and catalysis.

$AuCl_4^-$ had been used as an oxidant for oxidative polymerisation of pyrrole [34, 35], hexadecylaniline [25], *o*-anisidine [36] and aniline [26] resulting in formation of gold–polymer composite. Chemical synthesis of a gold–polyaniline composite is based on the oxidising properties of auric acid. $AuCl_4^-$ is reduced to Au^0 by aniline accompanying the simultaneous oxidation and polymerisation of aniline to polyaniline at acidic pH. One-step chemical synthesis of gold–polyaniline composite involves mixing of aniline and gold salt ($HAuCl_4$), and the redox reaction between them leads to the formation of gold–polyaniline composite. Preparation of gold–polyaniline composite using H_2O_2 [37], which acted as both oxidising and reducing agent, as well as using HBF_4 [38] was reported. Polyaniline nanoballs of a few microns size and decorated by gold nanoparticles (10–50 nm) were prepared in toluene solution by using a phase transfer catalyst [39]. Nanofiber-shaped polyaniline was synthesised using $HAuCl_4$ but polymer and metal particle got completely phase separated [40]. Two-step synthesis of gold–polyaniline composite was carried out using 10-bromodecylperoxide, which acted as a stabiliser of the gold nanoparticles as well as the oxidant for aniline [41]. Electrochemical synthesis of gold–polyaniline composite was also reported [29, 38]. For technological applications, it is desirable to have the gold–polyaniline composite of high surface area, high dispersion of gold nanoparticles into the polyaniline matrix, and an intimate contact between gold nanoparticles and polyaniline. Some of the preparation methods suffered from drawbacks, like poor dispersion of Au into polyaniline matrix or lack of intimate contact between gold and polyaniline that prevent the attainment of all the desired properties.

Mechanical properties such as miscibility, process ability, water resistance and transparency make PC an important matrix for dispersion of nanoparticles. Nanostructured composite film based on dispersion of thiol-coated gold nanoparticles in PC was prepared by evaporating a solution of PC and thiol-coated Au nanoparticles in $CHCl_3$ [42]. This composite film was developed for applications as optical lenses. PC membrane has been used as a template for the preparation of nanostructured materials [43]. Nanowires of metals and conducting polymer were electrodeposited in pores of PC membrane [44]. Synthesis of polypyrrole nanowires in PC membrane was reported using chemical method. PC membrane was placed between a two-compartment cell, pyrrole was added in one compartment and oxidant ($FeCl_3$) in other compartment. Pyrrole got converted to polypyrrole through a polymerisation reaction within each pore as oxidant diffused through these nanopores due to concentration gradient [45, 46].

In this communication, we report an in situ chemical synthesis route for the preparation of a gold–polyaniline composite in a PC membrane. PC membrane was placed in a specially designed two-compartment cell, separating the aqueous solution of aniline from $HAuCl_4$ solution. Concentration gradient across the membrane caused movement of $AuCl_4^-$ and anilinium ions in the pores of PC membrane. Nanopores existing in PC membrane acted as reaction vessels where aniline and $HAuCl_4$ were allowed to mix together, and the redox reaction between aniline and $HAuCl_4$ led to the formation of gold–polyaniline composite. The nanopores also control the growth of gold–polyaniline composite. These composites are promising to immobilze enzymes or other analyte selective molecules. Polycarbonate membrane with nanopores acts as a supporting matrix for immobilization of gold–polyaniline composites synthesised by chemical route. Studies were, therefore, carried out to characterise gold–polyaniline composite prior to exploiting them for various applications.

Experimental

Reagents

Nucleopore track-etched porous PC membrane with a pore diameter of 200 nm and thickness of 10 μm was obtained from Whatman Ltd. Hydrochloric acid, aniline and $HAuCl_4$ used were of analytical grade. Deionised water (18 MΩ/cm) purified by the MilliQ water purifier system from Millipore was used throughout the present studies.

Synthesis and characterisation of Au-PANI composite

The porous PC membrane (diameter = 1 cm) was sonicated in water for 5 min. It was placed in a specially designed two-compartment cell as shown in Fig. 1a. Solutions of 10 mM $HAuCl_4$ in water and 0.5 M aniline in 1 M HCl were filled in two compartments. The cell was

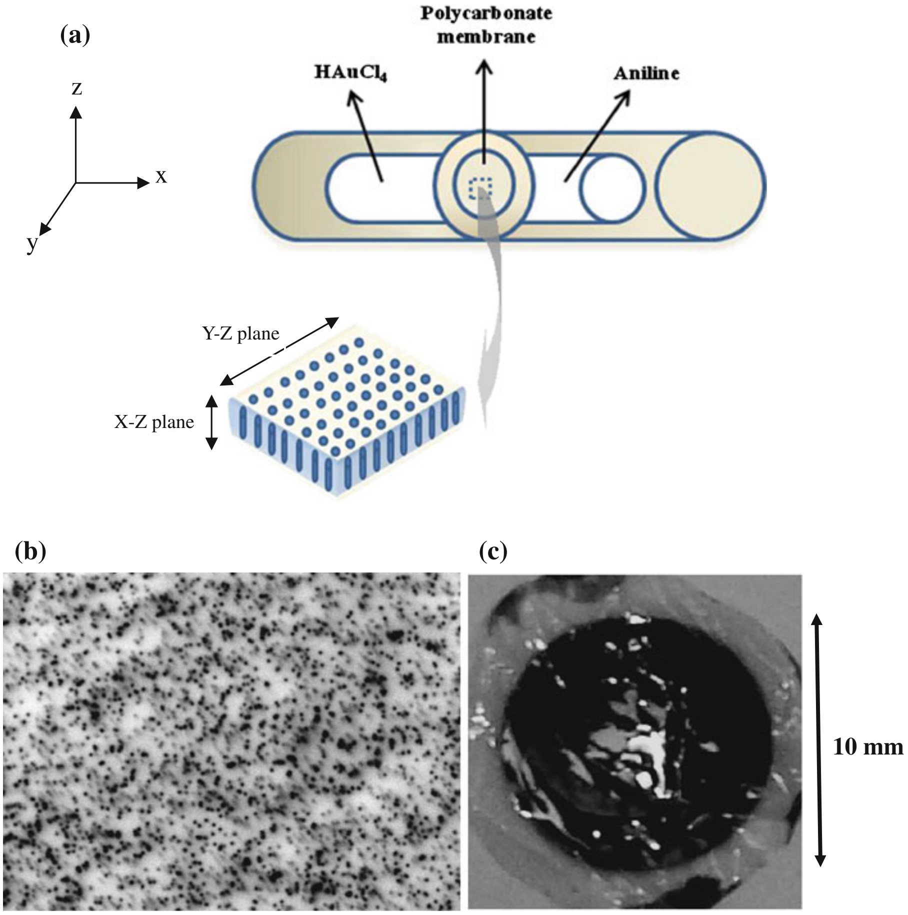


Fig. 1 **a** Schematic of two-compartment cell. **b** SEM image of the porous polycarbonate membrane (36 μm × 27 μm). **c** Photo of the PC membrane containing gold–polyaniline composite. Porous PC membrane separates the two compartments

kept undisturbed overnight to allow the redox reaction between aniline and $HAuCl_4$. The polycarbonate membrane has good chemical resistance in dilute acid solution. The cell was kept undisturbed overnight. The membrane was then washed thoroughly in water and allowed to dry in air. Similar experiments were repeated to prepare gold–polyaniline composite in PC membrane with different preparation times by keeping the cell undisturbed for 2, 4 and 8 h. Energy dispersive X-ray fluorescence measurement of membrane was carried out using Jordan Valley EX-3600 TEC EDXRF spectrometer having Rh target operated at voltage of 40 kV and current of 170 μA. XRD patterns were recorded on STOE XRD unit using Cu target (Cu $K_\alpha = 1.5406$ Å) with graphite monochromator. Absorbance spectra of membrane were recorded using a UV–Vis spectrophotometer (QE65000, Ocean Optic Ltd.). The absorbance spectra were measured in air by placing the membrane in a quartz cell. FTIR spectra were recorded in ATR mode using JASCO FTIR 610 spectrophotometer with a resolution of 4 cm^{-1}. TEM was performed using a JEOL 2000 FX microscope. Sample preparation for TEM experiment was carried out by dissolving the PC membrane containing gold–polyaniline composite in dichloromethane and solution was pipetted onto carbon-coated copper grids.

Results and discussion

Figure 1b shows the SEM image (36 μm × 27 μm) of the porous polycarbonate membrane. The black spots in the image are the nanopores present in the PC membrane. Pores are distributed randomly throughout the membrane surface. Figure 1c shows the photograph of gold–polyaniline composite loaded PC membrane. The dark-coloured 10 mm diameter circle is the region where gold–polyaniline composite is immobilized into nanopores in PC membrane. The loading and reduction of $AuCl_4^-$ by aniline in the pores of the 10 μm thick PC film was confirmed by EDXRF analyses. Significant difference in the concentration of Au was observed on $HAuCl_4$-exposed and aniline-exposed surfaces of the PC membrane where redox reaction between aniline and $HAuCl_4$ was allowed overnight. It is seen from Fig. 2a that the Au concentration is significantly higher on the side exposed to $HAuCl_4$ than the aniline-exposed side in PC membrane where redox reaction between aniline and $HAuCl_4$ was allowed overnight. Figure 2b shows the EDXRF spectra of gold–polyaniline composite in PC membrane when redox reaction between aniline and $HAuCl_4$ was allowed for 2 and 4 h. It can be seen that the concentration of Au is almost the same on

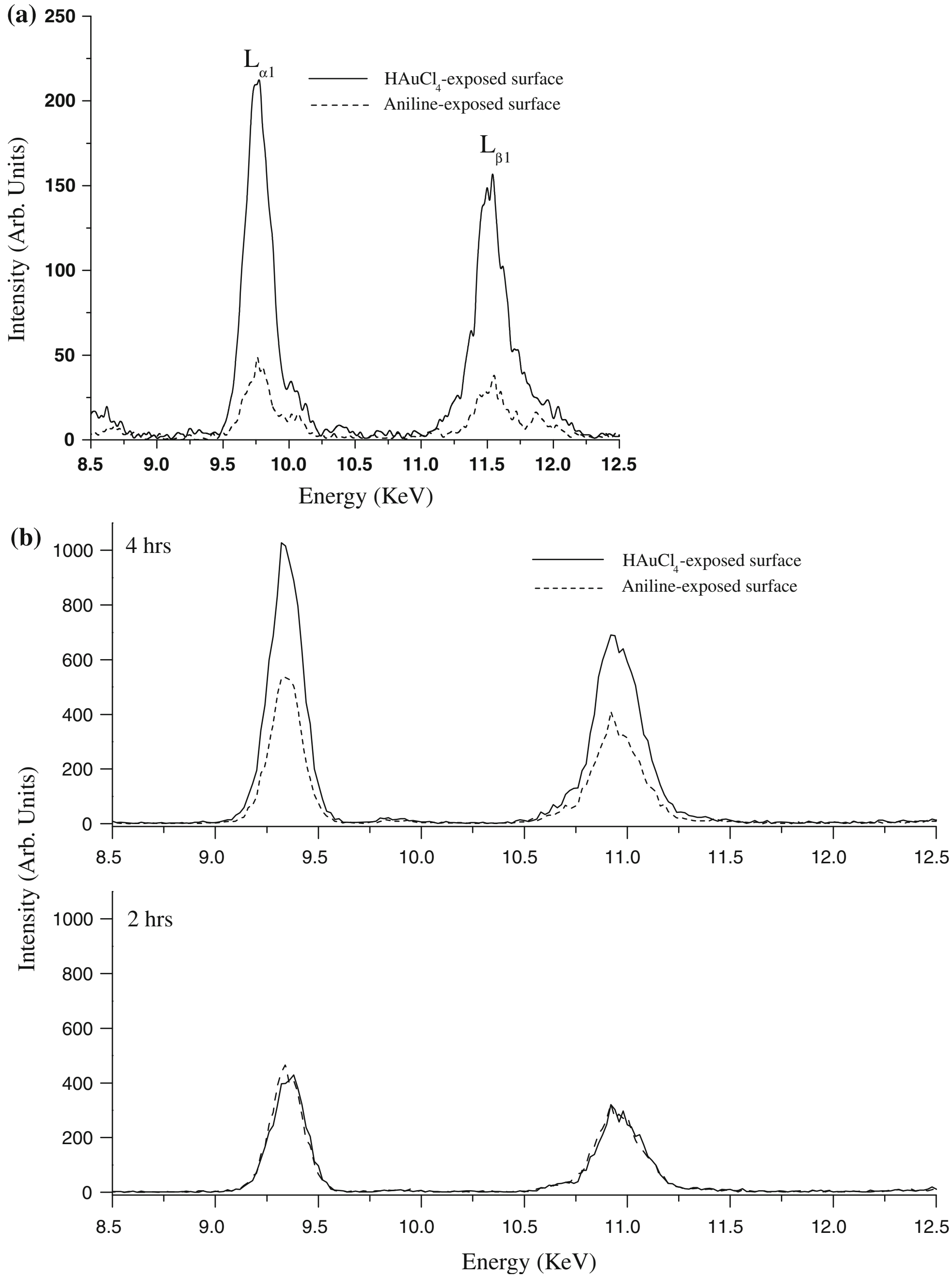
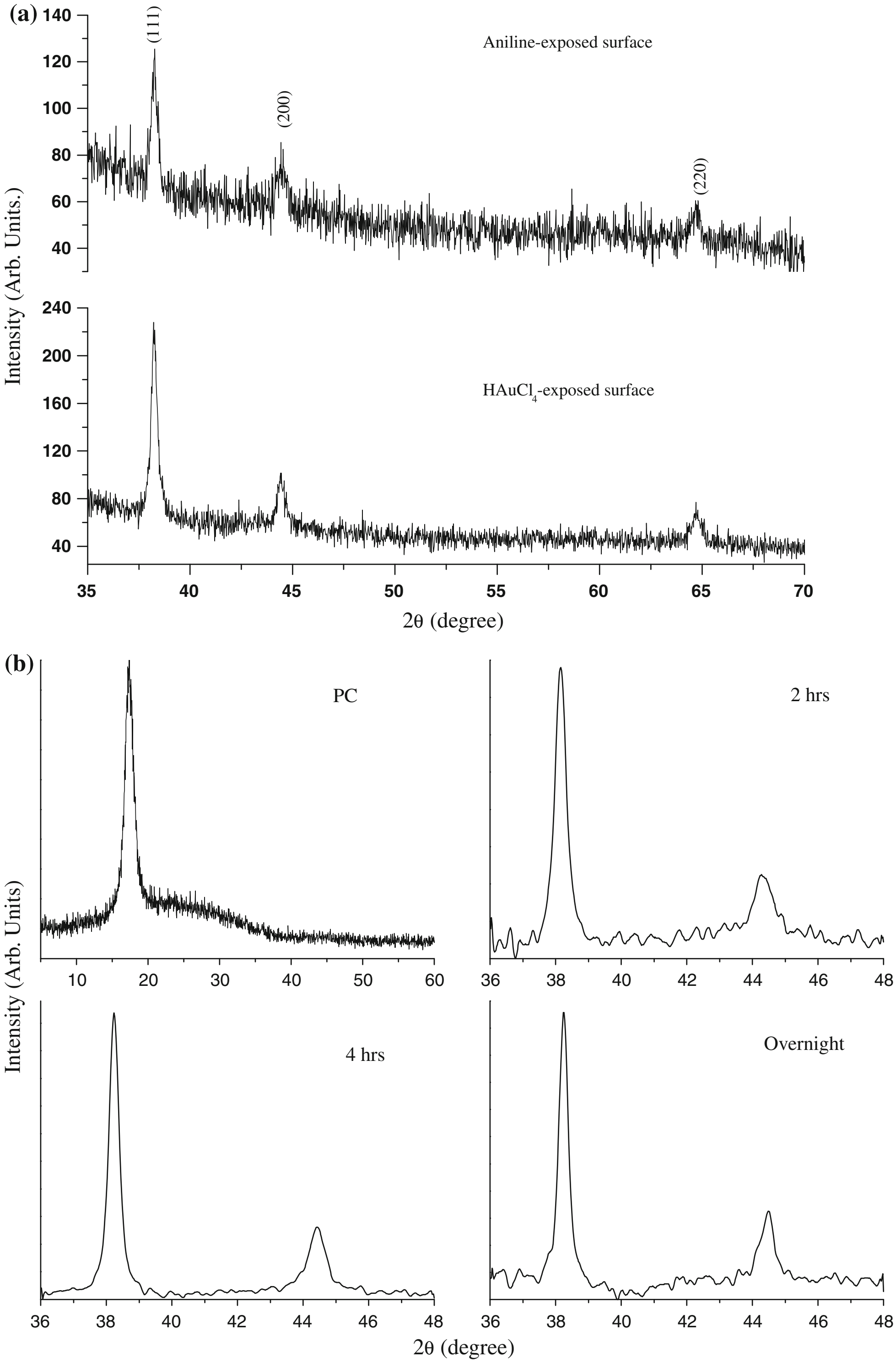


Fig. 2 **a** EDXRF spectra of PC membrane containing gold–polyaniline composite with preparation time of overnight. **b** EDXRF spectra of PC membranes containing gold–polyaniline composite with preparation time of 2 and 4 h

$HAuCl_4$-exposed and aniline-exposed surfaces of the PC membrane after exposing for 2 h. Differences in the concentration of Au were also observed on $HAuCl_4$-exposed and aniline-exposed surfaces of the PC membrane for 4 and 8 h. The presence of Au on both sides of the PC film suggests that the $AuCl_4^-$ ions diffused throughout the length of the pores of PC membrane because of concentration gradient.

X-ray diffraction patterns of PC membrane and gold–polyaniline composites in PC membranes (with preparation time of 2, 4, 8 h and overnight) were recorded. Figure 3a shows the X-ray diffraction patterns of both the surfaces of Au–polyaniline embedded PC membrane where redox reaction between aniline and $HAuCl_4$ was allowed overnight. The XRD patterns show broad peaks of the scattering angles (2θ) corresponding to the 111, 200 and 220 planes of the face-centered cubic phase of Au. This indicated that Au particles formed in the membrane are nanocrystallites. Therefore, broadening of the diffraction peak width of the (111) Bragg reflection was analyzed to estimate the size of Au nanocrystallites embedded in the membrane using the Scherrer equation. Figure 3b shows the XRD patterns of PC membrane and gold–polyaniline composites in PC membranes (with

Fig. 3 **a** X-ray diffraction pattern of PC membrane containing gold–polyaniline composite with preparation time of overnight. **b** X-ray diffraction pattern of PC membrane and PC membranes containing gold–polyaniline composite with preparation time of 2, 4 h and overnight



preparation time of 2, 4 h and overnight). XRD pattern of the PC membrane shows a peak at 2θ of ~17.3°. PC does not have any diffraction peak in the 2θ range where gold shows diffraction peaks. XRD patterns for gold–polyaniline composites in Fig. 3b show broad peaks of the scattering angles (2θ) corresponding to the 111 and 200 planes of the face-centered cubic phase of Au. The average size of Au nanocrystallites in gold–polyaniline composites with different preparation times was calculated to be about 24 ± 4 nm. Intensities of the diffraction peaks were different at $HAuCl_4$-exposed and aniline-exposed surfaces of the PC membrane. Intensity is higher on the surface exposed to $HAuCl_4$ than the aniline-exposed surface.

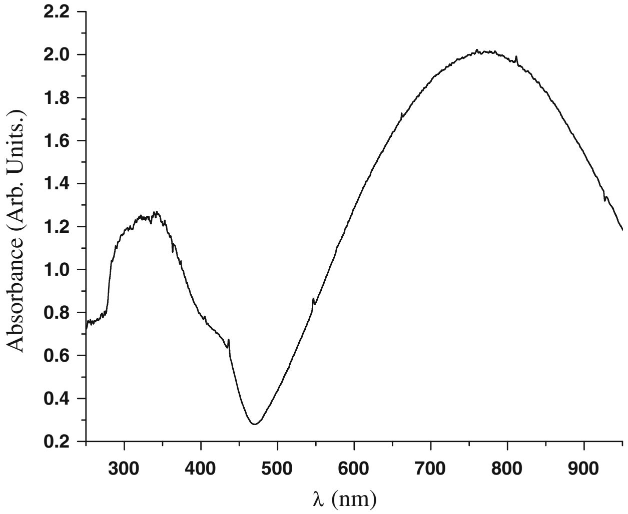


Fig. 4 UV–Vis spectrum of PC membrane containing gold–polyaniline composite in transmission mode

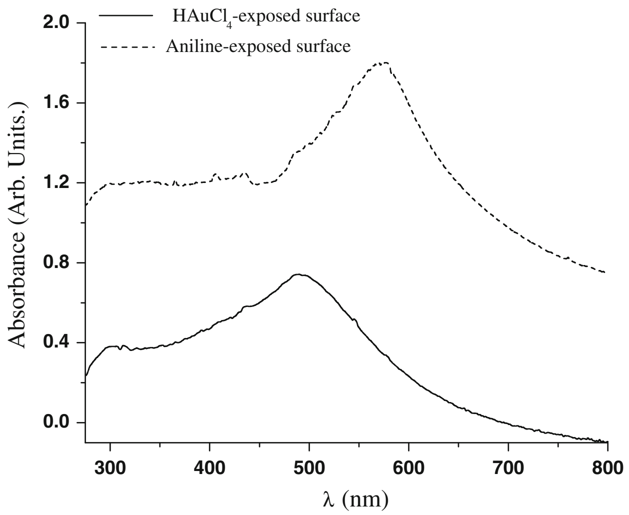


Fig. 5 UV–Vis spectrum of PC membrane containing gold–polyaniline composite in reflectance mode

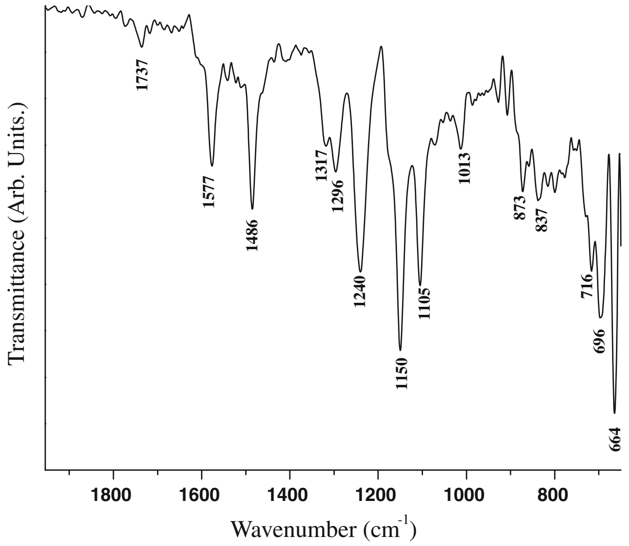


Fig. 6 FTIR spectrum of PC membrane containing gold–polyaniline composite in ATR mode

UV–Vis spectra of the composite material were recorded in both transmission and reflectance mode. The UV–vis spectrum in transmission mode showed characteristic absorption bands at 340 and 750 nm. A small shoulder at 430 nm was also observed resulting from polaron/bipolaron transition in polyaniline. The absorption band at 340 nm is due to the π–π* transition of the benzenoid rings. The band at $\lambda_{\max}$ 750 nm was very broad and corresponds to the transition from a localised benzenoid HOMO to a quinoid LUMO, that is, benzenoid to quinoid excitonic transition in polyaniline. The surface plasmon resonance peak of gold nanoparticles is not observed in transmission mode. In case of gold nanoparticles with spherical geometry, AuNPs show the maximum absorption at ~520 nm. Since it is a gold nanoparticle–polyaniline composite, the contribution of SPR of AuNPs at ~520 nm is superimposed by broad absorption band at $\lambda_{\max}$ ~ 750 nm. The reflectance spectra were recorded on both HAuCl$_4$-exposed and aniline-exposed surfaces. The spectrum of HAuCl$_4$-exposed surface showed a broad band with $\lambda_{\max}$ at 495 nm, which correspond to $\lambda_{\max}$ of surface plasmon band of Au nanoparticles in gold–polyaniline composite in pores of PC membrane. It is well known that surface plasmon bands of metal nanoparticles are sensitive to their surrounding environment. The absorption peak and intensity can change drastically if the dielectric constant of the medium is changed. The spectrum of aniline-exposed surface showed a broad band with $\lambda_{\max}$ at 595 nm, which corresponds to benzenoid to quinoid excitonic transition. It is seen from the UV–vis spectra that the surfaces of the PC membrane exposed to HAuCl$_4$ and aniline have significantly higher concentrations of Au nanoparticles and polyaniline, respectively. In present experiment, UV–Vis measurements gave contributions both from the polyaniline and surface plasmon band of gold nanoparticles (as shown in Fig. 4), and thus makes it difficult to interpret size of the gold nanoparticles. But from Fig. 5, we can predict that AuNPs were almost spherical and gold nanorods were not formed in cylindrical pores of polycarbonate as there is only one peak at 495 nm. In case of gold nanoparticles with spherical geometry, the major axis and minor axis of the particles are same and AuNPs show the maximum absorption at ~520 nm. When AuNPs deviate from spheroid and become elongated with increase in major axis, they show two plasmon absorption bands with one in the blue region near the original band position ~520 nm and the other in the red region >600 nm.

Figure 6 shows the FT-ATR-IR spectrum of the gold–polyaniline composite in the PC membrane. The peaks at

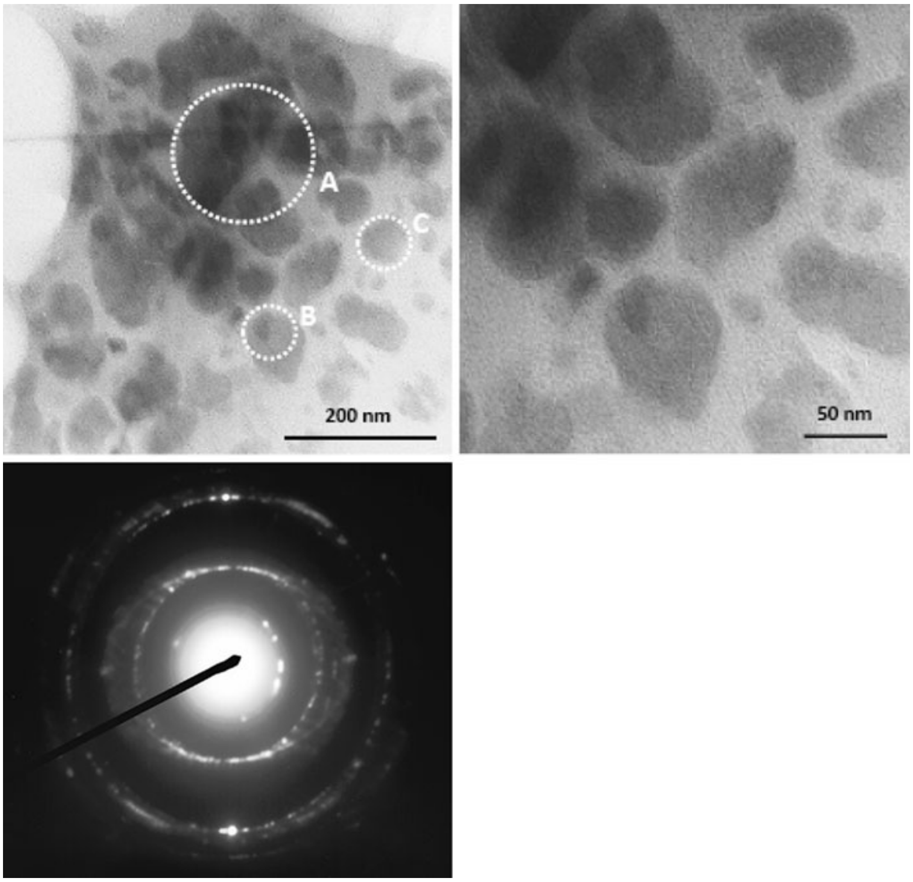


Fig. 7 TEM images of gold–polyaniline composite prepared in PC membrane and corresponding SAED pattern

1,577 and 1,486 cm^{-1} correspond to the stretching deformation of the N = Q = N and N–B–N, respectively, where Q is quinoid and B is benzenoid ring. The bands at 1,296 and 1,240 cm^{-1} correspond to the C–N stretching of the secondary aromatic amine and to the protonated C–N group, respectively. Figure 7 shows the TEM images of the gold–polyaniline composite prepared in the PC membrane and corresponding selected area electron diffraction (SAED) pattern. TEM images suggest that clusters of polyaniline were formed and gold particles (size < 50 nm) were randomly dispersed in these polyaniline clusters. The three circles marked as A, B and C represent three different regions based on number density of gold particles in polyaniline clusters. The dark spot in region A has higher number density of gold particles compared to regions B and C. SAED pattern corresponded to a characteristic polycrystalline ring pattern for a face-centered-cubic structure.

Conclusion

In situ one-step chemical synthesis of a gold–polyaniline composite in nanopores of PC membrane was carried out. Nanopores in PC membrane acted as reaction vessels where aniline and $HAuCl_4$ were allowed to mix together, and the redox reaction between aniline and $HAuCl_4$ led to the formation of gold–polyaniline composite. TEM images suggest that clusters of polyaniline were formed and gold particles were randomly encapsulated in these polyaniline clusters. Gold particles formed are nanocrystallites and average crystallite size is (24 ± 4) nm. EDXRF and other characterisation results show that the surfaces of the PC membrane exposed to $HAuCl_4$ and aniline have significantly higher concentrations of Au nanoparticles and polyaniline, respectively.

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