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Synthesis and characterization of gold–polypyrrole film composite

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Abstract Polypyrrole (PPy) coatings have potential applications in batteries, fuel cells, sensors, anti-corrosion coatings, and drug delivery systems. In this article, PPy film coating on the electrode of quartz crystal microbalance (QCM) was exposed to acidic aqueous $HAuCl_4$ solution. The reduction for gold ions took place and gold particles were produced at the film surface. The gold content at the PPy film was monitored by using QCM. The concentration of gold uptake increases as the original concentration of $HAuCl_4$ solution increases. The morphology of the film before and after the deposition of the gold particles was studied by the scanning electron microscopy coupled with energy dispersive X-ray spectrometry. The gold particles are of undefined shape and have diameters around 200–600 nm. However, the image of the composite powder shows that gold particles of sizes 100–120 nm are distributed over the surface of the polymer particles with some aggregation. Infrared spectroscopy and X-ray diffraction were used to characterize the composite.

Introduction

Gold has been extensively used in jewelry and many technological applications. The demand to recover gold from industrial waste has been increased. Most techniques to recover gold ions from solutions involve an adsorption method [1], photo-catalytic ZnO powders [2–4], and chicken egg-shell membrane/conjugated chitosan beads [5]. Fungus [6, 7] and algae [8, 9] were able to collect gold ions from water. Ion exchange resins [10, 11] were applied to select gold ions from aqueous solution. Additional processes were required to convert them into elemental gold. However, these methods are quite expensive.

Gold particles have unique properties, such as useful catalytic activities, optical properties, and biocompatibility and hence they have been extensively utilized in recent years. Several researches have been devoted to fabricate gold particles dispersed onto various substrates such as carbon paste electrode, self-assembled monolayer; conducting and non-conducting polymers [12–15]. Among the conducting polymers, polypyrrole (PPy) has been used as the supporting substrates for different noble metal or metal oxide because of its unique environmental stability and redox properties. Miao and co-workers [16] have synthesized the platinum–PPy nanocomposite that enhanced the electrocatalytic reduction of oxygen. Wang et al. [17] have prepared silver–PPy composites. The results indicated that two dimensional silver nanosheets were deposited onto the surface of the PPy. SiO_2–PPy nanocomposites were also reported [18, 19]. The nanocomposites presented good environmental stability and high electrocatalytic activity.

The literature gives several accounts of the ability of PPy to act as reducing agents for metal ions in solution. For example, it has been reported that gold ions can be reduced to gold metal by films of PPy [20–22]. We previously described the deposition of smooth and adherent films of PPy using a chemical route from an aqueous solution that contained $FeCl_3$ or $K_2S_2O_8$ as an oxidizing agent [23, 24]. The films were monitored using the quartz crystal microbalance (QCM). The optimum reaction conditions for the deposition of the PPy film were determined. The kinetic of the film formation was found to be governed by the concentration of the reactants in the bulk. Recently, we used

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the PPy film coating on the QCM electrode as sensors for the presence of silver ions in aqueous silver nitrate solution [25]. Silver nanoparticles have been deposited onto the PPy film after the reduction of silver nitrate with PPy. The mass of the PPy film increases due to the deposition of silver and the frequency of the quartz crystal holding the PPy film decreases correspondingly. Similar results were obtained in case of nanotubular conducting polymer, polyaniline, film coating on the QCM electrode in the presence of aqueous silver nitrate solution [26].

In the present article, PPy film was grown by the chemical oxidation of pyrrole [23, 24] on the electrode of QCM. The resulting set-up was then used to uptake and reduce gold ions from an aqueous acidic $HAuCl_4$ solution. Such process may simulate the recovery of noble metals from waste waters produced by industries using gold-containing compounds. On the other hand, the resulting gold–PPy composite may find applications in catalysis, medical, and environmental diagnoses. The generation of gold metal in the PPy film was monitored in situ by using QCM. The morphology and structure of the resulting composite was examined by the scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectrometry (EDX). The composite was analyzed using Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD).

Experimental

Chemicals

The pyrrole was obtained from Aldrich Chemicals and was purified by passing through a column of alumina neutral. $FeCl_3$ and $HAuCl_4$ were from BDH and used as received without any further purification.

Preparation of PPy film and deposition of gold

Polypyrrole film was prepared from the oxidation of 20 mmol L^{-1} solution of pyrrole dissolved in 50 mL of 0.2 mol L^{-1} HCl and 45 mmol L^{-1} $FeCl_3$ dissolved in 50 mL of 0.2 mol L^{-1} HCl. In this case, the molar ratio of $FeCl_3$ to pyrrole would be 2.25. All solutions were prepared in double distilled water. These solutions were then added to polypropylene bottle in which silicon wafers were immersed. A hole had been made in the cap of the bottle and a 5-MHz AT-cut quartz resonator, 1 inch in diameter, covered this hole and sealed with silicon rubber. Once the reaction was started, in situ PPy hydrochloride films were deposited onto the surfaces of the quartz resonator and the silicon wafers. The frequency was measured using a Fluke/Phillips PM 6654 frequency counter. Details of QCM experimental set-up and the experimental conditions were described previously [23, 24]. The mass per unit area of the film, m' (g/cm^2), was determined from the change in its resonance frequency using Sauerbrey equation [27], $\Delta f = -\left(2f_o^2/\sqrt{\rho_Q \mu_Q}\right) m'$, where f_o (Hz) is the natural frequency of the quartz crystal (unloaded resonator frequency), ρ_Q the quartz density has the value (2.649 g/cm^3), and μ_Q the shear modulus has the value (2.947×10^{11} N/cm^2). By the end of the polymerization, the films were washed with double distilled water and then with ethanol. The films were then dedoped by using 0.1 mol L^{-1} ammonia solution for 15 min and then exposed to a solution of $HAuCl_4$ dissolved in 10 mmol L^{-1} HCl until the frequency of QCM with time attains a steady-state condition.

Polypyrrole powder was synthesized using solutions of pyrrole and $FeCl_3$ like that used during the preparation of PPy films except the concentration of pyrrole and $FeCl_3$ were 0.2 and 0.45 mol L^{-1}, respectively. The synthesis was carried out for 4 h. The PPy hydrochloride thus obtained was dedoped in 0.1 mol L^{-1} ammonia solution. The final product was filtered, washed with ethanol and dried in dynamic vacuum. 0.2 g of PPy base was treated with 0.06 mmol L^{-1} $HAuCl_4$ solution. The suspension was stirred at room temperature for 2 h. After this time, the obtained composite was filtered, washed, and dried.

Characterization

The PPy film and its gold composite were sputtered with a thin layer of Pt/Pd and then used for SEM and EDX measurements using scanning electron microscope FESEM HITACHI H-8100. PPy powder and its gold composite were dispersed in acetone and then transferred onto silicon wafer substrates. The latter was sputtered with a thin layer of Pt/Pd. Wide-angle X-ray diffractogram of the powder composite was recorded on RIGAKU RINT2000 apparatus. FTIR spectra were recorded in the transmission mode on a Jasco FT/IR 460 plus apparatus spectrometer using the standard KBr pellet technique.

Results and discussion

The deposition of PPy film and gold ions uptake from solution

The frequency change (Δf) corresponds to the mass of the PPy base film was calculated and it equals 831 Hz. The electrode of QCM coated with the base film was exposed to an aqueous solution of 0.3 mmol L^{-1} $HAuCl_4$ dissolved in 10 mmol L^{-1} HCl solution (Fig. 1). It can be seen that the frequency decreases by time up to a steady-state condition. The decrease in frequency is attributed to a mass increase

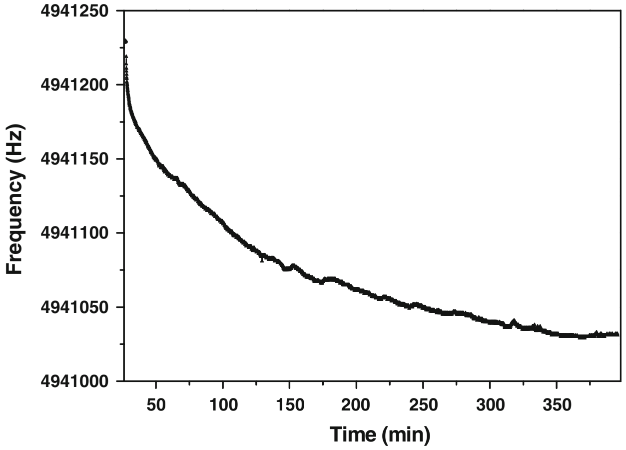


Fig. 1 Relationship between Δf of the PPy base film coating on the electrode of QCM when exposed to the 0.3 mmol L^{-1} $HAuCl_4$ (solution containing 0.01 M HCl)

in the film, corresponding to the deposition of metallic gold ($\Delta f_{Au} = 188$ Hz).

The mass of the metallic gold as a percentage was calculated from the ratio of Δf_{Au} in comparison to Δf, $(\Delta f_{Au}/\Delta f) \times 100$, and equals 22.67%. Different concentrations of $HAuCl_4$ solutions were exposed to different films of approximately Δf and hence of similar thicknesses and the values of the masses of the metallic gold as a percentage were calculated. A plot of the gold mass% against the original gold solution concentrations (0.015–0.3 mmol L^{-1}) is shown in Fig. 2. It can be shown that as the original gold solution concentration increases, the deposition of metallic gold from the solutions increases.

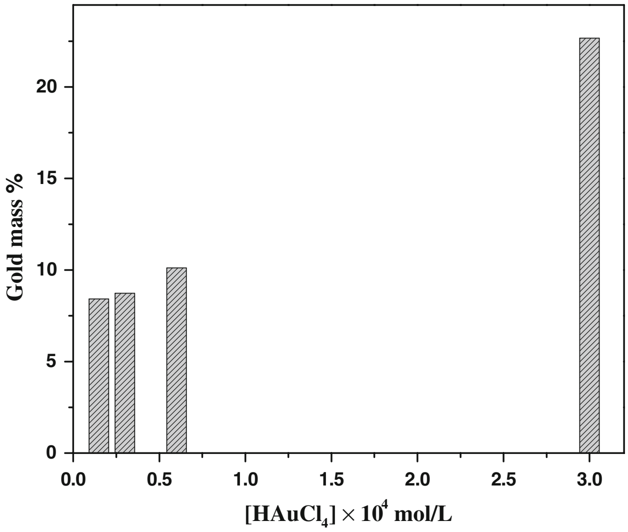


Fig. 2 Dependency of the gold mass% on the initial concentration of $HAuCl_4$ (solution containing 0.01 M HCl)

The morphology of PPy film and its gold composite

The existence of metallic gold onto the surfaces of PPy film was confirmed by the SEM and the EDX mapping images. The SEM image (Fig. 3a) of the PPy film grown onto the surface of the silicon wafer shows a smooth and homogeneous morphology. However, the corresponding image of the film exposed to 3 mmol L^{-1} $HAuCl_4$ solution (Fig. 3b) shows that gold particles decorate the surface and are

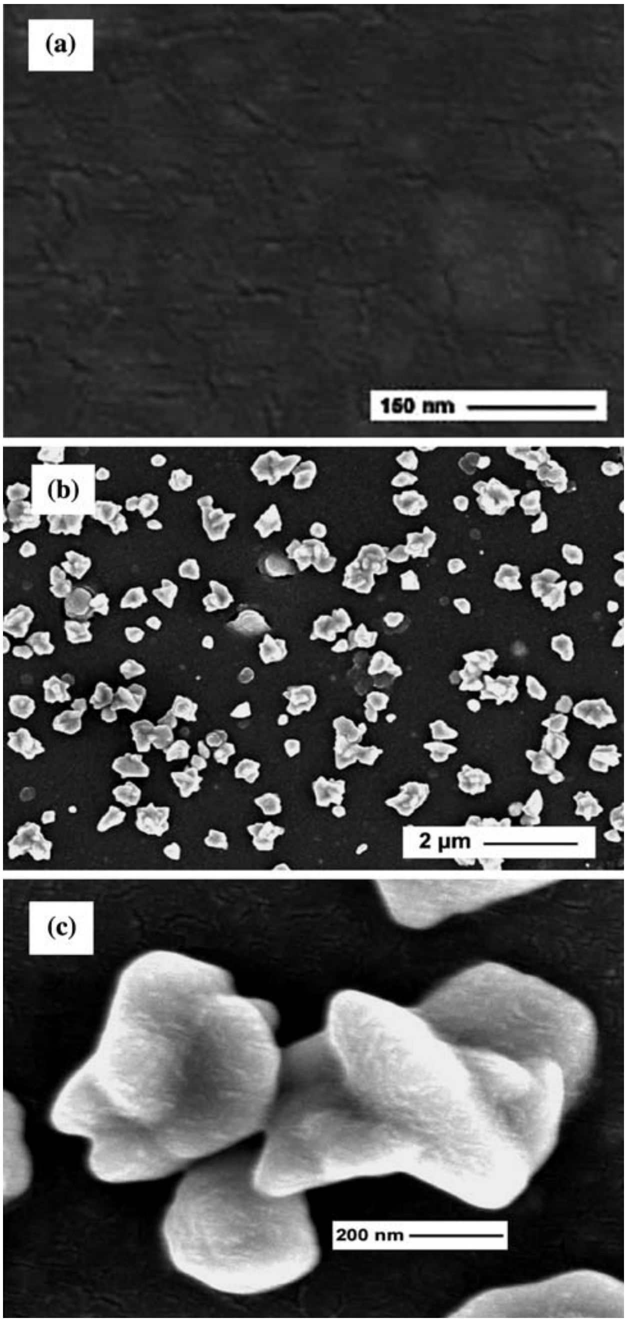


Fig. 3 The SEM of **a** PPy film, **b** gold–PPy film composite, and **c** the image of the composite at high magnification

distributed over the surface and there is no particles aggregation. Figure 3c is the image of the composite at high magnification.

The gold particles are of undefined shape and have diameters around 200–600 nm at the concentration of $HAuCl_4$ of 0.3 mmol L^{-1}. It is interesting to mention that, the size of the gold particles depends on the initial concentration of $HAuCl_4$ solution and time of exposure. It would be expected that as the concentration and time decrease, the size of the gold particles would be smaller, it is possible to finely control the average size of the gold particles in the composite. The EDX spectrum for the composite (Fig. 4) showed signal at $\sim E = 2.1$ keV indicating the exact presence of gold element in the tested area [28]. The line of oxygen (0.52 keV), nitrogen (0.39 keV), and carbon (0.28 keV) are indicating the constituents of the PPy structure.

The gold ions uptake by PPy film from the solution and the gold–PPy film composite formation are believed to involve the following stages: (1) the complex formation of gold ions (III) with the polymer, (2) the conversion of the gold ions near the PPy film to gold (0) at the surface [20–22, 29], and (3) the reduced gold particles are deposited onto the polymer substrate resulting in composite formation. The reduction of the gold ions and the oxidation of PPy occur simultaneously.

The characterization of PPy powder and its gold composite

The PPy powder was treated with 0.06 mmol L^{-1} $HAuCl_4$ solution. The gold–PPy composite powder was analyzed. The morphology of the PPy powder and its gold composite was studied (Fig. 5a, b). The image of the polymer powder shows granular particles of sizes 500–600 nm. However, the image of the composite shows that gold particles of sizes 100–120 nm are distributed over the surface of the polymer particles with some aggregation.

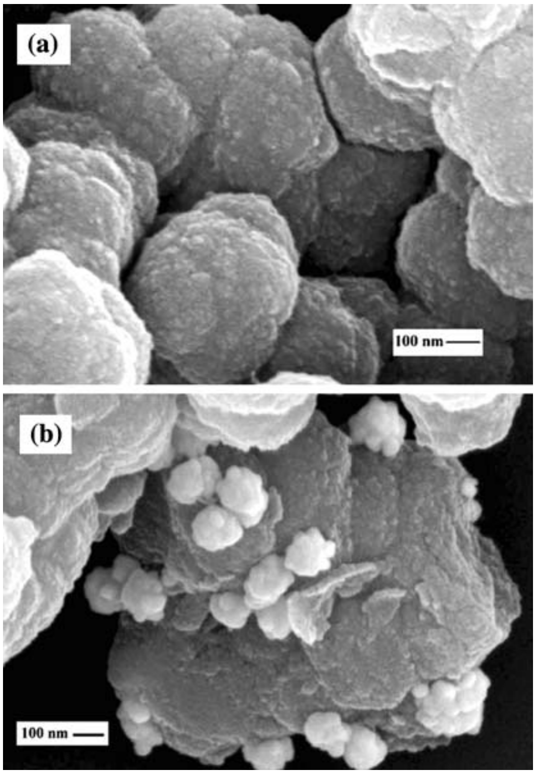
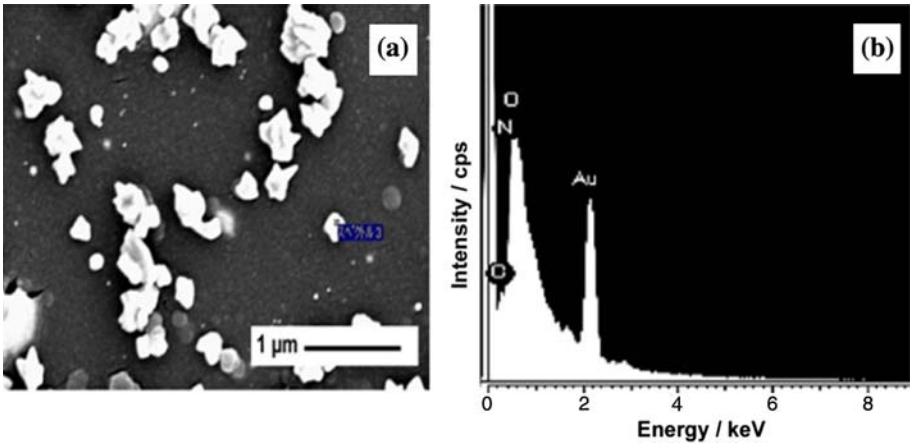


Fig. 5 The SEM of **a** PPy powder and **b** gold–PPy composite

Figure 6 represents the FTIR spectra of the gold–PPy composite. The spectra exhibit a strong band attributed to the C=C stretching of the PPy backbone at 1564 cm^{-1} and a symmetric C=N stretching band at 1471 cm^{-1}. The band at 1311 cm^{-1} is associated with the ring stretching of PPy and the antisymmetric C–H in plane bending [30], respectively. The band at approximately 1051 cm^{-1} is assigned to the C–H in-plane deformation of PPy and that about 935 cm^{-1} is assigned to ring deformation [31]. An additional peak at ca. 1715 cm^{-1} is observed, indicating the PPy is slightly overoxidized during the growth process [32]. This was supported by the increase in the intensity

Fig. 4 The EDX of the gold–PPy film composite



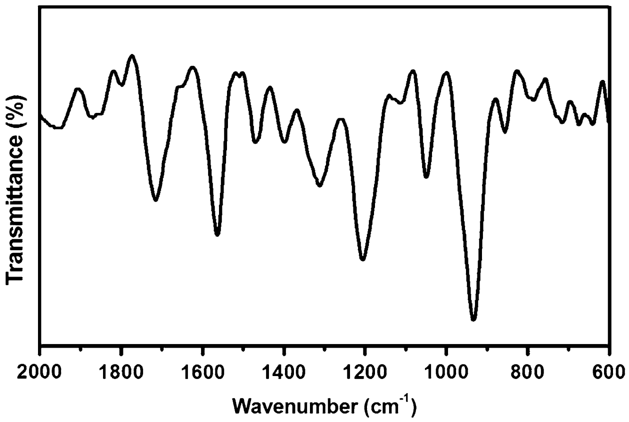


Fig. 6 FTIR spectra of the gold–PPy powder composite

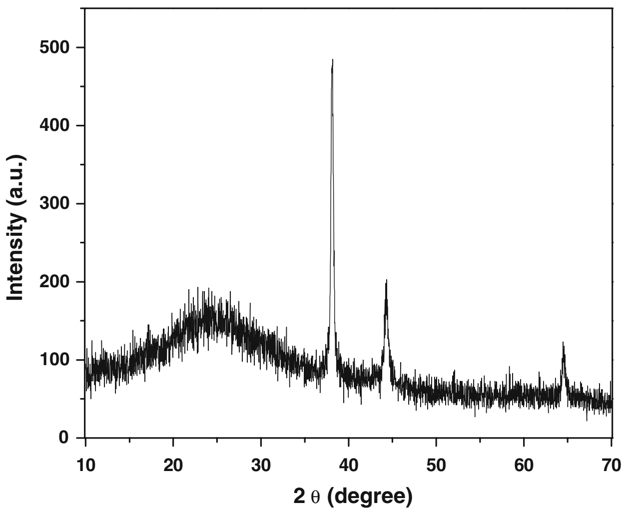


Fig. 7 The XRD pattern of the gold–PPy composite

ratio of the band at 1564 cm^{-1} to the band 1471 cm^{-1}. The characteristic bipolaron bands at 1207 and 935 cm^{-1} indicate the formation of PPy in its doped state [33].

The XRD pattern of the composite powder indicates the incorporation of the gold particles and is shown in Fig. 7. The polymer exhibits two broad peaks; the first centered at $2\theta = 26°$ and is less prominent than the other existed at $2\theta = 18°$. The diffraction lines at $2\theta = 38.04°$, 44.47°, and 64.5°, can be indexed to the (111), (200), and (220) planes due to gold particles, respectively. As expected due to the higher scattering intensity of the gold particles compared to the amorphous PPy structures, the peaks assigned to the gold crystal plains appear with a higher intensity than the bands of PPy.

Conclusions

The present study demonstrates the use of PPy film coating on the QCM electrode to uptake gold ions in acidic aqueous $HAuCl_4$ solution. Gold ions are reduced with PPy and the corresponding increase in mass would cause the easily detectable crystal-frequency change. The results showed that the mass of the PPy film increases due to the deposition of gold and the frequency of the quartz crystal holding the PPy film decreases correspondingly. The resultant composite can be used for catalytic oxidation and environmental diagnosis. The latter investigations are underway.

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