



Facile preparation of gold nanoparticles on the polyquinoline matrix: Catalytic performance toward 4-nitrophenol reduction



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ABSTRACT

Gold nanoparticles (AuNPs) have been introduced into polyquinoline (PAQ) matrix for the first time. For this purpose, 5-amino quinoline (AQ) and auric acid solution were used as a monomer and oxidant, respectively. Incorporation of gold nanoparticles into the PAQ matrix led to improved thermal stability: 5% of product was decomposed at 643 °C. Photoluminescence characteristics of resulting composite (Au@PAQ) were determined. Au@PAQ was also successfully utilized for the catalytic reduction of 4-nitrophenol (4NP) to 4-amino phenol (4AP). The reduction process was completed in only four minutes at 25 °C. Pseudo-first-order rate constant was estimated to be $3.05 \times 10^{-3} \text{ s}^{-1}$. The results were compared with the previous reported ones.

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1. Introduction

Hybridization of inorganic nanoparticles with the conjugated polymer has attracted major interest in the research communities. Among the various inorganic nanoparticles, AuNPs have gained considerable attention because they are one of the most stable metal nanoparticles. They have wide application areas [1] such as surface-enhanced Raman phenomena, optical device application and biomedical imaging [2–4]. Hence, gold is among the most innovative catalysts [5]. However, high prices of gold limits their large scale usage. To reduce this hindrance, gold clusters are often dispersed on the different polymer matrices [6]. In the other words, the suitable polymer matrices are highly demanded to avoid any undesirable aggregation.

Polyquinolines are members of electronically conductive conjugated polymers. Potential applications of polyquinolines include organic light-emitting diodes (OLEDs) [7,8], organic photovoltaic devices [9,10] and selective chemosensors [11,12]. To tailor the properties of polyquinolines, the various polymerization procedures have been developed: these are Friedlander condensation [13], Pd-catalyzed coupling [14], oxidative

polymerization [15,16], and electrochemical polymerization [17]. Thus, various polyquinoline copolymers, homopolymers, blends have been obtained and their chemical and physical properties have been investigated [15]. Up to now, dispersion of AuNPs on the different polymer matrices have been achieved including polyaniline [18], polyindole [19,20], polypyrrole [21], polycarbazole [22,23], polythiophene [24,25], polyfluorene [26] and polyvinylpyrrolidone [27]. However, to the best of our knowledge, the hybridization of AuNPs on the polyquinoline matrix has not been reported so far.

Herein, we describe the one step green protocol for preparation of Au@PAQ. In this process, 5-amino quinoline can reduce chloroauric acid (HAuCl_4) to elemental gold while itself of monomer is simultaneously oxidized polyquinoline. The elemental gold nanoparticles thus formed are dispersed on the PAQ matrix. The obtained composite is characterized with the different analytical techniques. Hence, its usability as a potential catalyst in the reduction of 4NP to 4AP is investigated.

2. Materials and methods

2.1. Materials

All solvents and chemicals were commercially purchased from Merck Chem. Co. (Germany) and used without further purification.

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A stock solution of gold trichloride ($\text{AuCl}_3 \cdot 3\text{H}_2\text{O}$) in deionized water (0.394 g/100 mL) was prepared.

2.2. Synthesis of Au@PAQ

The experimental procedure for preparation of Au@PAQ is as follows [28].

10 mL methanolic solution of AQ (0.200 g) was added into a 100 mL conical flask. 35 mL of auric acid solution (from stock) was added to this solution drop by drop with gentle stirring. After completing of oxidant addition, the reaction was stopped by addition of equivalent amount alkaline (0.05 N potassium hydroxide solution). Thus, the colloidal precipitated appeared at the bottom of the flask. Two microliters from this colloidal solution was taken for TEM analyses. The rest of the solution was centrifuged, washed several times with deionized water until effluent became colorless. The obtained product was dried in oven (130 °C).

2.3. Synthesis of PAQ

A representative protocol for the synthesis of the PAQ is as follows [36]:

In a glass flask, AQ (1.47 g, 10 mmol) was dissolved in aqueous solution of HCl (1 M, 10 mL) at 5 °C. An oxidant solution was prepared separately by dissolving ammonium persulfate (2.327 g, 10 mmol) in HCl aqueous solution (1 M, 5 mL). The oxidant solution prepared was added to monomer solution drop by drop. The mixture was stirred for further 10 h at 5 °C. After that, the polymer salts were isolated from the reaction mixture by filtration and washed with an excess of distilled water. The obtained product was dried in oven at 130 °C.

2.4. Catalytic reduction of 4NP

The catalytic reduction of NP with the Au@AQP was performed as given in the literature [29]. 3.5 mg Au@AQP was dispersed in 8 mL H_2O (solution A). The aqueous solution of NP (9×10^{-2} mM) was added to aqueous solution of NaBH_4 (0.65 M, 3.3 mL) (solution B). The solution B was mixed for a further 10 min to ensure the formation of phenolate anions [29] and then each solution (solution A and B) was mixed in an ultrasonic bath. 3 mL of the solution was taken from reaction the medium in determinate intervals for UV–vis measurements. The rate constant k was determined by measuring the changing the band observed in the 400 nm as a function of time.

2.5. Characterization techniques

UV–vis and infrared spectra were recorded on a PerkinElmer Lambda 25 and PerkinElmer FT-IR Spectrum one, respectively.

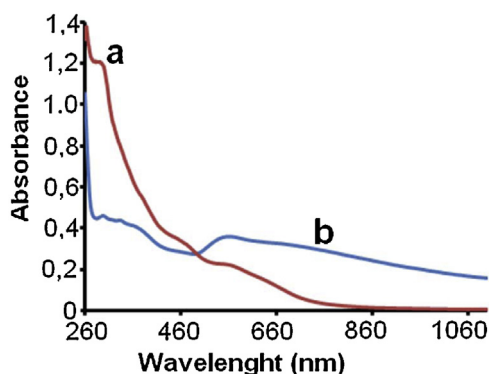


Fig. 1. UV–vis spectra of PAQ (a) and Au@PAQ (b).

Universal ATR sampling accessory (4000–550 cm^{-1}) was used in the FTIR instrument. Thermal data were obtained by using a PerkinElmer Diamond Thermal Analysis system. The measurements were conducted in nitrogen atmosphere with a heating rate 10 °C/min. A Bruker AXS diffractometer instrument with CuK_α radiation was used for X-ray analysis. SEM images of composite were recorded by using a JXA 8230 instrument. Tecnai G2 Spirit Biotwin model transmission electron microscopy (TEM) was used to determine the particle images. The samples were suspended in methanol and ultrasonically dispersed. 2 μL of this suspension were dried on a glass for SEM and TEM analysis. The sample was deposited onto a stab holding carbon tape for SEM analysis.

3. Results and discussion

One step oxidation of AQ was achieved by the auric acid solution (oxidant). As soon as oxidant added, initial yellow color of AQ solution was turned into reddish-brown and gradually became black within 2 h. Fig. 1 belongs to UV–vis spectra of Au@PAQ and PAQ. PAQ was prepared by oxidative polymerization using ammonium persulfate for comparison.

As seen this figure, PAQ exhibited an absorption maximum at 305 nm with a large tail up to 850 nm. This broad absorption band peculiar to conductive aromatic polymers [16] and assigns the presence of a polymerization product with different conjugation lengths. However, two strong absorption bands appeared in the absorption spectrum of Au@PAQ. The first one was observed at 333 nm due to $\pi(r)\pi^*$ transitions. The shoulder like absorption band observed at 384 nm was attributed to $n \rightarrow \pi^*$ transitions. The broad absorption band from 500–1100 nm was due to overlapping bands of polaronic excitations and surface plasmon resonance of Au nanoparticles [28].

The position of surface plasmon resonance (SPR) of gold is closely related to particle size and chemical surrounding: very small gold nanoparticles (<5 nm) do not show any plasmon adsorption [30]. Gold nanoparticles of 5–50 nm show a plasmon absorption band around 520–530 nm. As the particle size of gold nanoparticles increases, it is expected that SPR band is shifted to red. SPR band of Au@PAQ was observed at 550 nm. Therefore, it was conceivable to expect the formation of Au nanoparticles larger than 50 nm. SEM, TEM and XRD analysis also confirmed this suggestion as discussed in below.

Fig. 2 demonstrates the FTIR spectra of polymer and composite.

To better observe the structural changing after reaction, we also recorded the FTIR spectrum of PAQ. As compared with the FTIR spectrum monomer (not given), it was clearly observed that the

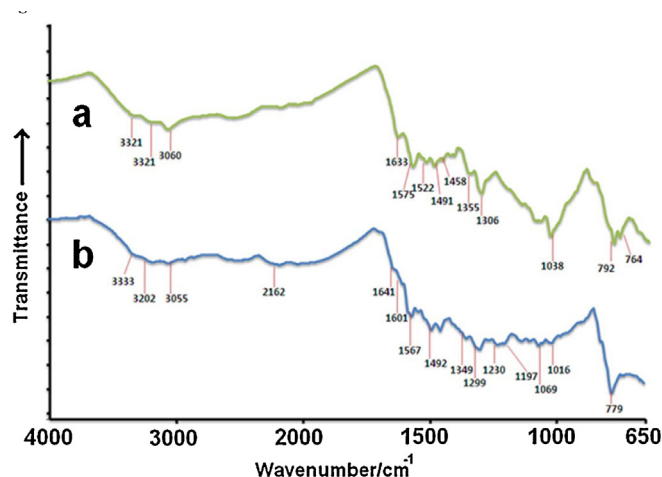


Fig. 2. FTIR spectra of PAQ (a) and Au@PAQ (b).

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