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SYNTHESIS OF GOLD NANOPARTICLES ATTACHED TO POLYPYRROLE NANOFIBERS

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Introduction

Polypyrrole is a frequently studied conducting polymer due to its application in sensing and catalysis.¹ Polypyrrole is considered among the most promising conductive polymers due to its stability and ease of conversion between conducting and insulating forms.² Different chemical and electrochemical methods are generally used in the synthesis of polypyrrole.² Despite many interesting applications, the use of polypyrrole is limited because of difficulty in processing it. Several approaches have been explored to improve the ability to process polypyrrole, including the use of emulsion, inverse emulsion, steric stabilizer, and microemulsion methods.¹

Several reports have also been published on the synthesis of polypyrrole-metal nanocomposites.³ The sensing and catalytic abilities of the polypyrrole composites are significantly better than those for polymer alone.⁴ As most of the important properties of the noble metals depend on their dispersion and surface properties in the surrounding medium, it is important to obtain evenly distributed Au nanoparticles in conducting polymer matrix. Here we report a simple and convenient procedure for the synthesis of polypyrrole and gold composites, where both polymer and metal morphologies can be controlled in a single set-up.

Experimental

Materials. Hydrogen tetrachloroaurate (HAuCl₄) was obtained from Alfa Aesar. Pyrrole and β -naphthalene sulfonic acid (NSA) were purchased from Aldrich Chemicals. Pyrrole was distilled before use and all other reagents were used as received.

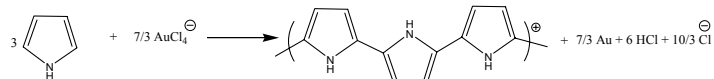
Instrumentation. Transmission electron microscopy (TEM) was used to determine morphology and size distribution of Au nanoparticles attached to polypyrrole. UV-Vis spectra of the nanocomposites were obtained with a Carey UV-Vis spectrophotometer using m-cresol as solvent. FT-IR spectra of nanocomposites pellets were obtained on a Nicolet FT-IR Nexus spectrometer.

Aqueous polymerization of pyrrole using NSA as dopant (PPY-Au-NSA).

The procedures reported by Wan et al. were used for synthesis of polypyrrole microtubules.⁵ In a typical synthesis, 0.02 M HAuCl₄ in 10 ml of water was added drop-wise to a 10 ml aqueous solution containing 0.07 M pyrrole and 0.1 M NSA. The samples were stirred for 12 h. After the polymerization, the samples were filtered. The solutions were washed with excess water, methanol and diethyl ether to remove excess dopant and oligomeric species.

Results and Discussion

Polypyrrole gold nanocomposites, synthesized using NSA as dopant, are shown before and after sonication in Figure 1 and 2, respectively. As shown in the TEM images, the resulting nanocomposites contain well-dispersed Au nanoparticles attached to polypyrrole nanofibers. The nanostructures of polypyrrole are 2-3 μ m in length and 50 nm in width. The reaction between the pyrrole monomer and AuCl₄⁻ is shown in Scheme 1. As the Au (III) salt can cause oxidative polymerization of pyrrole, an external initiator is needed. As a result, the resulting composites are free from by-products that arise when conventional initiators like ammonium persulfate are employed.



In polypyrrole-Au nanocomposites, most of the metal was found attached to the polypyrrole matrix, as shown in Figure 1. To determine particle-size distribution, all of the samples were sonicated before taking TEM images. An example of a sample after sonication is shown in Figure 2. The size of the Au nanoparticles in the polypyrrole-gold composites is around 10 nm. The size of Au metal particles, calculated from TEM and from Williamson-Hall analysis of peaks in XRD, is in close agreement with each other.

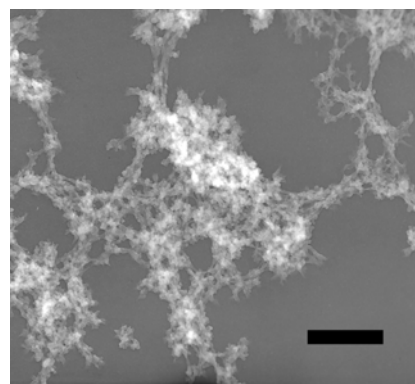


Figure 1. TEM images of polypyrrole-Au nanocomposites obtained using β -NSA as dopant. The scale bar represents 500 nm.

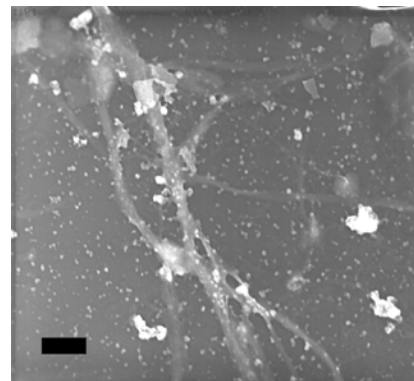


Figure 2. TEM images of polypyrrole-Au nanocomposites obtained using β -NSA as dopant after sonication. The scale bar represents 100 nm.

The UV-Vis spectra of polypyrrole-gold at different stages are shown in Figure 3. Because polypyrrole absorbs at wavelengths close to those where Au absorbs, it is difficult to detect the presence of Au nanoparticles with UV-Vis spectroscopy. The absence of absorption peaks corresponding to Au nanoparticles in the resulting nanocomposites has been noted in previous reports.⁶ This absence can be explained if, in the strongly acidic environment of the solutions, the oscillator strength is reduced, and consequently, no surface plasmon peaks are observed. This may also be due to overlap of the absorption of doped polymers in the same regions of the spectrum where the metal nanoparticles absorb. No absorption due to Au nanoparticles was observed, even in pH neutralized solutions. It, therefore, seems likely that the main reason for the absence of peaks corresponding to Au nanoparticles is due to overlap from polymer absorption. The UV-Vis spectra of polypyrrole-gold (Figure 3a and 3b), obtained during initial stages of polymerization, clearly shows a broad peak of around 450 nm, confirming the formation of Au nanoparticles. Selvan et al. have also found similar results and have confirmed the presence of Au nanoparticles using Mie-Drude analysis.⁶

To confirm the presence of stable Au nanoparticles in final composite, we have taken the XRD spectra. As shown in Figure 4, peaks due to (111), (200) (220) and (310) Bragg reflections of Au nanoparticles can be clearly observed in all the samples.

The FT-IR spectra of polypyrrole and polypyrrole-gold nanocomposites are shown in Figure 5. In the IR spectra of both polypyrrole and polypyrrole-Au composites, absorption peaks corresponding to the bipolaron bands were observed at 1220 and 910 cm⁻¹, in good agreement with spectroscopic characterization of polypyrrole.⁸ The shift in position of the peak at 1560 cm⁻¹, corresponding to -C-N stretch to higher wave numbers in the spectra, indicates an effective charge transfer between the Au and polypyrrole, as mentioned in previous reports.

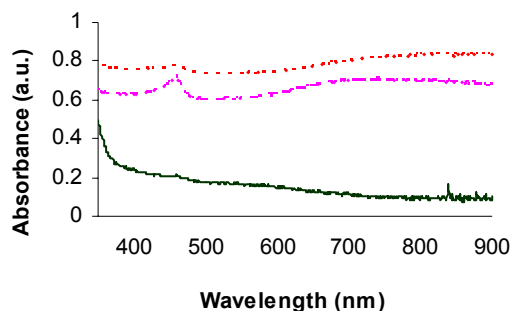


Figure 3. UV-Vis spectra of polypyrrole-Au-NSA nanocomposite during different stages of polymerization (starting from bottom to top).

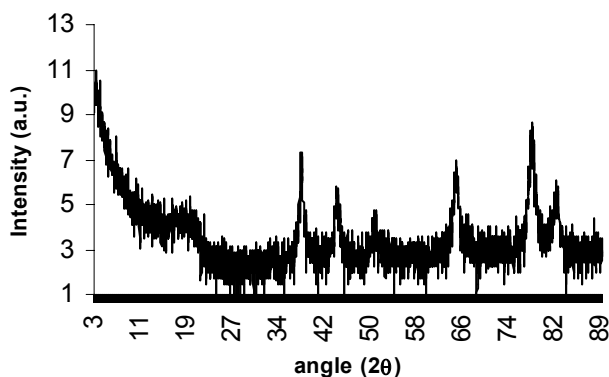


Figure 4. XRD spectrum polypyrrole-Au-NSA nanocomposite.

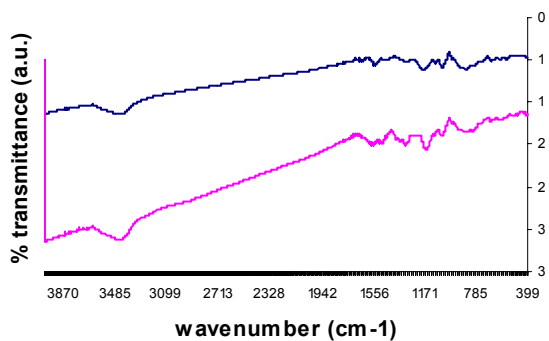


Figure 5. FT-IR spectra of polypyrrole-Au-NSA (bottom) and polypyrrole-NSA (top).

The electrical conductivity of the polypyrrole-Au-NSA composite powders was measured by the four-point probe technique. The conductivity of the NSA doped polypyrrole was 2.5 S/cm. After incorporation of gold nanoparticles, the conductivity values increased to 15 S/cm.

Conclusions

In this work we have developed a procedure for synthesis of polypyrrole-gold nanocomposites containing well-dispersed Au nanoparticles. This procedure results in formation of high surface area nanocomposites, where Au nanoparticles are attached to polypyrrole nanostructures.

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