In-situ chemical synthesis route for a fiber shaped gold-polyaniline nanocomposite

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Abstract

A facile synthesis route is described for the preparation of a gold-polyaniline nanocomposite material by polymerization of aniline hydrochloride using HAuCl_4 as the oxidant. It was found that the oxidative polymerization of aniline hydrochloride leads to the formation of polyaniline with a fiber-like morphology, while the concomitant reduction of HAuCl_4 results in the formation of gold nanoparticles of diameter 2-7 nm. The gold nanoparticles were highly dispersed and stabilized throughout the polyaniline fibers while being in intimate contact with the polymer. The combination formed a uniform metal-polymer composite material.

Introduction

Composites of electrically conducting polymers and metal nanoparticles are important in modern science and technology due to their potential applications and important physical properties [1]. Amongst the conducting polymers, polyaniline has been extensively studied because of its controllable electrical conductivity and interesting redox properties associated with the chain nitrogen [2]. One-dimensional nanostructured polyaniline nanofibers have attracted considerable research efforts since they are a kind of desirable molecular wire as a result of their large surface area and controllable conductivity. On the other hand, among the metal nanoparticles gold has been extensively studied due to its unique optical and catalytic properties [3]. Thus, a gold-polyaniline composite would acquire quality through the combination of both components, that is, good stability, high conductivity and the unique optical properties from the metal part while gaining easy processing, light weight, variable conductivity through doping, and the good optical properties from the polymer portion.

Chemical synthesis of a gold-polyaniline composite is based on the oxidizing properties of auric acid [4], which initiates the polymerization process of aniline. A gold-polyaniline composite obtained using a phase transfer catalyst has been reported in which polyaniline nanoballs several nanometres in size had become decorated with gold nanoparticles [5]. Nanofiber shaped polyaniline has been synthesized using auric acid as the oxidizing agent of aniline, but a complete phase separation was found between the polymer and the metal particles [6]. A report has been published for a two-step synthesis of a gold-polyaniline composite in which 10-bromodecylperoxide has been utilized as a stabilizer of the gold nanoparticles as well as the oxidizing agent of aniline [7]. Gold-polyaniline composites have also been produced by applying electrochemical [8] synthesis method. However, many of the above composites suffered from their overall low surface area, that is, the metal nanoparticles were dispersed in a bulk form of a polyaniline matrix and there was a lack of intimate contact between metal nanoparticles and polymer. The contact between the metal particles and polymer in a hybrid system plays a crucial role in molecular electronic devices since the charge transfer at the contact point, which indicates functionalization, plays an important role in many areas of technology.

In this communication, we report on an *in-situ*, one pot chemical synthesis route for the preparation of a gold-polyaniline nanocomposite material having a fiber-like morphology, in which 2-7 nm sized gold nanoparticles are highly dispersed in 15-40 nm diameter polymer fibers. Previously we demonstrated the synthesis of such gold-polyaniline composite obtained using aniline itself as oxidant with auric acid (hydrogen tetrachloroaurate) as reductant [9]. In the present work we describe the use of aniline hydrochloride. The use of the solid aniline hydrochloride is preferred to liquid aniline from the point of view of handling hazards [10].

Experimental techniques

Synthesis of fiber shaped gold-polyaniline nanocomposite

Aniline hydrochloride powder (0.2 g) was dissolved in methanol under mild stirring conditions. A stock solution of HAuCl_4 (1.5 mL) having a concentration $10^{-2} \text{ mol dm}^{-3}$ was added drop wise to the aniline hydrochloride solution. A dark green colour developed during the addition of HAuCl_4 after which the solution was kept under rest for 5 min. A green colloidal precipitation was formed slowly at the bottom of the beaker. The material was then allowed to settle for a further 10 min. Subsequently, the solution, taken from the bottom of the beaker, was pipetted onto lacey, carbon-coated, copper TEM grids. The remaining portion of the compound was used for IR and UV-visible spectra analyses. The whole process was carried out at room temperature ($\sim 25^\circ \text{C}$).

Result and discussion

The optical behaviour of the dark green product was studied by FTIR spectra[†] analysis. In the IR spectrum (Figure 1), the main peaks at 1600 and 1510 cm^{-1} correspond to the stretching deformation of the quinine and the benzene rings respectively. The band at 1375 cm^{-1} is attributed to the C-N stretching mode in the neighborhood of the quinoid ring. The band at 1305 cm^{-1} is assigned to the C-N stretching of the aromatic amine, whereas in the region $1010\text{--}1170 \text{ cm}^{-1}$, the aromatic in-plane C-H bending modes are observed. The out-of-plane deformations of C-H in the 1, 4-disubstituted benzene ring are located at 870 cm^{-1} . In the present study, the IR spectrum of the resultant compound resembles that of the typical spectra of HCl doped polyaniline [11, 12].

The resultant polymeric material was studied by transmission electron microscopy[‡] for an in-depth

understanding regarding the morphology of the polyaniline and the fate of HAuCl_4 after the reaction. Figure 2 (A and B) shows the structure of the resultant material at various magnifications illustrating the fiber-like morphology of the material. The diameter of the fibers varied from 15–40 nm. A typical EDX analysis (Figure 2D) obtained from the electron beam being focused onto a dark spot in the polyaniline fiber (Figure 2C) confirms that these spots are gold particles. Focusing the beam between the dark spots near the thin edge of the fiber yielded no gold X-ray peaks. Stereo images showed that the gold particles are distributed within the polymer. The gold particles were 2–7 nm in diameter.

In addition to this, electron energy loss spectroscopy (EELS) mapping for the gold particle distribution provided unambiguous confirmation that the dark spots are gold. This is most clearly illustrated in Figure 3 where a small portion of the gold-polyaniline composite was isolated such that the particles showed minimal overlap. Figure 3A is a zero-loss image of the composite. This is an energy filtered image such that it is only derived from electrons which have retained the beam energy when passing through a thin sample. This image contains no useful micro-analytical information. In contrast, Figure 3B is a gold map from the same region. This Au jump-ratio image was obtained by dividing the Au $\text{O}_{2,3}$ post-edge loss image (an image derived from the signal from an energy window placed just above the ionization energy of Au $\text{O}_{2,3}$ shell X-rays, the signal being the sum of the background signal at this position which contains no micro-analytical information, and the signal resulting from electrons that lost energy by generating Au $\text{O}_{2,3}$ shell X-rays) by the pre-edge image (an image derived from the signal from an energy window placed just before the ionization energy of Au $\text{O}_{2,3}$ shell X-rays, this image being a background image). From comparing the zero-loss and jump-ratio images, it can be seen that all the dark areas in Figure 3A correspond to all of the Au particles mapped in Figure 3B. This result was confirmed for all the other areas studied.

The electronic absorption spectra of the polyaniline salt have been documented in the literature. Polyaniline salt [6] shows three absorption peaks at 325–360 nm, 400–430 nm and 780–825 nm. In the present study, the UV-visible spectrum[§] (Figure 4) of the resultant material shows two sharp and prominent absorption bands at 320 and 423 nm. The absorption peak at 320 nm is due to the $\pi\text{--}\pi^*$ transition of the benzenoid rings. The peak at 423 nm is due to the polaron / bipolaron transition. A suppressed broad absorption band starting from 510 nm to 900 nm can be assumed to result from the combined effect of the gold nanoparticles and the transition from the localized benzenoid highest occupied molecular orbital to a quinonoid lowest unoccupied molecular orbital. In our earlier synthesis using liquid aniline and methanol [9] this transition produced a clear absorption maximum at 610 nm, showing that the detailed structure of the material obtained in the present synthesis procedure is slightly different. After deconvolution the appearance of the absorption peak at 560 nm reveals the plasmon absorption

Figure 1

IR spectrum of the composite material

Figure 2

TEM images of the composite material taken at different magnifications. The dark spots within the polymer fibers are gold nanoparticles as identified by EDX analysis (D), the copper peaks being from the TEM grid

Figure 3

(A) Zero-loss image of polyaniline encapsulated gold particles. (B) Au $O_{2,3}$ edge jump-ratio image of the area shown in (A). All of the dark regions in (A) can clearly be identified as gold nanoparticles

Figure 4

UV-visible spectrum of the gold-polyaniline composite material. After deconvolution the appearance of two absorption peaks at around 560 and 725 nm, red and blue dotted curves respectively, result from the plasmon absorption band for the gold nanoparticles and the benzenoid-to-quinoid excitonic transition respectively

band for the gold nanoparticles resulting from the collective oscillation of the conduction electrons. The other absorption peak at around 725 nm which is due to the benzenoid-to-quinoid excitonic transition generally shows a band in the 700–800 nm region. From the TEM images it is clear that the encapsulated gold nanoparticles in the polyaniline matrix are within the size range 2–7 nm. Generally, gold nanoparticles within the size range 5–50 nm show an absorption band in the 520–530 nm regions [13]. In the present study, a bathochromic shift of the plasmon absorption band of the gold nanoparticles has been observed. Nanosized gold particles have a high electron affinity and can strip off electrons from the surrounding matrix. These charged particles are stabilized by the matrix and the repulsive force between the charged particles prevents their aggregation. A process of forming such a complex naturally will alter the electron density of the nanoparticles surface. This then directly affects the surface plasmon absorption band which results in a bathochromic shift [14]. In the UV-vis spectra (Figure 4), the absorption band at 560 nm is due to the plasmon absorption band of the gold nanoparticles which are encapsulated by the polyaniline matrix. Since a shift of the plasmon absorption band was observed for the polyaniline encapsulated gold nanoparticles, this leads to the conclusion that functionalization of the gold nanoparticles by the polymer has taken place [15].

Conclusion

We have demonstrated a green chemical route to obtain a gold-polyaniline fiber-shaped nanocomposite material by using a one pot, *in-situ* and template-free synthesis method. The formation of a nanofiber-like morphology has been discussed previously [16]. From earlier reports, when HAuCl_4 was used as the oxidizing agent for aniline the formation of a nanoballs [5] and nanofiber-like [6] morphology was obtained with a phase separation between the gold and polymer being observed. A multi-step synthesis method also does not guarantee an intimate contact between the metal and the polymer [7]. The present synthesis route has achieved a nanostructured hybrid material with an intimate contact between gold nanoparticles and polyaniline through functionalization. The conductivity of this composite material has been found $0.7 \times 10^{-1} \text{ S cm}^{-1}$ at 300 K. The composite is expected to be advantageous compared to the other reported gold-polyaniline systems with respect to the nano-dimension as well as the composite formation. A superstructured nanomaterial, described here, has some novel properties which are technologically useful for the fabrication of electronic memory devices. Optimization of such a device is currently in progress.

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Notes and references

- † A Perkin-Elmer 2000 FT-IR spectrometer, operating within the range $850\text{--}1700 \text{ cm}^{-1}$ with a resolution 4 cm^{-1} , was used for the infrared spectral analyses. For this study, the sample was deposited in the form of a thin film on a sodium chloride disk.
- ‡ Transmission electron microscopy studies of the particles were carried out at an accelerating voltage of 197 kV using a Philips CM200 TEM equipped with a LaB_6 source. An ultra-thin windowed energy dispersive X-ray spectrometer and a Gatan Model 678 Imaging Filter (GIF) attached to the TEM was used to determine the chemical composition of the samples.
- § For UV-vis spectra analysis, a small portion of the solid sample was dissolved in methanol and scanned within the range 300–1000 nm, using a Varian, CARY, 1E, digital spectrophotometer.

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