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Palladium Nanoparticles in Poly(*o*-phenylenediamine): Synthesis of a Nanostructured ‘Metal-Polymer’ Composite Material

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We report here on an in-situ synthetic method for the preparation of a metal-polymer composite material. This technique offers a route to achieving an intimate contact between the polymer and the metal nanoparticles. Very small palladium nanoparticles (~3 nm) are uniformly dispersed and highly stabilized throughout the macromolecular chain, forming a uniform metal-polymer composite material. The resultant composite material was characterized by means of different techniques, such as IR and Raman spectroscopy, which offered information about the chemical structure of polymer, whereas electron microscopy images provided information regarding the morphology of the composite material and the distribution of the metal particles in the composite material.

Keywords composite material, Raman spectra, TEM, Pd-nanoparticles, poly(*o*-phenylenediamine)

Introduction

Nanocomposites are a special class of materials originating from a suitable combination of two or more types of nanoparticles or nanosized objects, which when utilizing an appropriate formation technique, result in new materials having unique physical properties and a wide range of applications in diverse areas (1). Electrically conducting polymers incorporating metallic nanoparticles have received extensive attention over the years due to their vast range of applications in areas such as biosensors (2), electrochromic capacitors (3), anti-corrosive coatings (4), and electro-catalysis (5). Polyaniline, as the most extensively studied conducting polymer, has been widely investigated for electronic and optical applications due to both its good environmental stability and its tunable electrical and optical properties (6, 7).

The preparation of gold-polyaniline composite material has also been undertaken utilizing preformed polyaniline and by exploiting the multi-oxidative state of the

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polymer (8, 9). Using hydrogen peroxide, formation of a gold-polyaniline composite with a gold particle size of 26 nm has been reported (10). We have successfully produced a gold-polyaniline composite material from a toluene solution by using a phase transfer catalyst, where polyaniline nanoballs, (a few micrometres in diameter) were decorated with the gold nanoparticles (10–50 nm) (11). In a separate communication (12), we reported the formation of a gold-polyaniline composite material with a narrow size distribution of the gold particles (~6 nm). Recently, a technique for incorporating 50 nm sized Pt nanoparticles on polyaniline has been published (13). The synthesis of a Cu-polyaniline composite material has been reported using both a sonochemical synthetic route (14), and using sodium borohydride to reduce copper nitrate and then mixing the resultant sol with aniline and ammonium persulfate (15).

Polyaniline derivatives have attracted growing scientific attention because their chemical properties are similar to those of polyaniline and they are more easily processed than the parent polymer (16).

Efforts have been made to produce Pd-poly (*o*-methoxyaniline) (16) and Pd-poly (*o*-toluidine) (17) composites using preformed polymeric material. A poly(*o*-toluidine) and copper nanoparticle composite material has been produced on preformed poly(*o*-toluidine) by exploiting various oxidation states of the polymer (18). An *in situ* protocol has been developed by us for the synthesis of Cu-poly(3,5 dimethyl aniline) (19) and Cu-poly (*o*-toluidine) (20) composite materials using cupric sulfate as an oxidizing agent. This results in copper nanoparticles with an average size of 5 nm, which are highly dispersed within the polymer. It has been recorded (21) that the polymerization of *o*-anisidine by HAuCl_4 forms a gold-poly(*o*-anisidine) composite material. In that report, much more emphasis was focused on the structure of the gold nanoparticles rather than the morphology and properties of the polymer that was generated simultaneously with the gold nanoparticles. Recently, the synthesis of poly(*o*-phenylenediamine) with a nanobelt-like morphology has been documented (22). This process started with *o*-phenylenediamine and employed HAuCl_4 as a polymerizing agent. The HAuCl_4 resulted in the formation of bulk gold particles. A complete phase separation between the polymer and metal particle was observed.

In the present communication, we report on a reaction between *o*-phenylenediamine and Pd-acetate that forms a yellow precipitation. The resultant precipitation was analyzed by means of different techniques including Raman and IR spectroscopy, which yielded the chemical structure of the product, whereas electron microscopy images provided information regarding the morphology and the physical structure of the material.

Experimental

Reagent grade Pd-acetate was purchased from Next Chimica. *O*-phenylenediamine was supplied by BDH, London. 0.42 g of Pd-acetate was dissolved in 100 mL toluene and used as the stock solution. In a typical experiment, 0.06 g of *o*-phenylenediamine was dissolved in 15 mL of toluene in a 25 mL conical flask under continuous stirring conditions using a magnetic stirrer. From the stock solution, 1.0 mL of Pd-acetate was added slowly, to the stirred solution. Initially, the solution developed a yellow colorization. However, after addition of all of the Pd-acetate, a yellow, cloudy precipitation appeared. Stirring was discontinued and the solution was left for 5 min during which time all the precipitation collected at the bottom of the flask. After collection of the TEM samples of the material from the bottom of the flask, the rest of the solution was filtered and the solid mass

collected was used for both IR and Raman analyses. The entire reaction was carried out at room temperature.

Infrared spectra, in the region 700–4000 cm^{-1} , were obtained from a Perkin-Elmer 2000 FT-IR spectrometer operating at a resolution of 4 cm^{-1} . The IR sample was deposited in the form of a thin film on a NaCl disk. Raman spectra were acquired using the green (514.5 nm) line of an argon ion laser. Light dispersion was carried out via the single spectrograph stage of a Jobin-Yvon T64000 Raman spectrometer. Power at the sample was kept very low (0.73 mW), and the laser beam diameter at the sample was $\sim 1 \mu\text{m}$.

Transmission electron microscopy (TEM) studies of the resultant material were carried out at an accelerating voltage of 200 kV using a Philips CM200 TEM. An ultra-thin windowed energy dispersive X-ray spectrometer (EDS) and a Gatan Imaging Filter (GIF) attached to the TEM were used to determine the chemical composition of the samples. TEM specimens were prepared by pipetting 5 μL of colloid precipitation onto lacey carbon coated copper TEM grids.

Results and Discussion

In this work, we first examined the spectroscopic behavior of the dried material by IR analysis within the spectral region 700 to 4000 cm^{-1} (Figure 1A). The peaks at 3373 and 3197 cm^{-1} result from N–H stretching, whereas peaks at 3030 and 2938 cm^{-1} correspond to aromatic C–H stretching. The peaks at 1618 and 1501 cm^{-1} correspond to the stretching deformation of the quinone and benzene rings, respectively. The band at 1250 cm^{-1} can be interpreted as the C–N⁺ stretching vibration of the polaronic structure (23). The band at 1134 cm^{-1} can be assigned to the vibrational mode of the –NH⁺= structure. This mode indicates the presence of positive charges on the chain and the distribution of the dihedral angle between the quinone and benzenoid rings (24). Aromatic C–H in-plane bending modes are observed at 1042 cm^{-1} . The out-of-plane deformations of C–H in the 1,2,4-trisubstituted benzene rings are located in the region 900–700 cm^{-1} .

The Raman spectra of the resultant material is given in Figure 1B and comparable spectral behavior has been observed for the polyaniline system (25). The present spectrum reveals the presence of the C–C deformation bands of the benzenoid ring at 1560 and 1590 cm^{-1} . The band at 1520 cm^{-1} corresponds to the N–H bending deformation mode. A strong band at 1470 cm^{-1} is due to C=N stretching mode of the quinoid units. The overlapping peaks between 1300 and 1430 cm^{-1} correspond to the C–N⁺ stretching modes of the delocalized polaronic charge carriers. The intensity of these peaks confirms the presence of a high concentration of charge carrier species in the polymer. A broad band at 1250 cm^{-1} can be assigned to the C–N stretching mode of the polaronic units. The CH benzene deformation mode is located at 1160 cm^{-1} and this indicates the presence of the quinoid rings.

Both the IR and Raman data documented the presence of the charge carrier species, i.e., the radical cations (conductive holes) and other neutral segments in this product compound. These are similar to the structure of polyaniline (23–25), which indicates that the resultant product was –NH₂ substituted polyaniline i.e., poly(*o*-phenylenediamine).

The TEM images in Figure 2 illustrate the fiber-like morphology of the poly(*o*-phenylenediamine). Figure 2A is an example of the large population of polymer fibers, while Figure 2B images part of a polymer fiber. Figure 2C is a higher magnification image

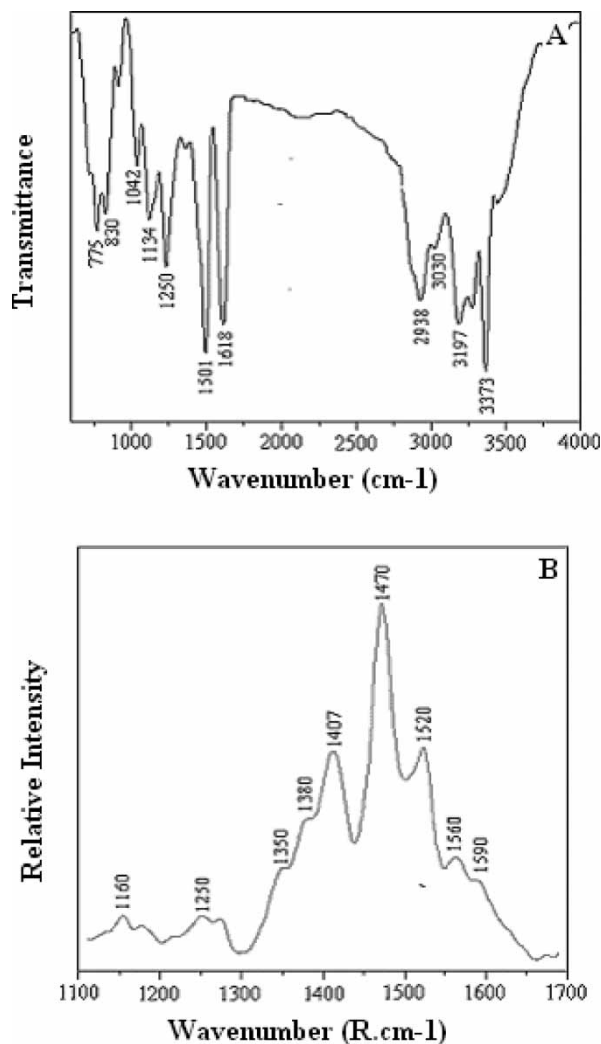


Figure 1. A) IR and (B) Raman spectra from the composite material.

derived from the boxed area indicated in Figure 2B, showing the surface morphology and internal microstructure of the polymer. It is clear that the surface is not smooth. The rough surfaces and the interior of the polymer are revealed by both these micrographs and stereo images to be composed of highly distributed dark regions of diameter about 3 nm. An EDS spectra (Figure 2D) from the area shown in Figure 2C was obtained when the electron beam was focused on a single dark spot and indicates the presence of palladium. EELS mapping of the distribution of Pd in the material has provided unambiguous confirmation that the dark spots are palladium. This is most clearly illustrated in Figure 3 where a relatively thin region of polymer composite was isolated such that the particles were not unduly overlapping. Figure 3A is a zero-loss image of this area, that is, it 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 microanalytical information. In contrast, Figure 3B is a palladium map from the same region. This Pd

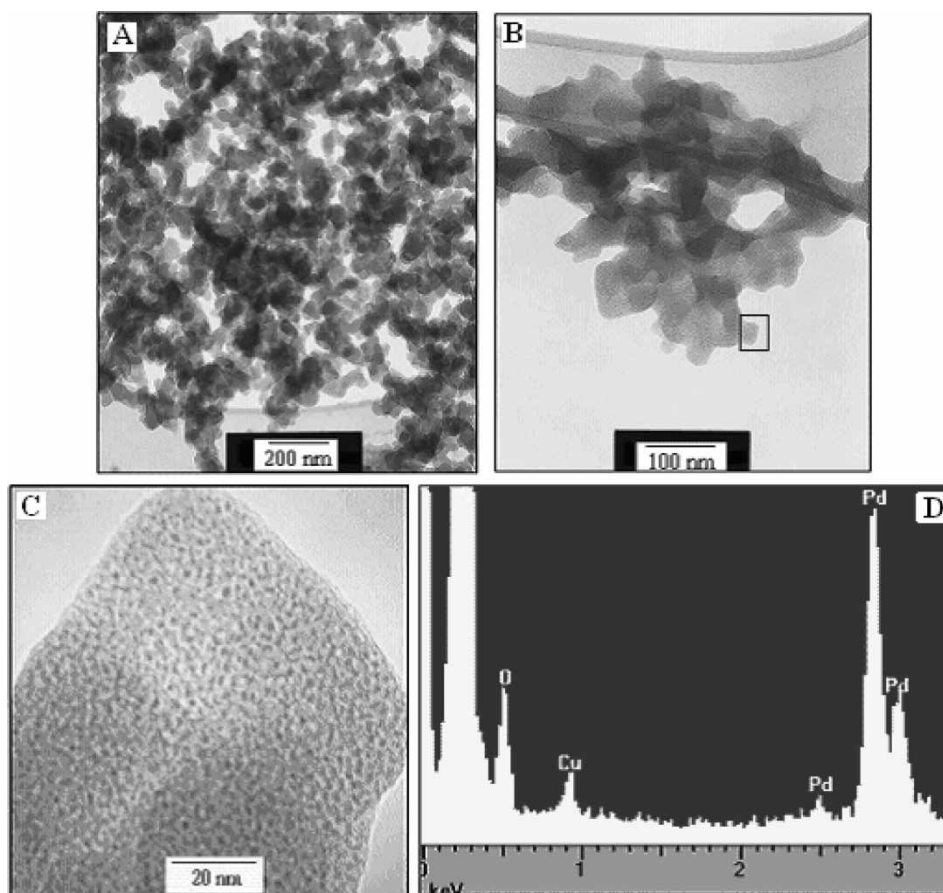


Figure 2. Bright field TEM images of the polymer: (A) Low magnification image showing the long chain morphology of the poly (*ortho*- phenylenediamine). (B) A small portion of the polymer chain revealing the overall morphology of the polymer. (C) A higher magnification image of the boxed area in (B) revealing the rough surface of the composite and the homogeneous distribution of the nanoparticles within the polymer. (D) EDS spectrum resulting from focusing the electron beam onto a single dark spot at the edge of the sample shown in (C). The copper peak is derived from scattering from the TEM copper mesh support grid.

jump-ratio image was obtained by dividing the Pd-N_{2,3} post-edge loss image (an image derived from the signal from an energy window placed just above the ionization energy of Pd N shell X-rays, the signal being the sum of the background signal at this position which contains no microanalytical information, and the signal resulting from electrons that lost energy by generating Pd N 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 Pd N shell X-rays, this image being a background image). From comparing the zero-loss and jump-ratio image, it can be seen that the dark areas in Figure 3A correspond to all the Pd particles (light regions) mapped in Figure 3B. It should be noted that when the electron beam was positioned on the composite there was neither a morphological change in the polymer nor any change in the position of any of the nanoparticles showing that the composite material including Pd nanoparticles were highly stabilized.

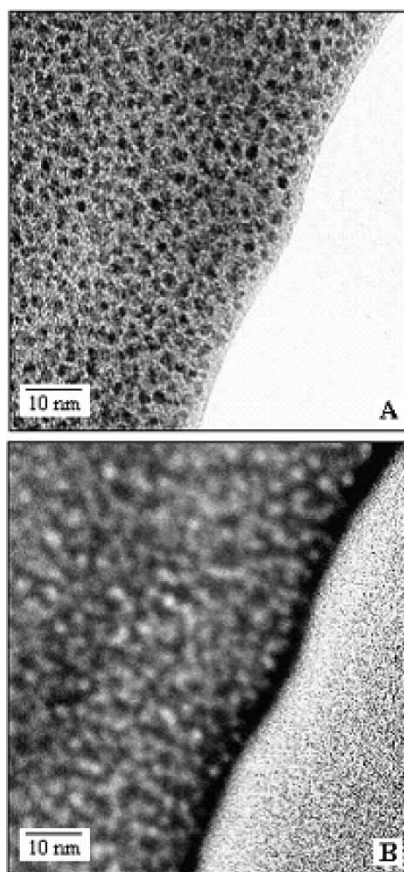


Figure 3. (A) A zero electron energy loss, high magnification image of the edge of the polymer composite. The dark spots in the polymer are ca. 3 nm diameter palladium nanoparticles. (B) A palladium jump ratio image of the area in (A) using the Pd-N_{2,3} edge. Palladium can only be seen in the areas corresponding to the dark regions in (A).

The formation mechanism of the oriented morphology of the polymer is not clear. However, according to the classical nucleation theory, the generally accepted mechanism is of a two-step process, such as, the formation of the nucleation centers followed by successive growth. In the first step, we can assume a covalent bond is formed between the $-\text{NH}_2^+$ group and the Pd (II), which results in the formation of radical cations on nitrogen $-\text{PhNH}_2^+$ and, under suitable conditions, that species develops an oligomeric form of (*o*-phenylenediamine). These oligomers are considered as the nucleation centers. The process of oligomerization is an oxidation pathway with each step being associated with the release of electron (26). These electrons then reduce the palladium ions to form palladium atoms, these atoms subsequently coalescing to form metal nanoparticles. It has been reported that gold nanoparticles catalyze the directional growth mechanism of the polyaniline nanofiber (27) and poly (*o*-phenylenediamine) nanobelts (22). In this study, a similar effect for palladium nanoparticles can also be expected. Since the formation of the palladium nanoparticles and the oligomeric form of the (*o*-phenylenediamine) takes place simultaneously, the palladium nanoparticles

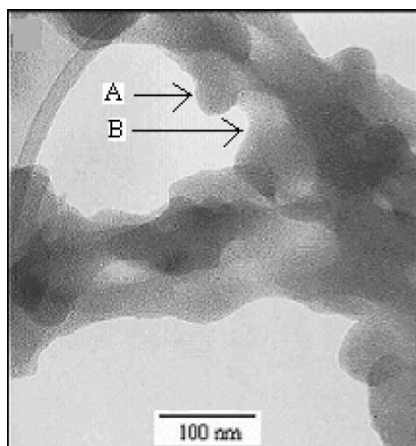


Figure 4. (A) Branching and (B) interconnecting network of the composite material.

can catalyze the oriented growth of the poly-(*o*-phenylenediamine) resulting in a fiber-like morphology. During the formation, a branching or interconnected network (Figure. 4) was also observed and can be explained as follows. A competition between a directional fiber growth process and the formation of additional nucleation centers takes place. Once a high density of nucleation centers is generated, the interfacial energy between the reaction solution and the nanofibers may be minimized such that rapid precipitation occurs in a disordered manner resulting in irregular shapes being produced (28).

Conclusions

In this work, we have demonstrated a facile synthesis route for the preparation of a palladium-poly(*o*-phenylenediamine) composite material having a branching and interconnected network. The palladium nanoparticles generated, having a narrow size distribution (~ 3 nm), were evenly dispersed within the poly-(*o*-phenylenediamine) matrix and catalyzed the directional growth, which resulted in the formation of a metal-polymer composite material with a fiber-like morphology. It is interesting to note that when HAuCl_4 was used as the oxidizing agent for the preparation of polyaniline fibers (27) and poly-(*o*-phenylenediamine) nanobelts (22), a complete phase separation was observed between the polymer and the gold particles. In contrast, in this work, we find a uniform palladium-poly-(*o*-phenylenediamine) composite forming a fiber network.

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