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Preparation of highly dispersed Pd-nanoparticles in poly- (*o*-aminophenol) needles: An 'intimate composite material'

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Poly- (*o*-aminophenol)-Pd nanoparticle composite can be prepared by a single step, one pot chemical synthetic route at room temperature. ∼2nm sized Pd-nanoparticles are encapsulated inside the needle-shaped polymer cage. IR and Raman spectra provide the information on the structure of the polymer. SEM and TEM images show the morphology of the polymer and the size of the metal particles respectively. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Polyaniline derivatives have attracted considerable scientific attention since their chemical properties are similar to polyaniline and their processing is much easier as they exhibit better solubility with common organic solvents. Electrically conducting polymers are important in modern technology as they have potential applications in optical and electronic devices, chemical sensors, catalysis, drug delivery and energy storage systems [1–5].

The incorporation of metal nanoparticles in conducting polymers provides for enhanced performance for both the 'host' and the 'guest', which can lead to interesting physical properties and important potential applications. The catalytic activity of palladium nanoparticles can be successfully combined with electrically conducting polymers in the form of hybrid composite materials. Efforts have been made to produce Pd- (polyaniline [6], polypyrrole [6], poly-*o*-methoxyaniline [7], poly-*o*-toluidine [8]) composites by using a chemical route. All of these composites have been prepared by using preformed polymeric material. The main disadvantage of this approach is the risk that there is a lack of intimate contact between the metal particles and the polymeric support.

We believe that this shortcoming is likely to be overcome by using a method in which both the polymer and the nanosized metal particles are produced simultaneously. In order to illustrate such an approach, we report on a single step, *in-situ* chemical synthetic route for the preparation of a Pd - [poly- (*o*-aminophenol)] composite material in which highly dispersed Pd nanoparticles of the order of 2 nm diameter are contained within the polymer matrix.

2. Experimental

2.1. Materials

Regent grade Pd-acetate was purchased from Next chimica. *O*-phenylenediamine was supplied by BDH, London. 0.42 g Pd-acetate was dissolved in 100 ml toluene and used for the experiment as a stock solution.

2.2. Instrumentation

Transmission electron microscopy (TEM) studies of the particles were carried out at an accelerating voltage of 200 kV using a Philips CM200 TEM equipped with a LaB_6 source. An energy dispersive X-ray spectrometer

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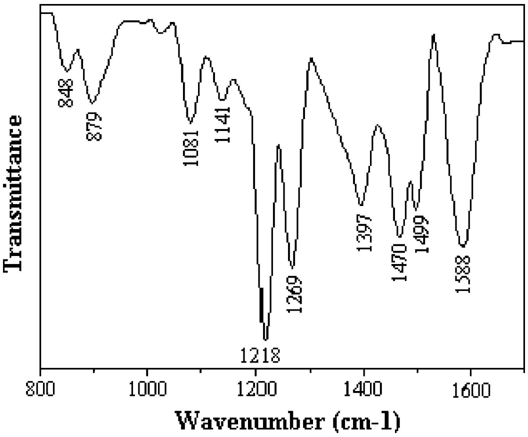

Figure 1. IR spectra of the composite material.

(EDS) attached to the TEM was used to determine the chemical composition of the samples. Palladium mapping was carried out using a Gatan EELS 678 Imaging Filter. TEM specimens were prepared by pipetting 2 μL of colloid solution onto a carbon coated copper grid.

Surface images were obtained of the TEM samples using a JEOL JSM-840 scanning electron microscope (SEM) operating at an accelerating voltage of 20 kV. As a precaution to prevent possible charging, the samples were sputter coated with a thin uniform layer of Au-Pd prior to viewing.

Raman spectra were acquired using the green (514.5 nm) line of an argon ion laser as the excitation source. Light dispersion was done via the single spectrograph stage of a Jobin-Yvon T64000 Raman spectrometer, using the microscope stage, and a CCD detector. Power at the sample was kept very low (0.73mW), and the laser beam diameter at the sample was ∼1 m.

Infrared spectra, in the region 4000–700 cm^{-1}, were collected using on a Perkin-Elmer 2000 FT-IR spectrometer at a resolution 4 cm^{-1}. The sample was deposited in the form of thin film on a NaCl disk.

2.3. Procedure

In a typical experiment, 0.09 g of ortho-aminophenol was dissolved in 15 ml methanol under continuous stirring conditions using a magnetic stirrer. 4 mL of palladium acetate solution[9] was added drop by drop to the solution. When the pH reached at 5.5, precipitation occurred resulting in a reddish yellow coloration to the solution. One drop of this solution then was pipetted onto a lacey carbon coated copper grid for TEM analysis. After completion of the TEM analysis, the same sample was used for SEM studies of the surface morphology of the polymer. The rest of the solution was dried under vacuum and the dry mass was used for IR and Raman analysis.

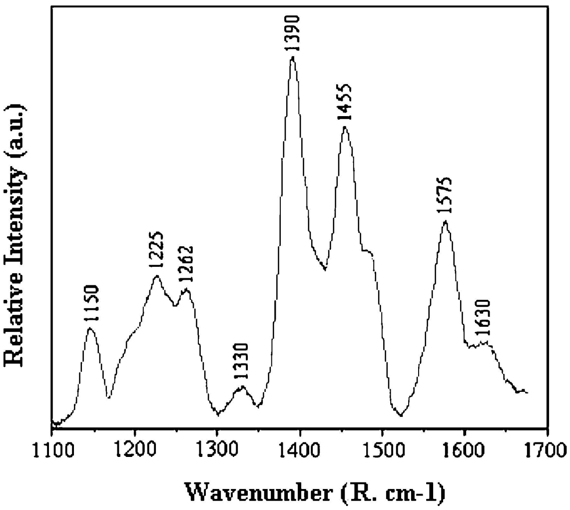

Figure 2. Raman spectra of the composite polymer.

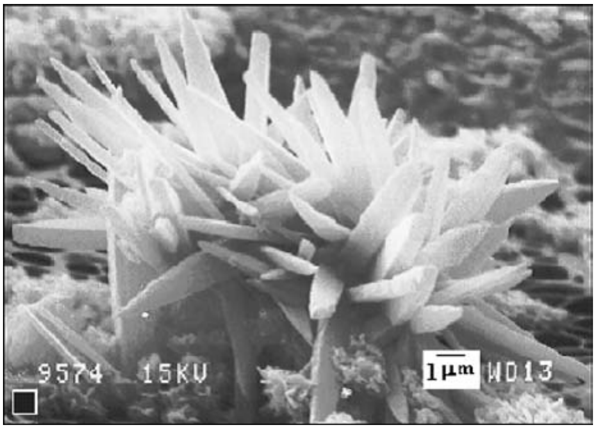

Figure 3. SEM image of the composite material showing a cluster of larger polymer needles.

3. Results and discussion

In the IR spectrum (Fig. 1), the characteristic band at 1588 cm^{-1} can be assigned to the $C = C$ stretching of the quinoid rings while the two peaks at 1499 and 1470 cm^{-1} are the characteristic bands of the $C = C$ stretching vibration mode for benzenoid rings. The bands at 1397 and 1218 cm^{-1} can be attributed to the C-O-H deformation vibration and the C-O stretching vibration respectively. The band at 1269 cm^{-1} results from the C-N stretching vibration, whereas the bands at 1141 and 1081 cm^{-1} are due to aromatic C-H in-plane bending modes. The out-of-plane deformations of C-H in the 1, 4- disubstituted benzene rings are located at 879 and 848 cm^{-1}.

In the Raman spectrum (Fig. 2), the position of the C-C and C-H benzene deformation modes are found at 1575 and 1150 cm^{-1} indicating the presence of quinoid rings. The band at 1225 cm^{-1} corresponds to the C-N stretching of the single bond while the band at 1262 cm^{-1} can be assigned to the C-N stretching mode of the polaronic units. The band at 1330 cm^{-1} corresponds to the $C-\overset{\cdot+}{N}$ stretching modes of the delocalized polaronic charge carriers that indicate the conducting nature of the polymeric compound. The peak at 1390 cm^{-1} is due to the electronic absorption of the free charge carriers. The band at 1455 cm^{-1} corresponds to the $C = \overset{\cdot+}{N}$ stretching mode

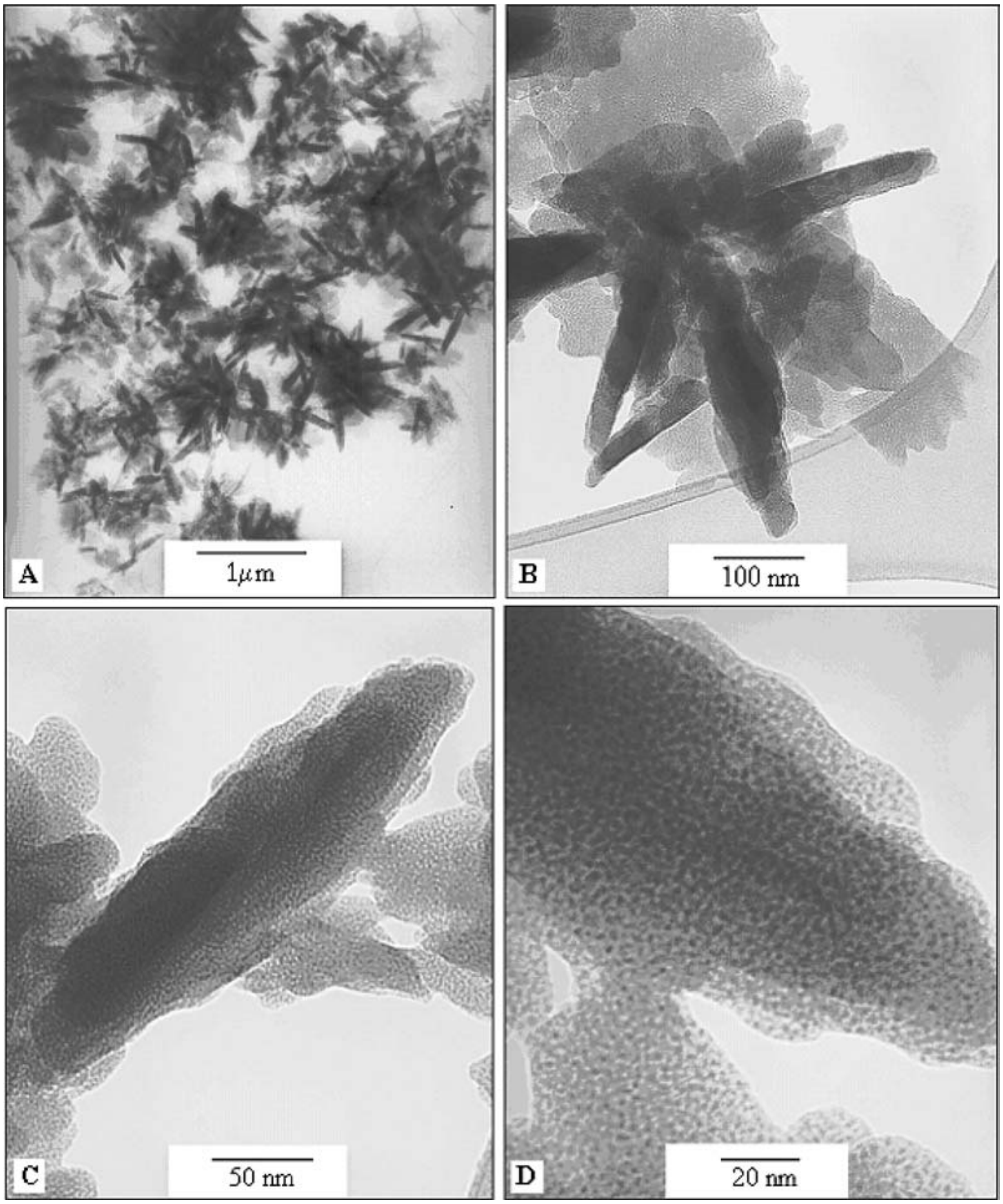

Figure 4. TEM images at increasing magnifications of the composite made up of nanoneedles and palladium nanoparticles (dark spots).

of the quinoid units. The C-C deformation bands of the benzenoid rings are observed at 1630 cm^{-1}.

The SEM image (Fig. 3) illustrates the needle-like morphology of the polymeric form of *o*-aminophenol. A similar morphology was obtained when the ratio of Pd acetate to *o*-aminophenol was altered. Various sized isolated clusters of these larger needles were seen scattered on the grid surface. Fig. 4 and 5 show a sequence of increasingly magnified TEM images of the poly-(*o*-aminophenol), the needles being smaller than in Fig. 3, but again exhibiting some marked clustering. In Fig. 4B– and 5, the dark spots result from the nanoparticles that are highly dispersed in the polymer. The inset EDS spectrum in Fig. 6 provides the confirmation that the particles are palladium, the spectrum being obtained by focusing the electron beam onto a single particle at the edge of a needle. This was confirmed by EELS element mapping using the Pd-$N_{2,3}$ edge, which revealed that Pd was only present in the particles. The Pd nanoparticles were encapsulated and highly dispersed within the polymer structure. They had a remarkably uniform size with a diameter close to 2 nm. The composite material was found to be structurally and chemically stable under the high electron doses that were utilized, and the associated elevated temperatures experienced, during the EELS element mapping as well as during the longer term, lower dose exposures.

4. Mechanism

The *in-situ* co-formation of the palladium nanoparticles and the *o*-aminophenol polymer suggests the operation of the following mechanism. The presence of an electron-

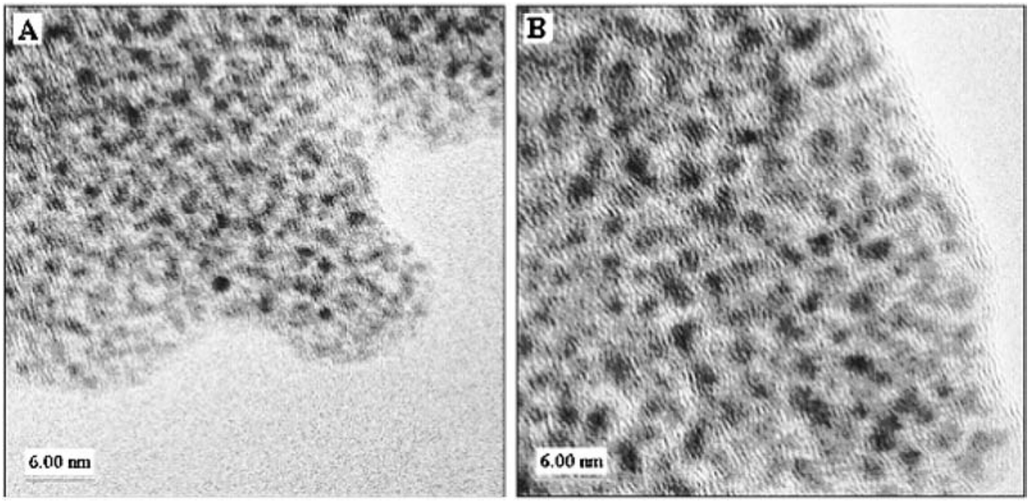

Figure 5. High magnification TEM images of the Pd nanoparticles in the polymer matrix.

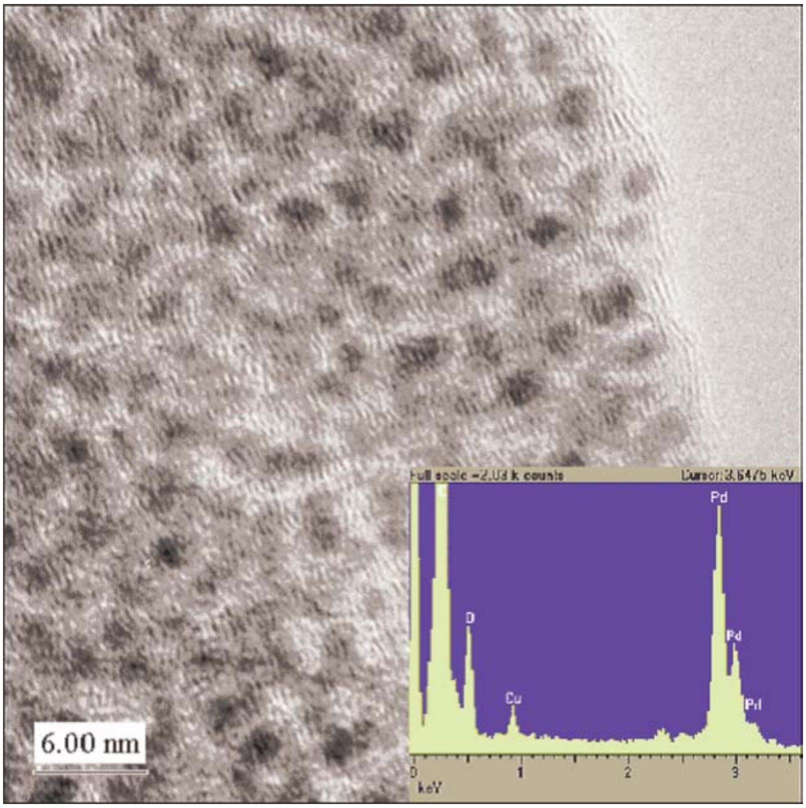

Figure 6. A high magnification TEM image of the composite material. The EDS spectrum, inset, was obtained from a spot analysis of a single nanoparticle located at the edge of a needle. The copper peak is derived from scattering from the copper support grid.

donating group (-OH) in aminophenol facilitates the relay of electrons through the $-\ddot{N}H_2$ group and forms an electrostatic bond with Pd^{2+} cation. During the electrostatic attachment, the$[(OH)ph-\overset{\cdot+}{N}H_2]$ like species are formed which, under acidic conditions, undergo polymerization, which is an oxidation process. Each step of the polymerization is associated with the release of one electron [9], which is then used in the reduction of palladium ions to form palladium atoms. These atoms subsequently coalesce and form clusters, which are stabilized within the growing polymer. From a consideration of the sequence of steps occurring at the nanoscale, an intimate contact between metal and polymer is likely to develop.

5. Conclusion

A single step, one-pot method such as that described above for the preparation of a ‘polymer-metal’ intimate composite material (ICM) could well be of importance in the synthesis of sensors, catalysts, electronics and other optical instruments while yielding improved performance of such devices.

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