

Effect of Particle Morphology and Content on the Properties of Palladium/Polycarbonate Nanocomposites

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ABSTRACT

In this paper, we study the effect of morphology on the properties of *ex situ* and *in situ* palladium/polycarbonate (Pd/PC) nanocomposites. Discrete Pd nanoclusters of ~ 15nm size were formed in the absence of PC in the reaction mixture (*ex situ* method) while agglomeration of Pd nanoclusters was noticed in the presence of PC in the reaction mixture (*in situ* method). The electrical conductivity measurement shows a dramatic difference between these nanocomposites with a significantly higher value for the *in situ* nanocomposite compared to the *ex situ* nanocomposite. Changing the Pd content and involving a phase transferring agent (tetraoctylammonium bromide-TOABr) found to influence the size of the Pd nanoparticles and thus the properties. With TOABr, the particle size were controlled to 3nm and 5nm for 1and 2vol.% *ex situ* nanocomposites respectively. The insulating nature of the TOABr involved Pd/PC nanocomposites confirmed the dependency of properties over the morphology.

Keywords: nanocomposites; *in situ* and *ex situ* synthesis, morphology; electrical conductivity

1. INTRODUCTION

Enhanced surface area and tunable properties have made the metal nanoparticles a better candidate for the optical, thermal and electrical applications. However, their applications are limited due to the difficulty in handling, quick oxidation of the metal particles [1]. Thus, protecting these nanoparticles by organic ligands [2] including polymers [3-5] becomes necessary. Polymers are preferred over the organic ligands due to the convenience in handling, reduced post-synthesis treatment and more direct applications.

In this paper, we report preparation of Pd/PC nanocomposites (*in situ*) by reducing palladium chloride (PdCl₂) in the presence of polycarbonate (PC) dissolved in dichloromethane. Nanocomposites were also synthesized by dispersing dodecanethiol protected Pd nanoparticles in PC solution (*ex situ*). Effect of varying Pd content and involving TOABr on the properties of the nanocomposites were studied.

2. EXPERIMENTAL SECTION

All analytical grade chemicals purchased were used as received. In the *ex situ* method, C₁₂H₂₅SH-protected Pd nanoparticles were prepared using Brust method [2]. The Pd nanoparticles were then homogeneously mixed with a solution of 40 mg of PC in 20 ml of CH₂Cl₂ (1.6 μM) followed by film casting at room temperature. In the case of the *in situ* method, PC (40 mg) was dissolved in CH₂Cl₂ (20 ml) (1.6 μM). 15 mg of PdCl₂ was first dissolved in 2ml of conc. HCl so as to form a complex [PdCl₄]²⁻, and was further dissolved in 48 ml water to form a 1mM solution. This biphasic mixture (along with or without 10ml of 0.5 mM TOABr) was stirred continuously using a magnetic stirrer for 30 minutes. A freshly prepared solution of NaBH₄ in 20 ml water (0.1M) was added drop-wise to the mixture. The color of the reaction mixture changed rapidly from golden yellow to black, indicating the formation of Pd nanoparticles. However, in the presence of TOABr the color change was from golden yellow to greenish yellow. After stirring for 3 hours, the organic phase was separated, washed thrice with 250ml of with ethanol/water mixture (60/40 v/v%) and was directly cast into film at room temperature.

3. RESULTS AND DISCUSSION

3.1 Morphology of Pd/PC nanocomposites

The TEM image of the *ex situ* nanocomposite with 1 and 2 vol.% Pd revealed dispersed Pd nanoparticles of 10 and 15 nm embedded in PC matrix (Figure 1). Based on earlier reports on the n-alkanethiol-protected Pd nanoparticles, the presence of dodecanethiol on the surface of the Pd nanoparticles in the present study is likely to ensure the separation of the nanoparticles even after mixing with PC. However, the average particle size of the Pd nanoparticles in previous studies was found to be ~ 5nm size; using the Brust method [2]. Although the identical metal salt: thiol ratio and reducing agent were used in the present study, an increase in the size of the nanoclusters was found. The effect of increased temperature of the reaction mixture and absence of any phase transferring agents may have contributed to the increased size of the nanoparticles [6]. A difference in the concentration of reducing agent may have also contributed to the increase in the average size of nanoparticles.

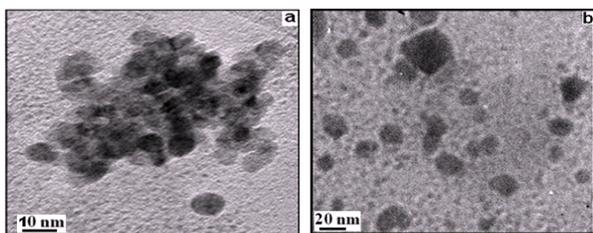


Figure 1: TEM images of the 1(a) and 2(b) vol.% *ex situ* Pd/PC nanocomposites.

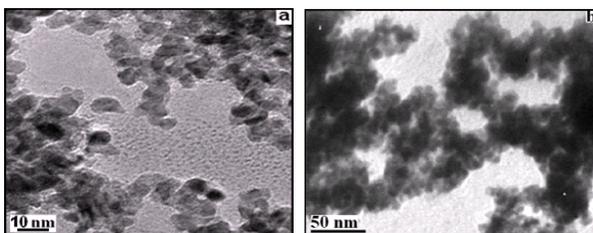


Figure 2: TEM images of the 1(a) and 2(b) vol.% *in situ* Pd/PC nanocomposites.

In contrast to the above system, *in situ* nanocomposite of Pd nanoparticles in PC showed significant agglomeration (Figure 2). Similar observations were reported by Chatterjee *et al* with Au/poly(dimethyl amino ethyl methacrylate-*b*-methyl methacrylate) [3] and Liu *et al* with Au/PMMA [5]. Wang *et al* have suggested that in order to obtain discrete nanoparticles, the rate of adsorption of organic ligands on the surface of nanoparticles should equal the rate of nanoparticle formation [7]. Accordingly, organic ligands with lower molecular weight have been found to be more effective in limiting the nanoparticles size.

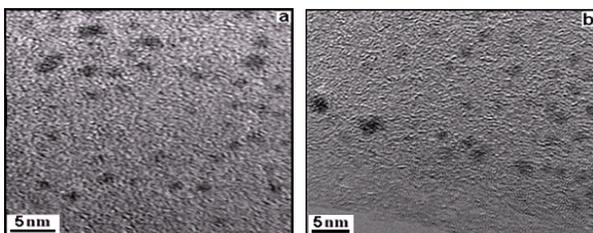


Figure 3: TEM image of the 1 (a) and 2 (b) vol.% *ex situ* Pd/PC nanocomposites with TOABr.

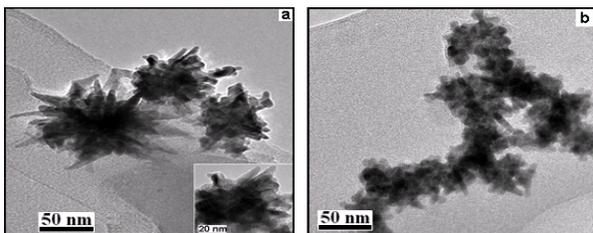


Figure 4: TEM image of the 1 (a) and 2 (b) vol.% *in situ* Pd/PC nanocomposites with TOABr.

Inclusion of TOABr reduced the size of the Pd nanoparticles in 1 and 2 vol.% *ex situ* nanocomposites

to 3 and 5nm size, respectively (Figure 3). Generally, the nanoparticles formed tend to grow into clusters due to their enhanced surface energy. Further growth of such nanoclusters can be terminated by protecting them with organic ligands. Thus, the size of the metal nanoclusters might possibly be controlled. As per Brust *et al* [2] and Liu *et al* [6] one major route is to expedite the process of shifting nanoclusters from aqueous phase to the organic phase by adding phase transferring agents (TOABr) which is proven in our case (Figure 3, 4).

3.2 Chemical interactions in Pd/PC nanocomposites

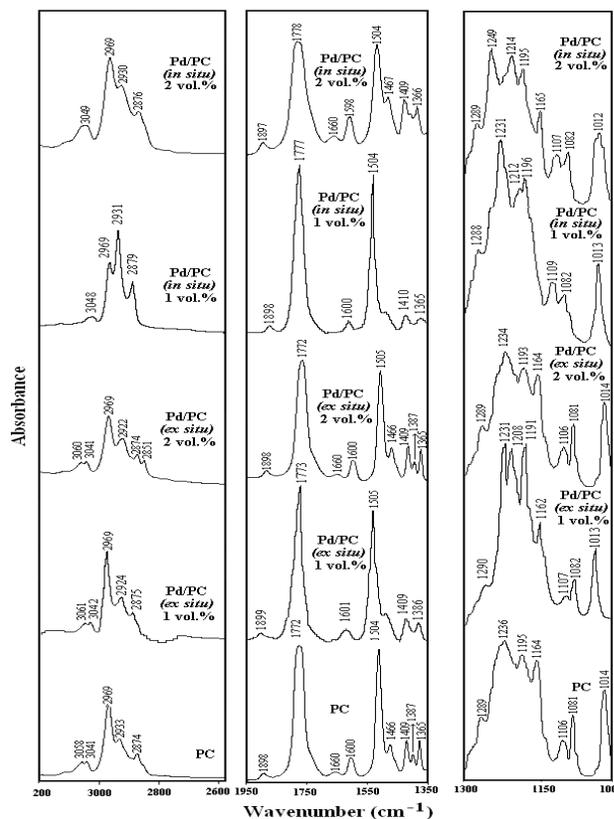


Figure 5a. FTIR peaks for the normal Pd/PC nanocomposites

FTIR spectra for PC, 1 and 2 vol.% *ex situ* and *in situ* Pd/PC nanocomposites are shown in the Figure 5a. From the figure, we can confirm that at high wavenumber region ($2600-3200\text{ cm}^{-1}$), no big difference is noted between PC and the *in situ* nanocomposites. However, with the 2 vol.% *ex situ* nanocomposites two new peaks at 2922 and 2851 cm^{-1} assigned for C-H asymmetric stretching for CH_2 groups were seen[8]. Similar Peak at 2924 cm^{-1} is also seen in the 1 vol.% *ex situ* samples. The appearance of these peaks may be due to the presence of alkyl chains (from dodecanethiol) in the *ex situ* nanocomposites. Changes in the FTIR peaks brought in by the inclusion of the TOABr are reported in the Figure 5b. The broadening

of the peaks in the 1 vol.% *in situ* nanocomposites shows the possibility of the increased interactions of the PC Chains with the Pd nanoclusters which is once again confirmed by the TEM images.

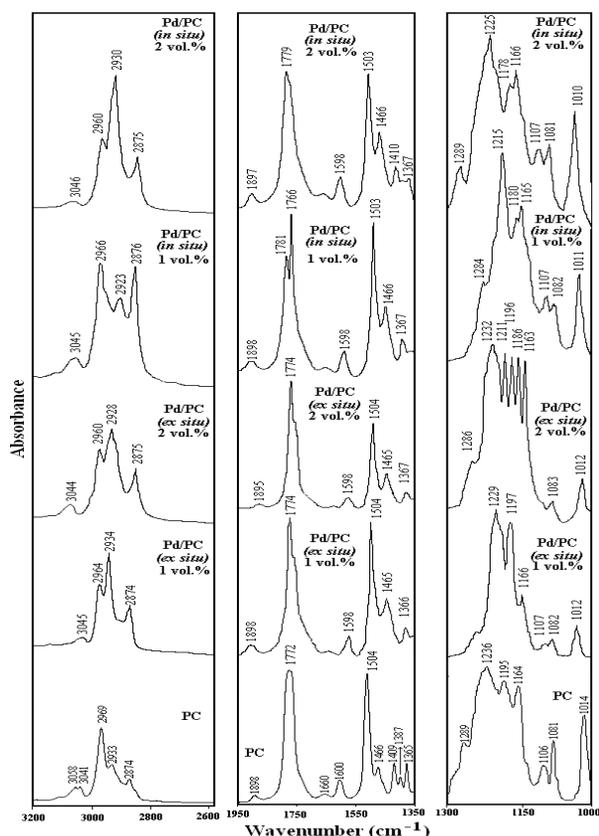


Figure 5b. FTIR peaks for the TOABr assisted Pd/PC nanocomposites

Formation of new peak at 1212 and 1214 cm^{-1} in the 1 and 2 vol.% *in situ* nanocomposites assigns the asymmetric stretching of C-O-C bond in the PC chains[9]. A huge increase in the intensity of this peak noticed in the TOABr assisted 1 vol.% *in situ* sample along with its morphology suggests the conformational changes in the PC chains. Our perception is once again supported by the reduction in the intensity of 1164 cm^{-1} in the *in situ* nanocomposites that corresponds to the decrease in the symmetric stretching of the C-O-C bond [9]. Further research is required to study the changes in the peak positions, intensities achieved after the TOABr inclusion.

3.3 Thermal Properties

Thermogravimetric analysis performed under nitrogen (Figure 6a) indicates in the thermal stability of the 1 and 2 vol.% *ex situ* nanocomposites from ~430 to ~455 and 470°C, respectively. In comparison, in the *in situ* nanocomposites with 1 and 2 vol.% Pd content, an improvement in thermal stability to ~438 and 450°C

was observed. For the given Pd content, the TOABr assisted nanocomposites were more thermally stable than the normal ones as shown in Figure 6b. T_{onset} of the TOABr assisted 1 and 2 vol.% *ex situ* nanocomposites to be 480 and 495°C. The T_{onset} was 450 and 460°C for the TOABr assisted *in situ* nanocomposites.

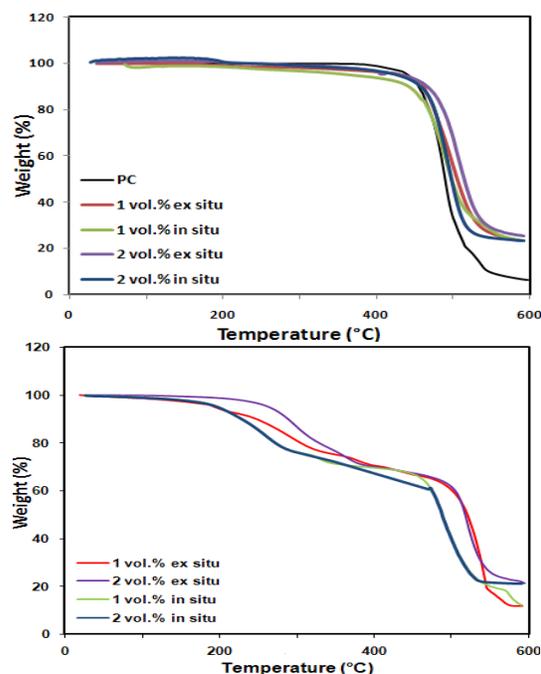


Figure 6: Thermogravimetric analysis of the normal (a) and TOABr assisted (b) 1 and 2 vol.% *ex situ* and *in situ* Pd/PC nanocomposites.

Aymonier *et al.* [4] observed that the thermal stability of the nanocomposites increase with decrease in particle size and agglomeration. It can be seen from the Figures 6a and 6b that any *ex situ* nanocomposite is more thermally stable than the *in situ* ones with equal or less Pd content. These results correlate with changes in the area of the polymer-nanoclusters interface. More is the interfacial area, better will be suppression of the chain collisions. Thus, the results we obtained are in close agreement with the TEM images revealing that the dispersed Pd nanoparticles with more interfacial area provide better thermal stability than the agglomerated ones.

3.5 Electrical Properties

No significant difference is observed for the 1 and 2 vol.% *ex situ* with resistivity of $7.2 \times 10^{13} \Omega\text{m}$. Similar results were also seen in the 1 vol.% *in situ* nanocomposites too. However, the *in situ* nanocomposite films having 2 vol.% Pd showed a linear increase in the current with the voltage indicating a constant resistance of about 442 Ω and thus a resistivity of $2.13 \times 10^5 \Omega\text{m}$ as shown in Figure 7a. Irrespective of the Pd content or mode of synthesis,

TOABr assisted nanocomposites were found insulating in nature with their resistivity measuring in the range of $10^{12} \Omega\text{m}$ as shown in the Figure 7b.

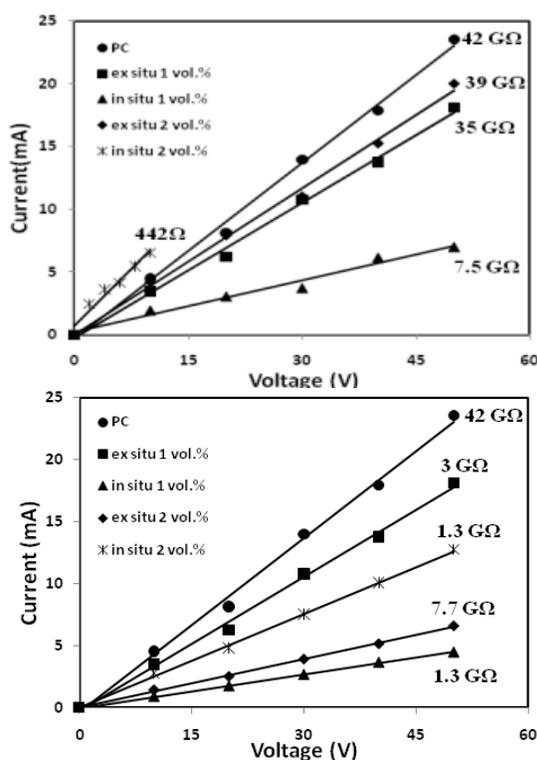


Figure 7: Electrical Properties of the normal (a) and TOABr assisted (b) Pd/PC nanocomposites.

Prior work by Athawale et al [10] on Pd/polyaniline nanocomposites reported similar increase in the electrical conductivity of the polymer matrix. However, these works involved conducting polymers for electrical conductivity studies on nanocomposites. We in our case involved electrically insulating polymer (PC) rather than a conducting polymer. The insulating nature of the *ex situ* nanocomposites might be because of the presence of discrete Pd nanoclusters. Here, the nanoclusters were separated from each other by dodecanethiol and were then embedded into the PC matrix. However, in the *in situ* nanocomposites, the agglomerated Pd nanoclusters might form continuous segments. This in turn might facilitate the electron transfer from one Pd cluster to another Pd cluster leading to a continuous electrical conductivity. Changes in the morphology brought in by the inclusion of TOABr might have affected the electrical behavior of the nanocomposites. Further studies are required to understand the effect of the metal salt: capping agent ratio, film thickness and molecular weight of capping agents on the electrical properties of the Pd/PC nanocomposites.

4. CONCLUSION

Pd/PC nanocomposites prepared by the *ex situ* and *in situ* methods exhibited marked differences in their morphology. The Pd nanoparticles produced by the *ex situ* method were well-dispersed while the Pd nanoclusters produced by the *in situ* method were agglomerated. In the absence of any capping agent such as thiol or polymer, stable Pd nanoclusters could not be obtained due to inadequate stabilization. Inclusion of TOABr as the phase transferring agent reduced the Pd particle to less than 5 nm in size. Expedition of phase transfer brought in by TOABr resulted in discrete nanoclusters of 100nm size in 1 vol.% in situ nanocomposites. Changes in the FTIR peak positions and intensities suggest the possibility of chemical interactions between PC chains and Pd nanoclusters and conformational changes in PC. For the same Pd content, the *ex situ* nanocomposites were found to transmit more light than the *in situ* nanocomposites in the UV-Vis-IR region. The onset of thermal degradation of the *ex situ* and *in situ* nanocomposites were found higher than that of PC. The thermal stability of the nanocomposites shows a proportional increase with the Pd content and reduction in particle size. Further research is required to explore the other factors possibly affecting the morphology of the nanocomposites.

5. REFERENCE

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