

Structure-property relationships in Pd/PC nanocomposites based chemical sensors

O.P. Valmikanathan*, D. Meka**, S. Prasad** and S.V. Atre*

* Oregon State University, Corvallis, OR 97331, sundar.atre@oregonstate.edu

**Portland State University, Portland, OR 97201, spasad@pdx.edu

ABSTRACT

In this paper, we study the effect of morphology on the thermal stability of palladium/polycarbonate (Pd/PC) nanocomposites. Pd/PC nanocomposites were synthesized via two different techniques, *ex situ* and *in situ*. 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). Variations in thermal stability were noted for the various Pd/PC nanocomposites as a function of their morphology. These results have implications for the operating life-times of chemical sensors containing Pd/PC nanocomposites as active elements.

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

1. INTRODUCTION

The enhanced surface area and the ability to tune the electrical characteristics have made 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 [2-3] including polymers [4-6] becomes necessary. Prior studies [4-5] show that the properties of the nanoparticles were controlled by the selection of the protecting agent as well as the distribution of the nanoclusters. Polymers are preferred over the organic ligands due to the convenience in handling, reduced post-synthesis treatment and more direct applications.

Generally, polymer-protected nanoclusters can be prepared by two different synthetic methods. In the *ex situ* method, organic ligand-protected nanoclusters are initially prepared followed by homogenous mixing with a polymer solution [7-8]. In contrast, the *in situ* method, involves the preparation of nanoclusters in the presence of a polymer [5-6]. This method generally does not involve additional organic ligands other than the polymer, as protecting agents. The resulting solutions from either method can subsequently be cast into films.

In this paper, we report an *in situ* method for preparing nanocomposite films by reducing palladium chloride (PdCl₂) in the presence of polycarbonate (PC) dissolved in dichloromethane. We also synthesized Pd/PC nanocomposite films by an *ex situ* method involving the

dispersion of dodecanethiol-protected Pd nanoclusters in a solution of PC in dichloromethane. It was found that the synthesis method had a significant impact on the morphological characteristics and the corresponding optical, thermal and electrical properties of the nanocomposite films. The effect of varying Pd content and involving a phase transferring agent (tetraoctylammonium bromide -TOABr) on the properties of the nanocomposites were also studied. The electrical conducting behavior of the *in situ* nanocomposites and the affinity of the Pd metal towards the Lewis acid gases have resulted in the construction of a SO₂ sensor out of the Pd/PC nanocomposites. The SO₂ sensing capabilities of the Pd/PC nanocomposites have been discussed in detail in another paper. In this paper, we present the results from our investigations in the synthesis and thermal stability of Pd/PC nanocomposites. These issues are of importance in determining the time and temperature combinations affecting the use of Pd/PC nanocomposite-based chemical sensors.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Pd/PC nanocomposites

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 homogenously 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. The schematic of the Pd/PC nanocomposites synthesis is given in Figure 1.

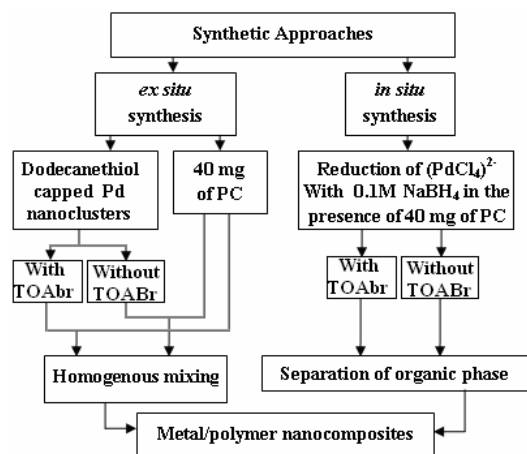


Figure 1: Schematic representation of *in situ* and *ex situ* Pd/PC nanocomposites synthesis.

3. RESULTS AND DISCUSSION

3.1. Morphology of Pd/PC nanocomposites

The TEM image of the *ex situ* nanocomposite with 2 vol. % Pd (on a stoichiometric basis) revealed dispersed Pd nanoclusters of ~15 nm embedded in PC matrix (Figure 2a). Based on earlier reports on the synthesis and morphology of n-alkanethiol-protected Pd nanoclusters, the presence of dodecanethiol on the surface of the Pd nanoclusters in the present study is likely to ensure the separation of the nanoclusters even after mixing with PC. However, the average particle size of the Pd nanoclusters 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 nanoclusters [9]. A difference in the concentration of reducing agent may have also contributed to the increase in the average size of nanoclusters.

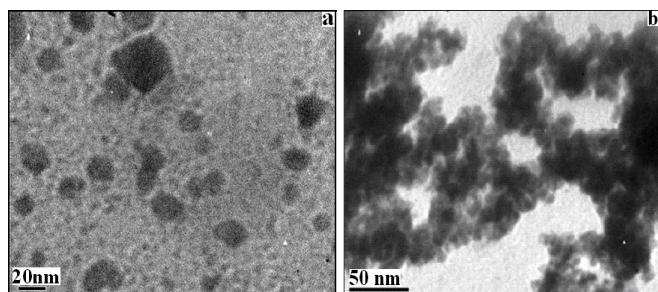


Figure 2: TEM image of the *ex situ* and *in situ* Pd/PC nanocomposites showing (a) dispersed Pd nanoparticles, and (b) agglomerated Pd nanoparticles, respectively .

In contrast to the above system, *in situ* nanocomposite of Pd nanoclusters (2 vol. % on a stoichiometric basis) in PC showed significant agglomeration (Figure 2b). Similar

observations on agglomeration were reported by Liu et al using Au/PMMA [6], and Chatterjee et al with Au/poly(dimethylamino ethyl methacrylate-*b*-methyl methacrylate) copolymers [4]. Thus, morphological changes in nanocomposites appear to be strongly dependent on the specific polymer system and reaction conditions.

However, when synthesized in the presence of phase transferring agents the size of the Pd nanoparticles in 2 vol. % *ex situ* nanocomposites were controlled to 5nm size (Figure 3a). The Pd nanoparticles size was further controlled to 3nm by reducing the Pd content to 1 vol. % (Figure 3b). Similar results were reported by Brust *et al.* [2] on Pd capped with dodecanethiol.

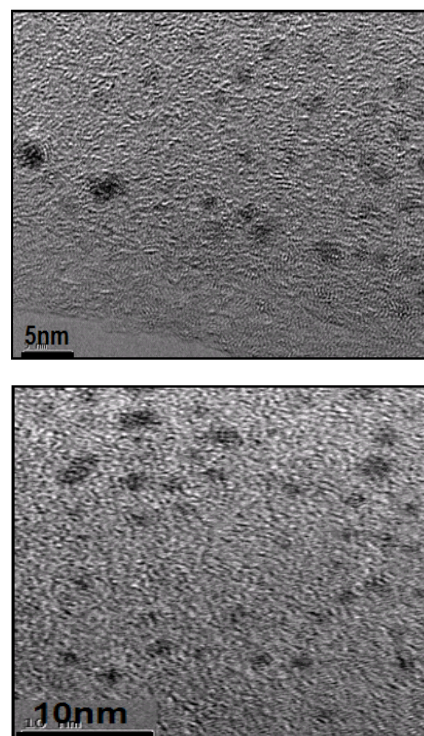


Figure 3: TEM image of the *ex situ* Pd/PC nanocomposites (2 vol.% and 1 vol.%) with phase transferring agents showing (a) dispersed Pd nanoparticles ≤ 5 nm size and (b) Pd nanoparticles ≤ 3 nm size, respectively.

The possible mechanism involved in the nanoclusters formation is given Figure 4. Now, when a metal salt is reduced into metal, 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 by various ways. 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 was proven in our case. Prior studies also talks about the other factors like metal content [5] and molecular weight of the capping agent.

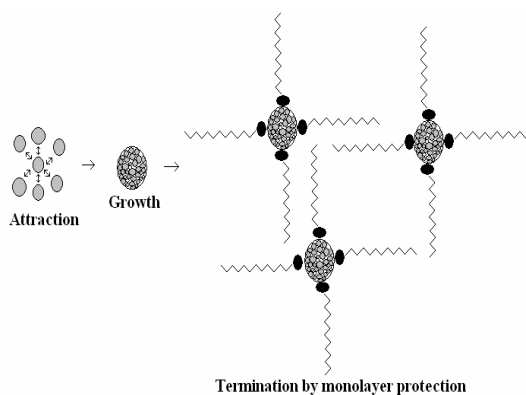


Figure 4: Mechanism involved in the Pd nanoclusters formation.

Wang *et al* have suggested that in order to obtain discrete nanoclusters, the rate of adsorption of organic ligands on the surface of nanoclusters should equal the rate of nanocluster formation [10]. Accordingly, organic ligands with lower molecular weight have generally been found to be more effective in limiting the nanoclusters size. The wide-ranging behavior of agglomeration in nanocomposites prepared by the *in situ* methods may also be due to the differences in the conformations of the polymer chain in the different studies. These conformational differences can arise from variations in molecular weight, solvent, and temperature. Consequently, the mobility of the polymer during adsorption on the nanocluster surface can be affected, thereby limiting the agglomeration of the nanoclusters. In addition, the nature of interactions between the polymer and the surface of the nanoclusters may also play a role in determining the morphology of the resulting nanocomposites. Further studies are needed to better understand the differences in morphologies observed between the *in situ* and *ex situ* nanocomposites when synthesized with varying TOABr concentration and also with PC of different molecular weight. The following sections examine the consequences of the differences in morphology on the resulting properties of the nanocomposites.

3.2. Thermal Properties

The thermogravimetric (TGA) curves for the Pd/PC nanocomposites and PC at different heating rates and atmospheres are shown in the Figure 5. For each sample, the corresponding differential thermogravimetric analysis (DTGA) plots in the Figure 6 revealed the temperature at which the maximum rate of weight loss (T_{max}) occurs. The DTA plots are represented with normalized weight Ψ (%) which can be expressed as,

$$\Psi = \left[\frac{W_i - W_{end}}{W_0 - W_{end}} \right] * 100 \quad (1)$$

where, W_i is the weight (%) of the sample at the given temperature, W_0 is the weight (%) at the starting of TGA experiment and W_{end} is the weight (%) at the ending of TGA experiment.

The onset temperature of degradation (T_{onset}) and the end temperature of degradation (T_{end}) can be obtained from the TGA. Their difference ΔT thus, represents the temperature range for thermal degradation of a given sample. The ratio of ΔT with the heating rates (r) gives the overall degradation time of the sample. From the data, it was seen that the thermal stability of PC and the nanocomposites increases with increase in the heating rates. The results are supported by the shifts in the values of T_{onset} and T_{max} to the higher range with increase in the heating rates. Also, the overall degradation time ($\Delta T/H$) for the sample decreases with increase in the heating rates. Similar results were obtained by Peng *et al* [11] for poly (vinyl alcohol)/silica nanocomposites. A possible reason for such behavior may be explained as follows. The rate of degradation depends on the rate of heat absorption by PC which once again depends on the heating rate. Thus, even though when the nanocomposites showed enhanced thermal stability at higher heating rates, their overall degradation time may highly get reduced.

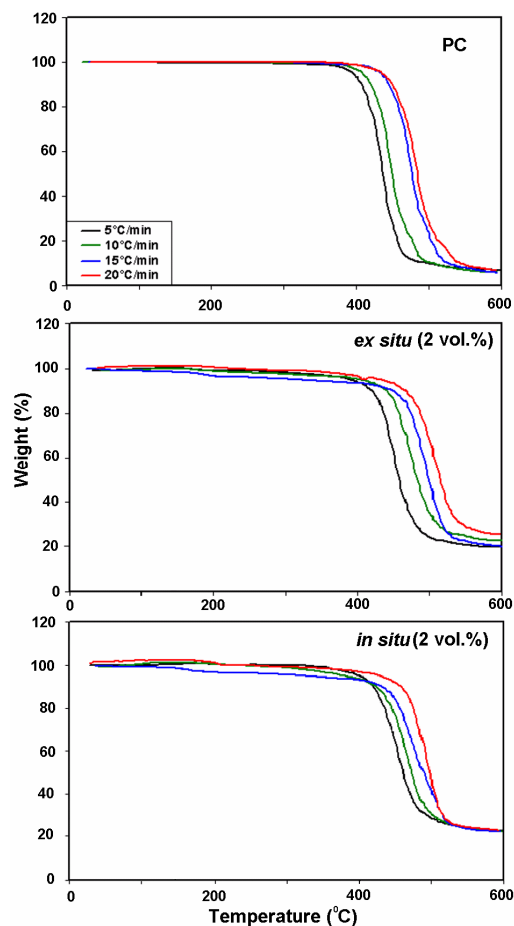


Figure 5: Thermogravimetric analysis of 2 vol. % Pd/PC nanocomposites and PC at different heating rates.

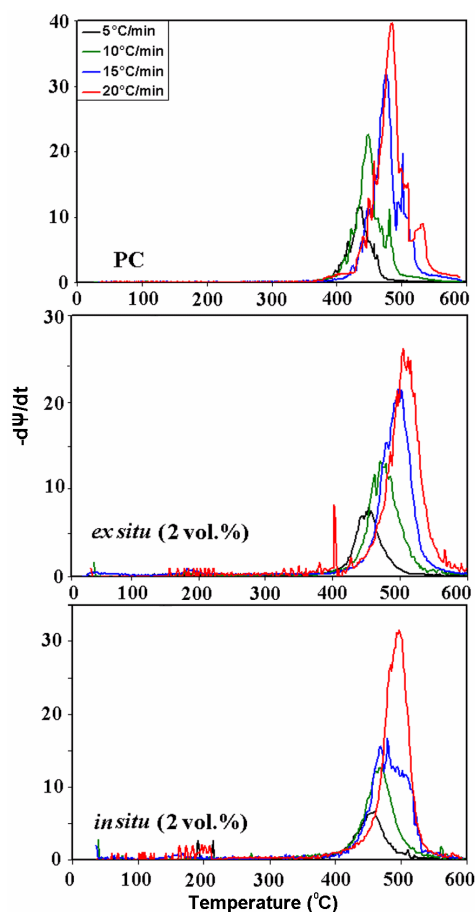


Figure 6: DTGA data for 2 vol. % Pd/PC nanocomposites and PC at different heating rates.

Further analysis of the data revealed that increasing the Pd content in the nanocomposites, increases the T_{onset} and T_{max} . Similar results were obtained by Aymonier et al [12] for Pd/PMMA (Pd content: 0.01 vol.%), Xia et al [13] for Cu/LDPE (Cu content : 17 wt.%) and Hsu et al [14] for Au/polyurethane (Au content: 0.065 wt%). The increment in the thermal stability may possibly be due to the increase in the PC-nanocluster interfacial area. Further research is required to find the existence of a percolation limit of Pd above which the thermal stability of the nanocomposites may remain unaffected.

It could also be determined that for any given Pd concentration, *ex situ* nanocomposite is more thermally stable than the *in situ* ones with equal or less Pd content. A similar increase in thermal stability was noted in earlier reports by Huang et al [7] for Au/poly(methyl styrene) (particle size: 3.5 nm and Au content: 5 wt. %), Aymonier et al [12] for Pd/PMMA (particle size: 2.5 nm) and Hsu et al [13] for Au/polyurethane (particle size: 5 nm). Aymonier et al and Hsu et al also observed that the thermal stability of the nanocomposites increase with increase in metal concentration and with decrease in particle size and agglomeration. These results roughly correlate with changes

in the area of the polymer-nanocluster interface and are in close agreement with the morphology of the nanocomposites.

4. CONCLUSIONS

Pd/PC nanocomposites were synthesized via two different techniques, *ex situ* and *in situ* respectively. The morphology was found to control the thermal properties and thus the time-temperature limits on the SO_2 sensing capabilities of the nanocomposites. The particle size and morphologies were found controlled by involving the phase transferring agent (TOABr) in the reaction mixture and by varying the metal content. Further research is required to explore the factors possibly affecting the morphology and properties of the nanocomposites. These studies will be useful for tailoring metal-polymer nanocomposites for chemical sensing applications.

REFERENCES

1. W.P. Wuelfing, S.M. Gross, D.T. Miles, R.W. Murray, *Journal of American Chemical Society*, 120, 12696, 1998.
2. M. Brust, M. Walker, M. Bethell, D. Schiffrin, and D.J. Whyman, *Journal of Chemical Society and Chemical Communication*, 20, 801, 1994.
3. M. Aslam, G. Gopakumar, T.L. Shoba, I.S. Mulla, K. Vijayamohanan, S.K. Kulkarni, J. Urban and W.Vogel, *Journal of Colloid and Interface Science*, 255, 79, 2002.
4. S.K. Jewrajka, and U. Chatterjee, *Journal of Polymer Science Part A: Polymer Chemistry*, 44, 1841, 2006.
5. C. Aymonier, D. Bortzmeyer, R. Thomann, and R. Mulhaupt, *Chemistry of Materials*, 15, 4874, 2003.
6. F.K. Liu, S.Y. Hsieh, F.H. Ko, and T.C. Chu, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 231, 31, 2002.
7. H. Huang, Q. Yuan and X. Yang. *Colloids and Surfaces B: Biointerfaces*, 39, 31, 2004.
8. S. Chattopadhyay, and A. Datta, *Synthetic Metals*, 155, 365, 2005.
9. K.Koga, T. Ikeshoji and K.Sugawara, *Physical Review Letters*, 92, 11507-1, 2004.
10. H. Wang, X. Qiao, J. Chen, and S. Ding, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 256, 111, 2005.
11. Z. Peng L.X. Kong LX, S.D. Li, and P. Spiridonov. *Journal of Nanoscience and Nanotechnology*. 6, 3934-3938, 2006.
12. C. Aymonier, D. Bortzmeyer, R. Thomann, and R. Mulhaupt. *Chemistry of Materials* 15, 4874- 4878, 2003.
13. X. Xia, S. Cai, and C. Xie. *Materials Chemistry and Physics* 95, 122-129, 2006.
14. S.H. Hsu, C.W. Chou, and S.M. Tseng. *Macromolecular Materials and Engineering* 289, 1096-1101, 2004.