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Synthesis and Characterization of Metal Nanoparticles and the Formation of Metal-Polymer Nanocomposites

Anshu A. Pradhan, [1,3] S. Ismat Shah[1,2,3] and Lisa Pakstis[1]

[1] Department of Materials Science and Engineering
[2] Department of Physics and Astronomy
   University of Delaware, Newark, DE 19716, USA
[3] Fraunhofer Center for Manufacturing and Advanced Materials, Newark, DE 19711, USA

ABSTRACT

Metal nanoparticles are highly prone to oxidation due to their high surface energy and affinity for oxygen which can lead to the complete oxidation of the particles. Studying and utilizing the unique properties of metal nanoparticles requires minimizing their interaction with the atmosphere. We have used the co-condensation technique to synthesize suspensions of metal nanoparticles in isopropanol. The solvent protects the nanoparticles from the atmosphere and minimizes agglomeration of the nanoparticles. The particles showed a lognormal distribution and the average particle size was below 20nm. Polymer-metal nanocomposites were made by dispersing the metal nanoparticles in PMMA matrix by spin coating and solution casting. Adherent films, fibers and free standing films could be obtained by varying the process conditions. The SEM images show that the nanoparticles in the spun coated films were non-agglomerated and well dispersed over a wide area. Morphology of the spun coated films was different from the solution cast films. Electrically conducting films having interconnected silver particle network could be obtained. Cytotoxicity studies show that the silver nanoparticles and the PMMA-Ag nanocomposite films are antibacterial in nature. We have also dispersed the nanoparticle into pump oil and measured the thermal conductivity of the resultant mixture. The thermal conductivity of the oil could be increased by over 50% by adding an extremely small fraction of the silver nanoparticles.

INTRODUCTION

Metal nanoparticles have received tremendous interest due to their unique optical, electrical and magnetic properties.[1-4] Several chemical and vacuum techniques have been used to synthesize metal nanoparticles.[5,6] In general, chemical techniques produce smaller nanoparticles with a narrower particle size distribution, while vacuum techniques produce higher purity nanoparticles. In this paper, we report on the synthesis of silver nanoparticles by Co-Condensation (COCON) technique which combines the advantages of chemical and vacuum routes of nanoparticle synthesis. COCON is derived from an earlier technique called Vacuum Evaporation onto a Running Oil Substrate (VEROS) demonstrated by Yatsuya and his co-workers[7]. The technique was modified by Klablunde[6,8] who used an organic liquid in place of the oil used in VEROS. The COCON technique involves the co-deposition of metal vapors from an evaporation source, and a suitable solvent onto the cryogenically cooled walls of an evacuated chamber. The supercooling of the metal vapors as they move away from the evaporation source leads to the formation of metallic nuclei. These nuclei are deposited on the chamber walls together with the remaining metal vapors and the solvent. No growth occurs on

cold chamber wall, however, on warming the reactor the nuclei grow to form metal nanoparticles. The solvent molecules surround the growing metal nuclei and prevent agglomeration. This solvation effect is critically important as it not only disperses the nanoparticles within the liquid medium, it also prevents oxidation of the nanoparticles which is a common problem in the synthesis of metal nanoparticles. The COCON technique is also easily scalable. We have used a scaled up reactor to produce silver nanoparticle suspensions. The nanoparticles were dispersed into a poly-methyl methacrylate (PMMA) matrix by spin coating and solution casting. These films have non-agglomerated silver nanoparticles dispersed over a wide area and allow the exploitation of the large surface area of the nanoparticles. In addition, process conditions can be varied to yield conducting films. It is also known that silver nanoparticles are antibacterial in nature.[9,10] Thus, the PMMA-Ag nanocomposites can be used as low cost flexible antibacterial surfaces.

EXPERIMENT

A schematic of the COCON reactor is shown in Fig. 1. The reactor is 2m long and 0.4m in diameter. An effusion cell acts as the source of metal vapors. The reactor is pumped down after which the liquid nitrogen and the flow of 2-propanol is started. The pumping is then stopped and the low pressure is maintained by the solvent freezing along the sides of the reactor. The crucible is heated to a temperature of around 1400°C which causes the metal to vaporize. The growth of the nanoparticles occurs both in the vapor phase as the metal vapor travels towards the reactor wall and when the frozen solvent layer with the embedded metal nuclei melts. The nanoparticles are obtained in a suspension with the solvent. The particle size was determined by Transmission Electron Microscopy (TEM) and by X-Ray Diffraction (XRD).

Fig. 1: Schematic of the COCON

To form metal-polymer nanocomposites, PMMA (MW = 88K) was dissolved in a 1:1 mixture of the methyl ethyl ketone (MEK) and the silver suspension. The polymer concentration was between 8 mg/mL and 30 mg/mL. Films on silicon and glass substrates were fabricated by either spin casting at 600rpm or solution casting by allowing the solvent to evaporate slowly by saturating the atmosphere around the films with the solvent. The silver concentration in the suspensions and the films was determined with Thermo Gravimetric Analysis (TGA). The films were imaged by SEM and optical microscopy. The sheet resistance of the films was measured with a 4-point probe. Antibacterial studies were carried out by placing E.Coli cells grown to the mid log phase in contact with the films and the nanoparticles. For the suspensions, the 2-propanol was evaporated to eliminate the effect of the solvent. The cells were placed in an incubator at 37 °C for 24 hours. The number of colony forming units (CFUs) was then counted to determine the antibacterial nature of the particles and the films.
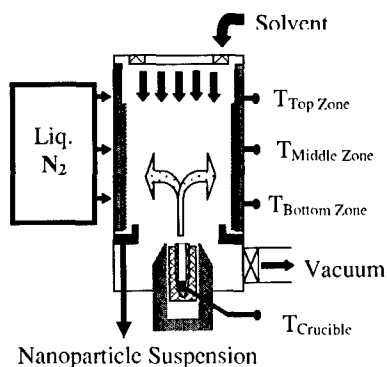
RESULTS AND DISCUSSION

Fig. 2a shows a TEM micrograph of the nanoparticles deposited with the crucible temperature of 1380°C. The particles show a log-normal distribution (Fig. 2b). Since vacuum phase synthesis of nanoparticles commonly show a log-normal distribution[11], this suggests that at least a part of the growth occurs in the vapor phase. The particle size increases slightly with temperature while the size distribution gets narrower at higher temperatures (Fig. 2c). Fig. 3
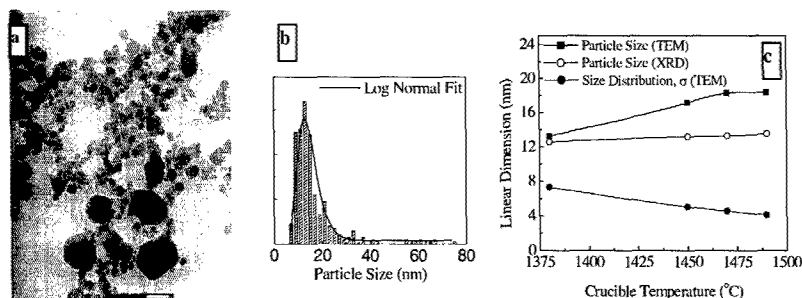

Fig 2: Variation of the particle size and size distribution of the nanoparticles

shows a high resolution TEM image of the silver nanoparticle and the associated diffraction pattern. It can be seen that the nanoparticle is a single crystal with few defects.

To form the metal-polymer nanocomposites, PMMA was chosen since it is a commonly used transparent polymer and is soluble 1:1 mixture of 2-propanol and MEK. As the solvent used in the COCON process was also 2-propanol, PMMA was dissolved in 1:1 mixture of MEK and 2-propanol. Fig. 4a shows the SEM images of the films deposited by spin coating from the PMMA-Ag solution. The silver nanoparticles can be seen as lighter regions in the darker PMMA matrix. It can be seen that the nanoparticles are non-agglomerated and well dispersed over a large area. At high polymer concentrations (30

Fig. 3: HR-TEM image of a silver

mg/mL), fibers are formed in addition to the films during spin coating. The fibers are a few cms long and 0.5 mm in diameter. SEM of the fibers (Fig. 4b) also shows that the individual nanoparticles are dispersed in the polymer matrix. The SEM images are very different from TEM images of the silver nanoparticles (Fig. 2a). This suggests that the agglomeration seen in the TEM image is due to the capillary force which concentrates the nanoparticles into an ever-decreasing volume as the solvent evaporates. The film obtained by spin coating shows a "snapshot" of the silver nanoparticles in the suspension because the rate of solvent loss is higher. Thus, it can be seen that the solvation of the metal nanoparticles, which prevents the
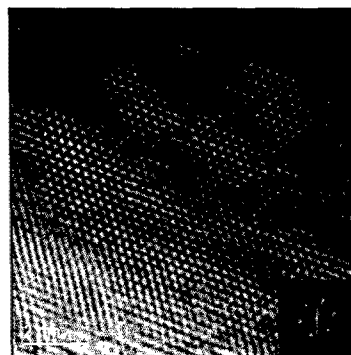
agglomeration of nanoparticles in the suspension, leads to the dispersion of the nanoparticles in the films. These nanocomposite films hold the nanoparticles in a stable matrix and allow us to take full advantage of the large surface area of the nanoparticles.

The films deposited by solution casting (Fig. 5) show a considerably different morphology from the spun cast films. In addition, the morphology is strongly dependent on the
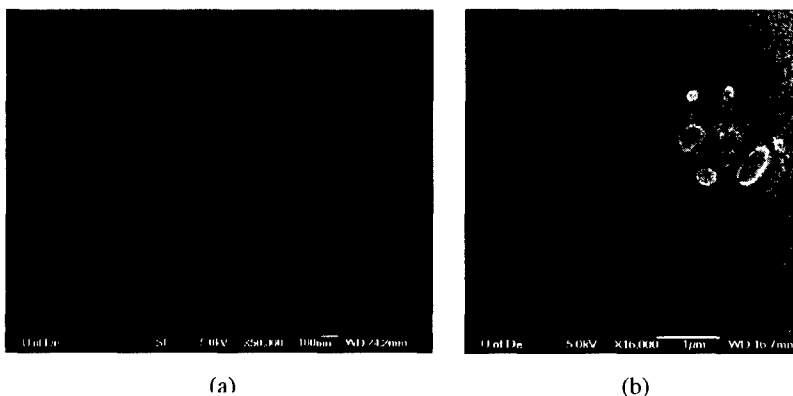

(a)

(b)

Fig 4: SEM micrographs of spin coated PMMA-Ag

PMMA-Ag ratio. Fig. 5a shows an optical micrograph of a film deposited from a 1mL solution containing 30mg PMMA and 1.5mg Ag, while Fig. 5b is of a film deposited from a 1mL solution containing 15mg PMMA and 1.5 mg Ag. The film dimensions were 3cm x 3cm and the thickness was approximately 5µm. Since the techniques used to form these films are non-specific, the silver nanoparticles can be imbedded in almost any polymer matrix. Films deposited at higher polymer concentrations contain individual sub-micron silver regions distributed in a PMMA matrix. We believe that the slow evaporation of the solvent decreases solvation of the nanoparticles which allows the agglomeration of the nanoparticles. This
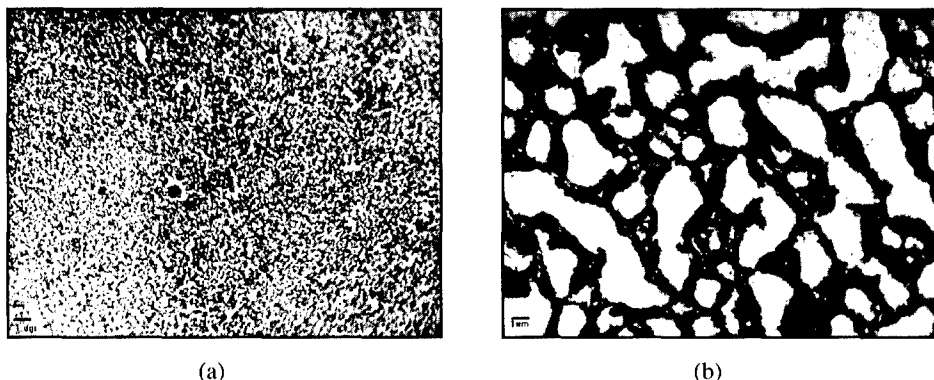

(a)

(b)

Fig. 5: Optical micrographs of solution cast PMMA-Ag films

hypothesis was tested by gently heating the silver nanoparticle suspension. The silver immediately precipitated out of the suspension, which suggests that reduction in solvation by

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providing kinetic energy to the solvent molecules that allows increased interaction amongst the nanoparticles leading to agglomeration of the nanoparticles. Films having a connected silver network (Fig. 5b) were found to be electrically conducting. The sheet resistance of the PMMA-Ag nanocomposite was around 4500 $\Omega/\square$ which is 11 orders of magnitude lower than the sheet resistance of PMMA (10^{15} $\Omega/\square$). Thus, these films can be used for applications such as transparent large area collectors for solar cell, soft electrically conducting bio-electrical interfaces, etc. The spun coated films (Fig. 2) and the solution cast films with discrete silver islands (Fig. 5a) were electrically insulating. Therefore, varying the solution evaporation rate makes it possible to control the properties and the morphology of the nanocomposite films.

Cytotoxicity studies were carried out to determine the effect of silver nanoparticles on bacterial growth. Fig. 6 shows the effect of the silver nanoparticle concentration on bacterial growth. It can be seen that addition of 10^{-4}g of silver leads to complete elimination of E.Coli colony forming units. Solution cast films containing the silver nanoparticles are also cytotoxic and inhibit bacterial growth.

We have also added silver nanoparticle suspensions obtained from the COCON reactor to enhance its thermal conductivity. Fig 7 shows the variation of the thermal conductivity of the mixture with the silver concentration. The thermal conductivity of a mixture of pump oil and 2-propanol was also measured to determine the effect on the solvent on the thermal conductivity. The addition of 2×10^{-4} wt% silver increases the thermal conductivity of the mixture by over 50%. The heat capacity and the electrical conductivity of the mixture remain unchanged. The oil-silver nanoparticle mixture is ideally suited for application such as lubricant in electrical motors, which require high thermal conductivity without jeopardizing the electrical properties.
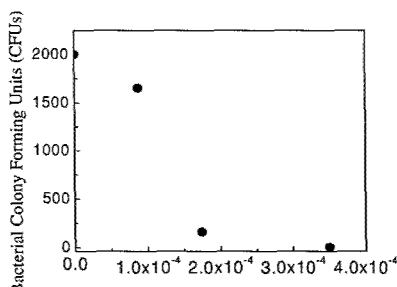

Fig. 6: Effect of silver concentration on the antibacterial properties of PMMA-Ag films

Fig. 7: Variation of the thermal conductivity of pump oil with addition of silver suspension

CONCLUSION

We have used the COCON technique to synthesize suspensions of silver nanoparticles in 2-propanol. The particles had a log-normal distribution and the particle size was below 20nm. Polymer-metal nanocomposites were made by dispersing the silver nanoparticles in a PMMA. The morphology of the films could be varied from having individual isolated nanoparticles in a

polymer matrix to interconnected silver web structures. Films with the interconnected silver network were found to be electrically conducting. Cytotoxicity studies carried out on the films proved that the nanocomposites were antibacterial in nature. Silver nanoparticle suspension was also added to pump oil to enhance its thermal conductivity. The thermal conductivity increased by 50% on addition of 10^{-4}wt% of silver.

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Poster Session