1-1-2007

Irradiation and Metal-Containing Conjugated-Polymer Nanocomposites

Frank D. Blum
Missouri University of Science and Technology

Zhe-Fei Li

Sunil K. Pillalamarri

Massimo F. Bertino
Missouri University of Science and Technology

IRRADIATION AND METAL-CONTAINING CONJUGATED-POLYMER NANOCOMPOSITES

Frank D. Blum,[a,b] Zhefei Li,[b] Sunil Pillalamarri,[a,c] Massimo F. Bertino[d]

[a] Department of Chemistry
[b] Department of Materials Science and Engineering
[c] Current Address: Freescale Semiconductor, Inc, Austin TX
[d] Department of Physics
University of Missouri-Rolla
Rolla, MO 65409

Introduction

In recent years, there has been considerable interest in inorganic/organic hybrid materials that combine the desirable properties of both classes. These composite materials may find significant application in a variety of applications such as sensors, memory and energy conversion, to name just a few.

In our laboratories, we have recently made a series of studies on the production of polymer nanofibers and their composites with nanometals. Much of this work has focused on the production of polyaniline (PANI) nanofibers that have been made from one-pot syntheses in aqueous solutions where the polymerization was influenced by γ-radiation[1] or UV-radiation.[2] In the latter case, the polymer can be patterned with an appropriate mask.

It has also been shown that if certain metal salts are added to the precursor solutions, metal nanocomposites can be produced. For example, we have been able to make polyaniline composites using γ-irradiation with silver[3,4] and gold[4] nanoparticles.

Experimental

Generally, the nanocomposites can be made from aqueous solutions of monomer, a free radical activator such as hydrogen peroxide or ammonium persulfate, a dopant such as *p*-toluenesulfonic acid or other strong mineral acid, and a soluble metal ion salt(s). It is important to note that these are all one-pot reactions. These solutions are then irradiated with either γ-irradiation in the University's nuclear reactor, or a standard ultraviolet lamp.

The resulting composites were characterized using transmission electron microscopy (TEM), FTIR, X-ray and UV-vis spectroscopy.

Results and Discussion

A variety of structures can be made from the techniques specified above. The resulting nanostructures are typically a function of the compositions of the various components, the irradiation and reaction times. For simplicity, we focus this report on nanometal structures attached to conjugated polymers.

In Figures 1 and 2, TEM micrographs are shown for polyaniline/metal nanocomposites with Ag and Au, respectively.[4,5] The micrographs show the presence of polyaniline nanofibers with metal clusters attached. These materials were prepared using γ-irradiation.

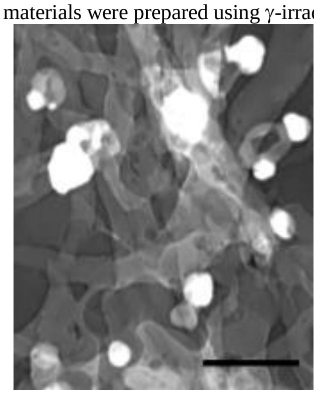


Figure 1. TEM of polyaniline/Ag composite nanoparticles. The Ag nanoparticles (bright spots) are attached to polyaniline fibers (medium brightness). The scale bar represents 50 nm.

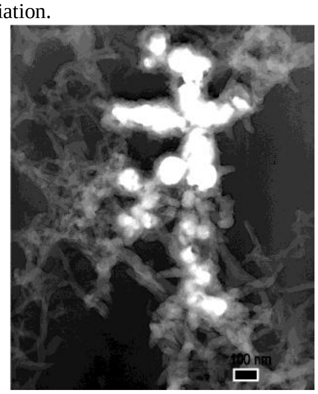


Figure 2. TEM of polyaniline/Au composite nanoparticles. The Au nanoparticles (bright spots) are attached to polyaniline fibers (medium brightness). The scale bar represents 100 nm.

Polyaniline nanofibers can also be produced using standard UV radiation. Shown in Figure 3 are a series of micrographs of polyaniline irradiated through a mask, demonstrating the ability of this technique to be used with conventional photopatterning.

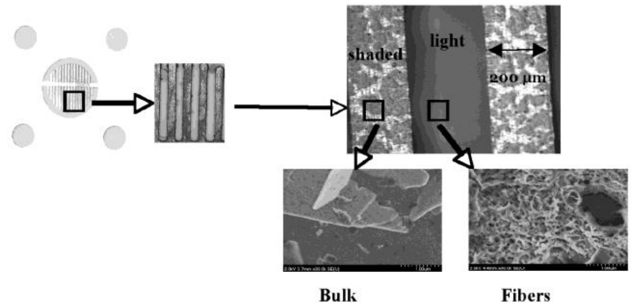
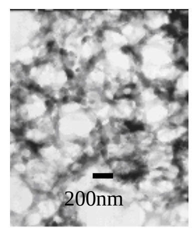


Figure 3. (L) Optical microscopic image of the patterning employed to produce bulk/nanofiber polyaniline thin films. (R) Optical and SEM images of patterned polyaniline thin films. The darker, uniform region was illuminated, and consisted of nanofibers. The shaded areas consisted of bulk polyaniline.

Lastly, we have been able to polymerize (3,4-ethylenedioxythiophene) (EDOT) to its polymer PEDOT alone and in the presence of cadmium and sulfur producing salts. One of the resulting structures is shown in Figure 4, along with the selected area electron diffraction results indicating the presence of CdS.

(a) 

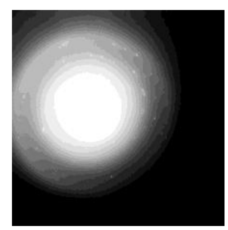
(b) 

Figure 4. (a) TEM image of PEDOT/CdS nanocomposite. (b) SAED image showing the reflection from (101), (110) and (103) planes of CdS.

Conclusions

It is clear that a variety of nanocomposites containing nanometal clusters and polymeric nanofibers can be made using relatively simple procedures. These materials can be made from aqueous solutions, avoiding the use of environmentally problematic solvents and can be made from a single pot. While some problems such as low yields need to be resolved, these synthesis techniques show promise for advanced materials preparation.

References

(1) Pillalamarri, S. K.; Blum, F. D.; Tokuhiro, A. T.; Story, J. G.; Bertino, M. F. *Chem. Materials*, **2005**, *17*, 227.
(2) Werake, L. K.; Story, J. G. ; Bertino, M. F. ; Pillalamarri, S. K.; Blum, F. D. *Nanotechnology*, **2005**, 16, 2833.
(3) Pillalamarri, S. K.; Blum, F. D.; Bertino, M.; Tokuhiro, A. K. *Polym. Mater. Sci. Eng.*, **2004**, 90, 264.
(4) Pillalamarri, S. K;. Blum, F. D.; Tokuhiro, A. T.; Bertino, M. F. *Chem. Materials*, **2005**, 17, 5941.
(5) Blum, F. D.; Pillalamarri, S. K.; Werake, L. K.; Story, J. G.; Bertino, M. F.; Tokuhiro, A. K. *Polymer Preprints* **2006**, 47(1), 405.