Synthesis and Characterization of ZnO Nanostructures Templated Using Diblock Copolymers

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ABSTRACT: The development of self-assembled ZnO nanoparticles within a diblock copolymer matrix using wet chemical processing specific to ZnO is reported. Diblock copolymers consisting of polynorbornene and poly(norbornene–dicarboxcylic acid) (NOR/NORCOOH) were synthesized with a block repeat unit ratio of 400 for the first block and 50 for the second block, to obtain spherical microphase separation. The block copolymer self-assembly was used to template the growth of ZnO nanoparticles by introducing a $ZnCl_2$ precursor into the second polymer (NORCOOH) block at room temperature and processing the copolymer by wet chemical methods to substitute the chlorine atoms with oxygen. X-ray photoemission spectroscopy (XPS) verified the conversion of $ZnCl_2$ to ZnO by monitoring the disappearance of the Cl 1*s* peak and the shift in the binding energy of the Zn $2p^3$ peak in the high-resolution spectra. The substitution of Cl by O was found to be a highly preferential process, whereby only one approach using a weak base (NH_4OH) succeeded in effectively replacing Cl with O to result in spherical ZnO nanoparticles having a size ranging from 7 to 15 nm, as determined by transmission electron microscopy. The development of such block copolymer-templated ZnO nanoparticles% is important in enabling the functionalization of large-area nanodevice technologies. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1058–1061, 2003

Key words: block copolymers; templates; nanocomposites

INTRODUCTION

The formation of self-assembled nanostructures has recently attracted significant interest, as it presents a very promising approach to the development of functional nanodevices. One approach to the growth of nanoparticles is the microphase separation observed in diblock copolymers. The synthesis of nanoparticles within microphase-separated diblock copolymers based on diffusing the doping agent (metal or semiconductor) into the copolymer matrix in the solid phase has been extensively reported.[1–11] In the present work, a novel synthetic approach tailored to the specific production of zinc oxide within the copolymer is reported. Having both metal and polymer constituents of the nanocomposite dissolved in a common solvent allows rapid diffusion of the metal to the functional groups of the block copolymer and results in more uniformly dispersed ZnO nanostructures, which are produced using a wet chemical processing at room temperature. The templating strategy used in our experiments is similar to the "universal" approach to synthesizing metal nanoparticles within diblock copolymers as proposed by Clay and Cohen,[12] but has been modified for the specific templating of ZnO nanoparticles. ZnO is of significant importance due to its electronic and optical properties. It is a wide band gap (E_g = 3.3 eV) metal oxide semiconductor with piezoelectric and optical properties in the UV range.[13] It crystallizes in the wurtzite structure and displays piezoelectric properties when its *c*-axis is oriented perpendicular to a substrate. For this reason, it is found in many electroacoustic applications such as sound sensors, SONAR emitters and detectors, and pressure transducers. ZnO is used as the clear top electrode in solar cells[13] and has potential in the area of information storage as a piezoelectric memory device. Furthermore, new and enhanced properties are expected due to confinement in nanoscale dimensions when controlled nanocrystalline forms of this system are developed. The development of ZnO in its nanocrystalline and/or nanocomposite form and its successful integration into current and future device technologies is one of the goals of our research.

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EXPERIMENTAL

Monomer and polymer synthesis

Norbornene (NOR), ethyl vinyl ether, and dichloromethane (CH_2Cl_2) were purchased from Aldrich

(Milwaukee, WI). Bis(tricyclohexylphosphine) benzylidine ruthenium(IV) dichloride (Grubbs's catalyst) was purchased from Strem Chemicals (Newburyport, MA). CH_2Cl_2 was distilled over calcium hydride under argon. The diblock copolymer of norbornene/norbornene dicarboxylic acid (NOR/NORCOOH) was synthesized using ring-opening metathesis polymerization (ROMP) with a ruthenium-based catalyst developed by Grubbs. ROMP is advantageous because it results in a narrow molecular weight distribution of the polymer, which is important in this templating application to produce uniformly sized well-dispersed nanostructures. ROMP also allows the presence of specific functional groups on monomers, which other polymerization processes might not tolerate. Based on the chosen volume fractions of the two blocks of the copolymer, a spherical nanoparticle morphology was targeted in this work. NORCOOH was synthesized and capped with trimethylsilane (TMS) similarly to literature procedures.[14] The polymer synthesis took place in an inert atmosphere in an MBraun Labmaster glove box. An example of a typical synthesis is presented here: For a diblock copolymer with a *m/n* block length ratio of 400/50, 1 equivalent (0.74 mL) of the Grubbs catalyst solution (0.15 g/5 mL) is added to 400 equivalents (1 g) of the NOR monomer in 25 mL of THF. This mixture is stirred for 1 h, after which 50 equivalents (0.43 g in 3 mL of THF) of TMS-capped NORCOOH is added. This solution is stirred for 24 h, then removed from the glove box and terminated with ethyl vinyl ether. The polymer is then precipitated in a mix of methanol (500 mL), deionized H_2O (25 mL), and acctic acid (12 mL) to acidify the TMS group in the second polymer block. The block copolymer is then filtered from this solution, washed with methanol, and then dried under a vacuum for 24 h.

ZnO-doped polymer film formation

The dried block copolymer (0.15 g) was dissolved in THF over 48 h to make a 0.5% (w/v) solution. A stoichiometric amount of $ZnCl_2$ (0.5*M* solution in THF, purchased from Sigma–Aldrich, Milwaukee, WI) was introduced to the polymer solution. This solution stirred for 24 h to allow the Zn^{+2} cations to associate with the carboxylic groups on the second block of the copolymer. The solution was poured into an evaporation boat made from Teflon-coated aluminum foil, from which the solvent was allowed to evaporate slowly over 36 h. The resulting film (approximately 0.05 mm in thickness) was peeled from the boat and placed under a vacuum for 24 h to remove any residual solvent. The film was then stirred in concentrated NH_4OH for 24 h, followed by washing in H_2O to remove water-soluble salts and to decompose unstable zinc hydroxides to ZnO.

Materials characterization

Data was recorded in 32 scans through the 4000 to 400 cm^{-1} range. X-ray photo-electron spectroscopy (XPS) data was obtained on a Perkin–Elmer spectrophotometer. Samples, 1 × 1 cm, were sputtered with Ar ions

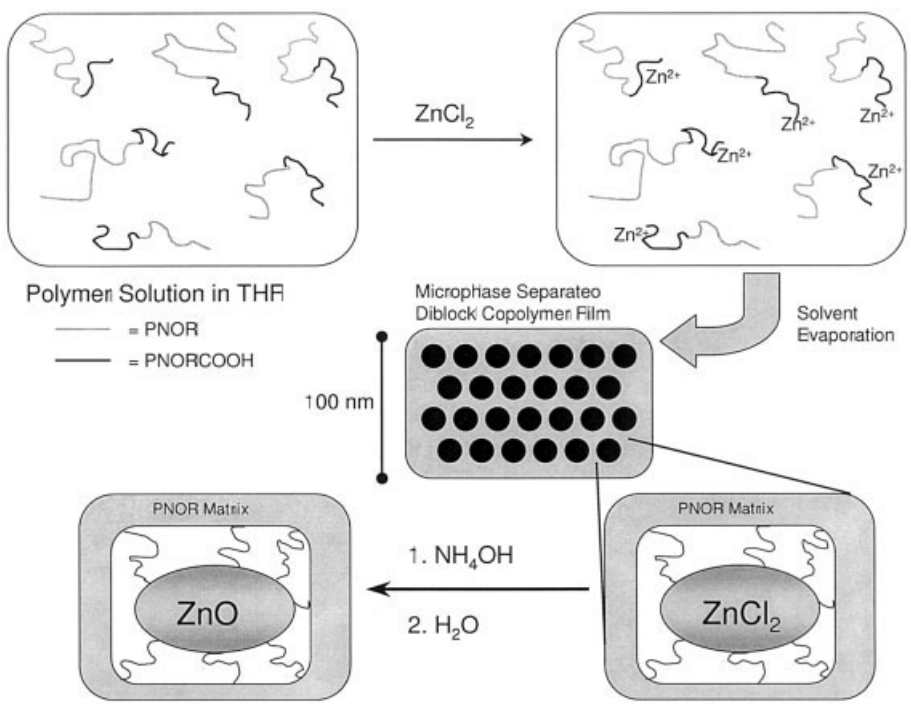

Figure 1 Room-temperature wet chemical synthesis scheme for ZnO nanostructures.

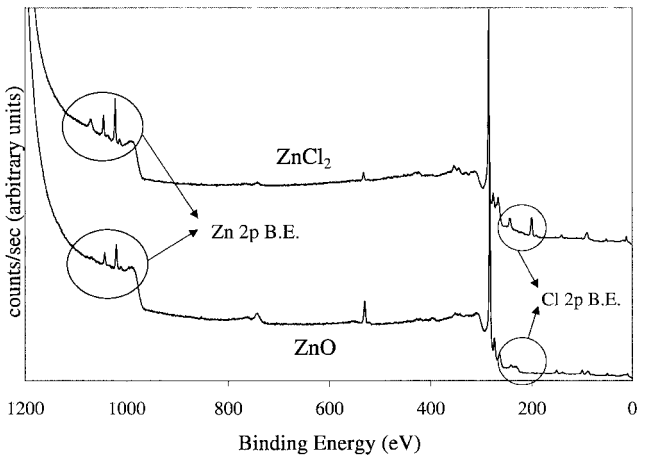

Figure 2 XPS spectra for the block copolymers containing $ZnCl_2$ and ZnO.

for 20 s prior to obtaining data to penetrate the surface of the polymer. Block copolymers were embedded in epoxy, and ultrathin (100 nm) samples for transmission electron microscopy (TEM) observation were prepared by solvent casting from benzene directly onto a carbon-coated nylon TEM grid. The morphology of the $[NOR]_{400}[NORCOOH]_{50}$–ZnO nanocomposites was studied using a HITACHI H-600 transmission electron microscope operated at 100 keV. At least five separate nanocomposite samples were examined by XPS and TEM to ensure reproducibility of the results.

RESULTS AND DISCUSSION

Diblock copolymers of $(NOR)_m/(NORCOOH)_n$ were synthesized with *m/n* ratios of 400/50. Gel permeation chromatography (GPC) confirmed that the distribution of the polymer was unimodal and was relatively narrow as given by the polydispersity index (PDI) of 1.15. A schematic representation for the self-assembly

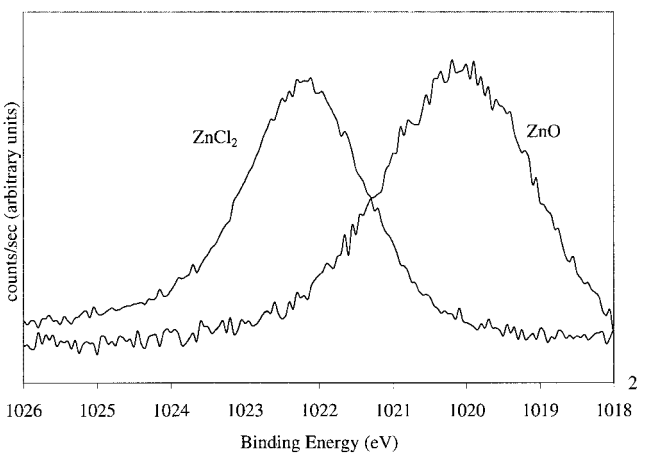

Figure 3 High-resolution XPS spectra of the Zn $2p^3$ binding energies for diblock copolymers containing $ZnCl_2$ and ZnO.

TABLE I
Zn $2p^3$ Binding Energies (B.E.'s) Determined Through High-resolution XPS

% Compound	Experimental B.E.'s (eV)	Literature B.E.'s (eV)
$ZnCl_2$	1023.1	1023.3
ZnO	1021.4	1021.7

of ZnO nanostructures using the templating strategy described earlier is shown in Figure 1. In our work, the templating is markedly different from previous work in that the metal salt is introduced while the polymer is in solution, before any microphase separation of the two blocks can occur. Earlier block copolymer nanoreactor synthesis schemes[1,5,12,14] introduced the metal salt by diffusion of a metal salt solution into a spin-cast or static-cast microphase-separated solid film. The advantages which our templating process presents are a rapid diffusion and attachment of the metal to the second (minority) polymer since both are in the liquid state and resulted in more uniform self-assembled nanostructures at room temperature through wet chemical methods, thus making it an appropriate process to integrate with current and future semiconductor processing technology, without additional thermal cycling steps.

Strong bases, such as NaOH, which have been used in the past in similar templating schemes,[12] were unsuccessful in oxidizing the $ZnCl_2$-containing nanodomains, because the ZnO product is soluble in strong bases. Our research determined that conversion to zinc oxide will only occur following treatment with a weak base, such as concentrated NH_4OH.

The XPS data from such treatment with NH_4OH, shown in Figure 2, demonstrate the successful conversion of $ZnCl_2$ to ZnO. When NaOH or KOH was used to oxidize the $ZnCl_2$-containing nanodomains, XPS showed that no Zn remained in the sample following the treatment, because ZnO solubilizes in these alkali bases, while it remains insoluble in NH_4OH. Figure 2 shows the disappearance of the Cl 1*s* peak in the XPS electron binding energy spectrum following the treatment of the $ZnCl_2$-doped films with NH_4OH, while the Zn $2p^3$ electron peak is still present.

High-resolution XPS (Fig. 3) performed on the doped samples showed a shift to a lower binding energy for the Zn $2p^3$ electron peak following treatment with NH_4OH, as expected for ZnO formation. The averaged binding energy values for untreated and treated samples were 1023.1 and 1021.4 eV, respectively, as shown also in Table I. These values are in good agreement with those in the literature for $ZnCl_2$ and ZnO, respectively,[15–18] and clearly demonstrate that the conversion of $ZnCl_2$ to ZnO nanoparticles was successfully achieved through this room-temperature wet chemical process.

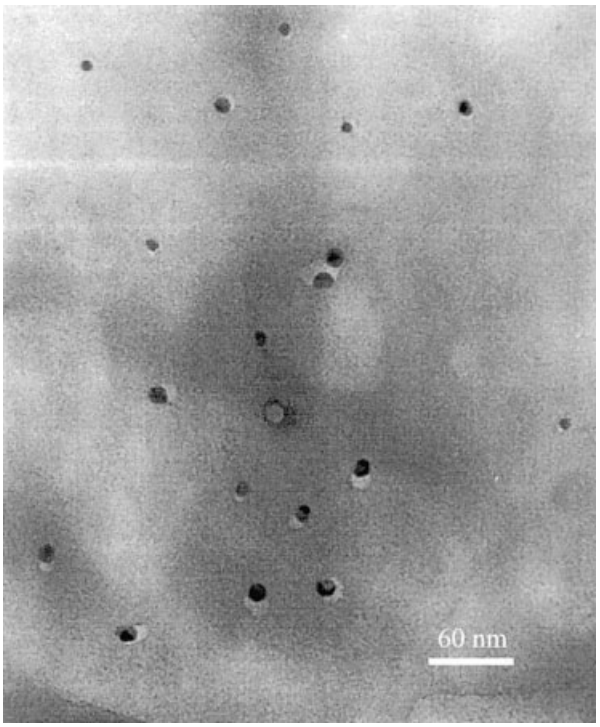

Figure 4 TEM image of ZnO nanoparticles.

To establish the physical (size, dispersion, morphology) parameters of the nanostructures, TEM was employed. Samples were prepared by direct casting onto the sample out of benzene on the TEM grid. Figure 4 shows a TEM sample with ZnO nanoparticles. The nanoparticles demonstrate a spherical morphology as targeted by the choice of the relative volume fractions in the synthesis of the constituent blocks in the diblock copolymer and have a relatively narrow size distribution with radii between 7 and 15 nm.

CONCLUSIONS

We successfully synthesized and characterized ZnO nanoparticles through wet chemical processing at room temperature using the self-assembly of microphase-separated block copolymer templates. XPS confirmed the conversion of the metal salt precursor to the metal oxide by monitoring of the Zn $2p^3$ binding energies in $ZnCl_2$ and ZnO. XPS also demonstrated that the polymer is able to retain the metal nanoparticles during the wet chemical treatments. TEM showed that ZnO nanoparticles synthesized in our scheme have spherical morphology, as targeted by the chosen volume fractions in the synthesis of the constituent blocks in the diblock copolymer.

This room-temperature wet chemical processing templating method is compatible with semiconductor manufacturing technology. It is an example of how block copolymers can be developed to form nanostructured materials for the realization of large-areas low-cost nanodevice technology.

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