

Preparation of Ordered Multilayer Titania/polymer Nanocomposite Thin Films by Evaporation-induced Self-assembly

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(Received August 23, 2004; CL-040993)

The ordered multi-layer TiO₂/Poly(DMCB) nanocomposite thin films were prepared by an evaporation-induced self-assembly method on a glass substrate. In the nanocomposite thin films, the surfactant DMCB was used as both structure-directing agents and monomers. The structures of the films were characterized using FTIR, XRD, and TEM. The results indicated that the films were composed of organic and inorganic layers with orderly interlaced arrangement and the interlayer distance between organic layer and inorganic layer was 7.17 and 6.26 nm before and after polymerization, respectively.

The construction of organic-inorganic nanocomposite films with an ordered structure, especially a multilayer structure has been an important target of functional materials research because of their wide applications as sensors, integrated optics, friction-reducing coatings, biological surfaces, light-emitting devices (LEDs), or surface-orientation layers.¹⁻⁴ From the application point of view, most of these applications require the preparation of stable and well-organized films with fast fabrication processes. But recent synthetic efforts to obtain such materials have focused on nanocomposites, prepared mainly by slow procedures like Langmuir-Blodgett method,^{5,6} monomer or polymer infiltration of inorganic nanostructures,^{7,8} or sequential deposition, i.e. layer-by-layer self-assembly.^{3,4,9} Recently, Lu and Zink et al. reported a very rapid method, so-called evaporation-induced self-assembly to prepare ordered inorganic-organic nanocomposite materials.^{1,2,10-14} In this method, surfactants used as structure-directing agents and inorganics can form ordered organic-inorganic nanocomposite materials in very short time, unfortunately this structure is unstable. However, if monomer and crosslinker were added or polymerizable surfactant were used in the preparation process and then initiated the monomer and crosslinker or the polymerizable surfactant to polymerize, the structure can be locked in and become stable.^{1,2} The poly(DMCB)/SiO₂ nanocomposite thin films was reported by our group using this method.¹⁵ So far, the articles about evaporation-introduced self-assembly are almost limited to silicate-based materials.

TiO₂ in the nanometer range is currently intriguing because of their excellent optoelectronic properties for solar cells and photocatalysts. However, there have been only a few reports on the fabrication of organic/TiO₂ multilayer films by the Langmuir-Blodgett⁵ and layer-by-layer self-assembly method.⁹ As mentioned above, these two kinds of processes require many repeated deposition steps to build up a practical film thickness. Here, we synthesized a polymerizable surfactant used as both structure-directing agents and monomers to prepare organic/TiO₂ nanocomposite thin films with ordered multilayer structure.

Film substrates, ordinary glass, were cleaned with 'Piranha solution,' a 30:70 mixture of 30% hydrogen peroxide (H₂O₂) and concentrated sulfuric (H₂SO₄) at 80 °C for 1 h followed by extensive rinsing with secondary distilled water, a final rinsing with absolute ethanol and dried in an oven. Crosslinker hexanedioldimethacrylate (95%) and initiator 1,1'-azobis(1-cyclohexanecarbonitrile) (97%) were obtained from Fluka and used without further purification. Methacrylic acid 2-dimethylaminoethyl ester (98.5%) obtained from Tokyo Kasei Kogyo Co., Ltd. TiCl₄ and 1-bromohexadecane(chemical pure) obtained from Shanghai Chemical Company were used without further purification.

The cationic surfactant, methacryloxyethylhexadecyltrimethylammonium bromide (coded as DMCB) which was synthesized according to the literature published elsewhere.¹⁵ The product was characterized by FTIR and NMR and was identified to be the target.

FTIR spectra of the films were taken on a Nicolet Avatar 360 spectrophotometer. X-ray diffraction (XRD) patterns were taken with a Philips X'pert-MRD instrument using Cu K α ($\lambda = 1.542 \text{ \AA}$) irradiation through a Ni filter. The measurement in a θ - 2θ scan mode was carried out over an angular range of 0.6-10.0° at 0.005° intervals in 2θ . The TEM micrographs were obtained with a JEM-2010 transmission electron microscope at 200 kV.

Precursor solutions were prepared by addition of DMCB, crosslinker hexanedioldimethacrylate and initiator 1,1'-azobis(1-cyclohexanecarbonitrile) into titania sol which was synthesized according to the literature published elsewhere.¹⁴ Finally, a small amount of water was added.

The films were prepared by dip-coating with a speed of 38.5 cm/min at room temperature in ambient conditions. Then the films were heated at 120 °C for 2 h in an oven to prepare polymerized films. The unheated and heated films were named unpolymerized (as-deposited) and polymerized films respectively.

FTIR analyses of the polymerized and as-deposited films were conducted to verify whether polymerization occurred in the heat treatment. Figure 1 shows the FTIR spectra of the as-deposited and polymerized films. It is seen that there exists obvious difference in the FTIR spectra of the two films, which provides an evidence of the organic polymerization of the film subject to heat treatment.² Namely, the peak at 1635 cm⁻¹ assigned to the C=C stretch vibration of the monomer disappears after heat treatment of the as-deposited film (Figure 1b), indicating that C=C is transformed to C-C. At the same time, the peak at 1719 cm⁻¹ assigned to the stretching vibration of C=O in the as-deposited film (Figure 1a) shifts to 1738 cm⁻¹ after heat treatment (Figure 1b), which indicates that the polymerization of the as-deposited film to generate methacrylate is involved in the heating process and thus the conjugated C=O is transformed

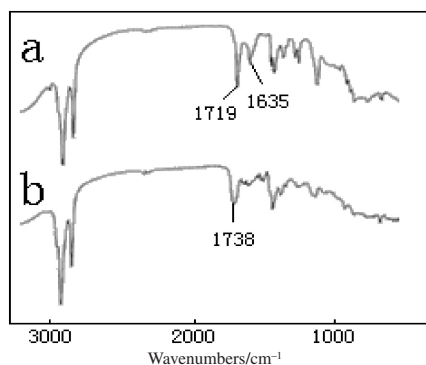


Figure 1. FTIR of un-polymerized and polymerized films.

to the unconjugated C=O.

Figure 2 shows the XRD patterns of the as-deposited and polymerized films on glass substrates. Both the two XRD patterns are characterized by (00 l) diffraction, which indicates that the films have lamellar structures. The as-deposited film shows XRD peaks assigned to (001), (002), (003), and (004) diffractions, indicating that the as-deposited film has an excellent lamellar structure. The periodicity d , i.e., the spacing between the organic and inorganic layers of the nanocomposite films, can be calculated from the corresponding d_{00l} values in Figure 2, from the equation: $d = l \cdot d_{00l}$. Where l is equal to 1, 2, 3, and 4, and refers to the order number corresponding to the number of each diffraction peak. The average spacing between the organic and inorganic layers of the as-deposited and polymerized films were calculated to be $d = 7.17$ and 6.26 nm, respectively. Thus the spacing was reduced after heat treatment of the as-deposited film and its subsequent polymerization.

The TEM image of the polymerized film is shown in Figure 3. It can be seen that the polymerized film has a laminated structure. The average spacing between the organic and inorganic layers of the polymerized films was calculated to be about 6 nm, which is in good agreement with the XRD results.

On the basis of the above results, the formation process of the films can be inferred as follows. The process starts with a homogeneous solution of soluble titania, surfactant, crosslinkers, and initiators prepared in ethanol/water solvent with an initial surfactant concentration (c_0) below the critical micelle concentration (c_{mc}). During dip-coating, preferential evaporation of ethanol progressively enriches the concentrations of water,

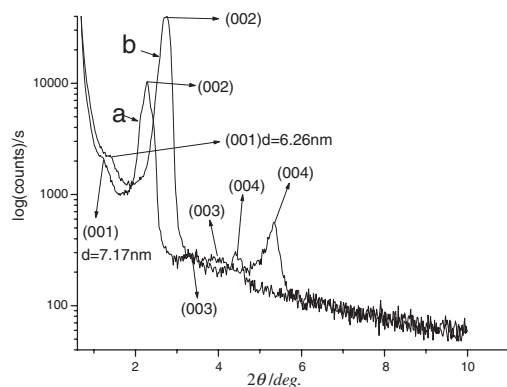


Figure 2. XRD of un-polymerized(a) and polymerized thin films(b).

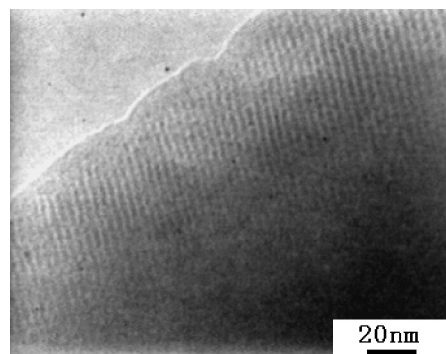


Figure 3. TEM of polymerized thin films.

HCl and the nonvolatile solution constituents within the depositing film. Continued evaporation promotes cooperative assembly of these (titania-surfactant-monomer) micellar species into interfacially organizes liquid-crystalline mesophase, thereby simultaneously organizing both the inorganic and organic precursors into a desired laminated structure in a rapid, continuous process. And the organic phase in the nanocomposite architecture can be well locked by heating to initiate and complete polymerization.

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