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Ordered luminescent nanohybrid thin films of $Eu(BA)_3Phen$ nanoparticle in polystyrene matrix from diblock copolymer self-assembly

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ABSTRACT

A simple route for fabricating highly ordered luminescent thin films based on hybrid material of diblock copolymer and europium complex, assisted with self-organization of polystyrene-block-poly(ethylene oxide) (PS-b-PEO) diblock copolymer upon solvent annealing, is presented. PS-b-PEO self-organized into hexagonal patterns and europium complex of $Eu(BA)_3Phen$ was selectively embedded in PS blocks after solvent annealing in benzene or benzene/water vapor. During benzene annealing, the orientation of the PEO cylindrical domains strongly depended on the $Eu(BA)_3Phen$ concentration. In contrast, when the hybrid thin films were annealed in mixture of benzene and water vapor, high degree of orientation of the PEO cylindrical domains is more easily obtained, which is independent of $Eu(BA)_3Phen$ concentration. Furthermore, preferential interaction of PEO domains with water induces a generation of nanopores in the hybrid thin film. Atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were used to characterize the long-range lateral order and phase composition of the hybrid thin films. The ordered nanohybrid thin films kept the fluorescence property of $Eu(BA)_3Phen$ and showed a strong red emission under the 254 nm light's irradiation. The fluorescence property was confirmed by photoluminescence (PL) spectra.

1. Introduction

Highly ordered nanohybrid materials in thin films have attracted much attention for their fascinating self-assembly nanostructure, as well as the potential applications in optical, optoelectronic, magnetic, and micromechanical devices. Block copolymer, one class of self-assembling materials, offer an attractive route to fabricate nanometer-scale structures, since they spontaneously form a range of periodic structures for proper compositions and under adequate conditions, owing to the microphase separation between dissimilar blocks [1–4]. Hence, much effort has been made to use self-assembled block copolymers as a tool for fabricating functional nanomaterials, such as noble metal [5–8], semiconductor [9–15], and inorganic oxide nanoparticles [16–20]. Very recent examples include the fabrication of well-defined surface patterns of functional hybrid materials in thin films based on PS-b-P4VP diblock copolymer and Au nanoparticles through metallization of the pyridine units' in situ using a wet chemical process [21], the use of cooperative self-assembly of polystyrene-block-poly(2-vinylpyridine) (PS-b-P2VP) copolymer and TTIP-based sol–gel precursors to prepare 2D arrays of strings of TiO_2 nanoparticles [22], and the preparation of ordered silicon nanodot arrays using linear-brush-type polystyrene-block-polycarbosilane (PS-b-PCS) diblock copolymer thin films combined with acetone vapor annealing [23]. Since a rapid route for orienting the cylindrical microdomains of asymmetric polystyrene-block-poly(ethylene oxide) diblock copolymer (PS-b-PEO) normal to the surface of a substrate by utilization of solvent was addressed by Russell and co-workers [24,25], examples have revealed that thin films of asymmetric (PS-b-PEO) diblock copolymer were successfully used as scaffolds for various nanostructures. One example is the fabrication of ordered inorganic oxide nanoparticles arrays which could be grown selectively on top of the PEO domains on the surface of ordered PS-b-PEO thin films by chemical vapor deposition [26,27]. Another and more extensive example involves the use of sol–gel chemistry to prepare hexagonally packed arrays of titania nanodomains with PS-b-PEO block copolymer as template [28,14,29,30].

Phosphor thin films have attracted considerable attention because of their potential application in high-resolution devices such as electroluminescent (EL) display, field emission displays (FEDs), and cathode ray tubes (CRTs) [31]. Compared with conventional powder phosphors, thin film luminescent structure used as display have higher contrast and resolution, superior

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thermal conductivity, better adhesion as well as a high degree of uniformity [31,32]. Hence, the fabrication of high-quality phosphor thin films has always been hot spot of study over the past few years [33–35]. On the other hand, the patterning technologies of phosphor screens have a great effect on the resolution of flat panel display devices [36]. Yu et al. have prepared pattered nanocrystalline phosphor films using sol–gel process combined with soft lithography [37], overcoming the high expenditure and complexity of traditional fabrication process, but the obtained patterns are in micrometer scales. Cong et al. have used micelles of PS-b-P4VP as nanoreactors to synthesize Eu(III)-block copolymer complex with the presence of 1,10-phenanthroline as cooperative ligand, and have successfully prepared hexagonally ordered luminescent thin films in nanometer scale [38]. However, the degree of lateral order of the thin films is low and the method is limited to the complexation between rare earth and polymer.

In this work, we report the use of solvent-induced ordering to fabricate highly ordered luminescent nanohybrid thin films via spin-coating from solutions containing europium complexes of $Eu(BA)_3Phen$ and PS-b-PEO, combined with solvent annealing; the europium complex was selectively incorporated into PS domain due to its hydrophobic. Annealed in pure benzene or benzene/water mixture vapor, the hybrid film showed highly ordered hexagonally packed PEO cylindrical microdomains embedded in $PS/Eu(BA)_3Phen$ matrix. The ordered nanohybrid thin film exhibits highly efficient red luminescence of $Eu(BA)_3Phen$. Atomic force

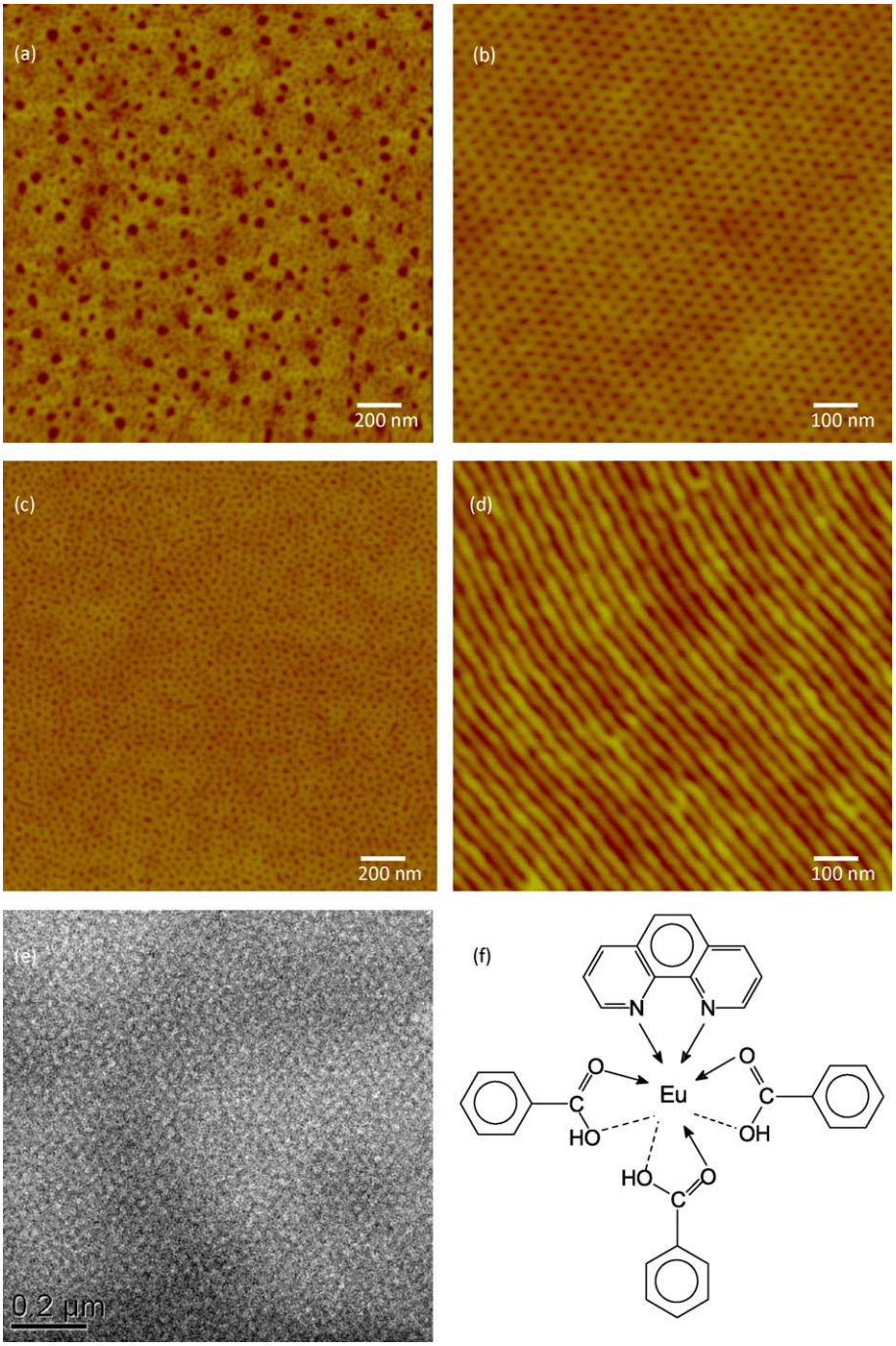

Fig. 1. Height AFM images of nanohybrid thin films (a) as spun and (b) after benzene annealing and pure block copolymer (c) as spun and (b) after benzene annealing. Dark parts correspond to low height values. (e) Corresponding TEM image of (b). (f) The molecular structure of europium complexes of $Eu(BA)_3Phen$.