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Unconventional tailorable patterning by solvent-assisted surface-tension-driven lithography

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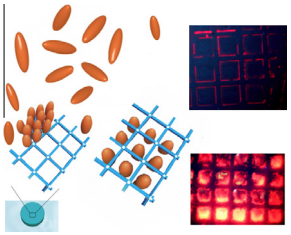
GRAPHICAL ABSTRACT



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ABSTRACT

Unconventional nanopatterning methods are emerging as powerful tools for the development of controlled shapes and ordered morphology of nanostructured materials with novel properties and tailorable functions. Here, we report a simple yet straightforward and efficient approach for patterning through unconventional dewetting that involves surface tension driven process. Using this innovative approach, we have successfully demonstrated to be able to prepare surface micro-patterns over large areas deposited through Eu^{3+}:TiO_2 nanoparticles providing rational control over the local nucleation of nanoparticles. Remarkably, these features could be addressed by polar or apolar solvents, suggesting potential applications in bottom-up nanodevices. This paper represents the first such attempt to create an inorganic materials non-lithographic template for the directed deposition of Eu^{3+}:TiO_2 or related metal oxides. The technique, which is driven by the unique chemical properties and geometrical layout of the underlying patterned micrometer-sized templates, enables the construction of micro- and nano-structuration of dispersed inorganic functional materials suitable for electrooptical and photonic applications.

1. Introduction

Fluorescent nanomaterials materials have promising applications in sophisticated display technologies [1,2]. An accurate patterning would also have a paramount effect on the resolution of display devices. Unconventional nanopatterning methods are emerging as powerful tools for the development of controlled

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shapes and ordered morphology of novel nanostructured materials with novel properties and tailorable functions. In particular, stimuli-responsive materials have been attracting increasing interest due to the possibility to significantly change their mechanical or optical properties in a predictable or controllable manner in response to their external stimuli of their environment, such as pH, temperature, surface tension, electric or magnetic fields [3,4].

Further to this, combining mechanically useful nanoparticles with the optical properties of rare earth ions, such as europium(III) ions, offers enormous technological potential in the area of photonic applications such as solid state lasers, sensors, optical amplifiers, scintillators, phosphors and optoelectronics displays and devices [5]. This could be particularly advantageous because Eu^{3+} ions produce an intense red photoluminescence with narrow atomic emission profiles and provides an inexpensive, long lifetime and nontoxic method for fluorescence imaging compared to organic fluorophores [6–8]. Nanocrystalline TiO_2 is expected to be a potential host matrix for the design and fabrication of efficient photosensitive materials. Besides, embedding a lanthanide complex in a hybrid matrix is also favorable for its unique optical properties such as long fluorescence lifetime and good luminescence efficiency combined with high photochemical stability of the hosts. Furthermore, titania is an excellent material for Eu^{3+} being highly transparent to visible light and due to its thermal, chemical, and mechanical properties and several synthetic approaches of Eu^{3+} doped TiO_2 films, nanoparticles, and particles have been reported [9–12]. The ability to pattern functional materials at different length scales is therefore essential for many research fields including electronic and optoelectronic devices [13,14]. However the challenges confronted by conventional lithography as high cost and time consuming may limit the applications. A high-throughput, low cost, patterning can be obtained by taking advantage of the combination of alternative unconventional lithographic techniques. In particular, control of self-assembly of functional materials based on dewetting is immensely important for realizing the possibility of adapting processing technologies to fabricate desired patterns over large areas [15–19]. Owing to impressive progress in materials science, a broad range of strategies used to pattern nanoparticles have been designed given rise to a variety of top-down methods such as advanced photolithographic techniques (EBL) [20,21] (soft embossing, decal transfer microlithography (DTM) [22], imprinting [23], soft lithography [24], micro-contact and microtransfer printing [22–25]. However, elastomeric stamps can contaminate solutions with unreacted oligomers [26] and swell upon contact with nonpolar solvents (e.g., hydrocarbons, toluene, and dichloromethane) [27]. Bottom-up methods such as Surface Tension-Driven (STD) techniques [28] and Lithographically Controlled Wetting (LCW) [29] assemble the atomic or molecular components into organized surface structures, and it is highly desirable to develop alternative approaches for the bottom-up fabrication. Similarly, techniques such as "confined dewetting lithography" (CDL) reported the assembly of particles into controlled patterns on various chemically modified substrates, where the grid floated on the solution [30]. What makes patterning by dewetting challenging is that different forces influence the instability of the film resulting from its interaction with the substrate subject to long range force of van der Waals, short range polar and molecular forces [31,32]. Normally it is almost hard to control the dewetting process for preparing surface nanopatterns with well-confined features. Moreover, wetting or dewetting phenomena might occur depending on the wettability of the substrate with respect to the deposited solution [33,34]. From this, it is clear that understanding the key mechanisms driving the assembly of particles at a micrometer scale brings new strategies for fabrication of well-ordered arrays of micron-sized objects.

In this paper, we present a solvent-assisted Surface Tension Driven (STD) patterning method through control of the patterning in different arrangements by choosing appropriate polarity of solutions used. Fluorescent patterns made of Eu^{3+} doped TiO_2 nanoparticles have been prepared. In this approach, the Eu^{3+}:TiO_2 surface pattern on the glass substrate is established by the template confined deposition on a micrometric scale (which is an effective method to control surface nanopatterns with aggressive solutions, large pattern areas, and to accomplish a high throughput), while the dewetting process is induced by polarity of the solvent. Specifically, we demonstrate how the polarity properties of the solvent offer control over the confined topography of the deposited film, shaping it into ordered squares. The proposed technique was applied as a general process to fabricate Eu^{3+}:TiO_2 surface nanopatterns, as representative functional material which in turn provides an excellent model sample for investigating the dependency of the dewetting process on different chemical parameters. Moreover, it is believed to the best of our knowledge, that this strategy is the first to use the various relative polarity of the solution to manipulate the different dewetting behaviors of Eu^{3+}:TiO_2 thin inorganic films dominated by various driving forces, which at the same time can improve our understanding of the influencing factors on the dewetting patterning mechanisms.

2. Materials and methods

2.1. Synthesis of Eu^{3+}:TiO_2 nanoparticles

All starting materials were obtained from commercial suppliers and used without any further purification. Eu^{3+}:TiO_2 nanoparticles were synthesised using a modified low temperature hydrolytic method reported previously in literature [35]. In a typical synthesis, 0.165 g of europium(III) acetate hydrate was added at room temperature to 35 g of oleic acid in a three-neck flask under vigorous stirring. The mixture was degassed at 120 °C for 2 h under nitrogen flow, and then cooled down to 100 °C. At 100 °C, 3.24 ml of Ti(IV) butoxide was added. The reaction was then allowed to stir for 10 min after which 2.8 ml of triethylamine first, and 7.2 ml of H_2O then, were rapidly injected into the flask, causing a rapid drop of temperature to 80–85 °C. The reaction was reheated to the initial injection temperature in a few minute and allowed to stir for 24 h under mild reflux. Excess of water was removed under vacuum. Finally, the nanoparticles were precipitated from the solution with addition of an excess of ethanol at room temperature. The resulting precipitate was isolated from the mother liquor by centrifugation and washing twice with ethanol to remove the excess of oleic acid. Finally, it was dispersed in apolar/polar solvents.

2.2. Microstructure fabrication by STD

For controlled dewetting the template-confined surface tension driven deposition process is shown in the scheme in Fig. 1. Micropatterns are realized by depositing few micro liters of 1% (w/v) of Eu^{3+}:TiO_2 in polar/non-polar solutions on different stamps used as geometrical constrain. First a transmission electron microscopy (TEM) copper (Cu) grid (300 mesh) with 60 μm wide square holes and 20 μm wide bars was used as the mask for the patterning. The grid was fixed under a metallic template placed onto the corning substrate. The Cu templates were fixed, by metallic clips, on the glass surface.

The surface energies were interpolated by the contact angle goniometer (OCA20, Dataphysics) software by using the polar and dispersion components of contact angles, respectively obtained by the use of water (H_2O) and diiodomethane (CH_2I_2).