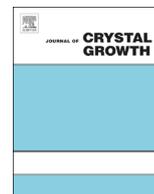




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A novel micropatterning of luminescent barium carbonate nanowires controlled by a phosphonated copolymer



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ABSTRACT

Novel luminescent BaCO₃ nanowires have been successfully synthesized in the presence of mixed additives of a phosphonated copolymer and an organic dye. The nanowires show a time-dependent self-assembly into various microstructures over different length scales. With the combination of a microcontact printing technique, the selective growth of uniform NWs was achieved through application of substrates with different wettability and roughness. In this strategy, microstructures, location and growth orientation of BaCO₃ NWs are well controlled.

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1. Introduction

Crystal arrays of inorganic, organic and their hybrids have received wide-ranging attention in recent years due to their potential applications in the fields of biosensing, solar cells and photoelectric device [1]. Nature provides various examples of biogenic materials with orderly arrays which endow organisms with extraordinary abilities. For instance, geckos and some beetles have nearly five hundred thousand keratinous hairs or setae on their foot, which enable them to climb up smooth and vertical surfaces [2]. In the ears of vertebrates, vibration of arrayed nanofibers is responsible for the perception of sound [3]. Spiral arrangement of nanofibers on water-striders' legs makes them stand and move quickly on the water [4]. Nature also provides alternative fabrication strategies to pattern single crystals (i.e. eyes of brittle star, and sea urchin spin). Crystals with exquisite microstructures usually develop in preorganized frameworks of organic matrices. These insoluble organic matrices provide confined spaces for controlling over nucleation, orientation, assembly and distribution of minerals. Meanwhile, soluble matrix (e.g., proteins and polysaccharide) effectively controls over mineral polymorph and morphology. But principles underlying the formation of many sophisticated biomaterials are still unknown and need further study.

Inspired by nature's ingenuity, scientists have undertaken many attempts to control the organization and location of various materials. The most widely used approaches are the micropatterned self-assembled monolayers (SAMs) [5,6], but they were

limited to several especial substrates, such as Au and Ag [7]. Polymer or plastics films as substrate expanded the crystal growth with regular arrays onto the curved substrate [8,9]. Recently, Meldrum et al. reported the synthesis of nanofibers with highly ordered arrangements via polycarbonate track-etch membranes [10]. Other strategies require the complex lithography and etching techniques [11]. However, these methods were not so straightforward. It remains challenging to control distributions of crystals in the specific locations for the construction of highly ordered arrays.

In this article, we demonstrate a selective growth method via microcontact printing technique (μ CP) [12] to produce photoluminescent BaCO₃ NWs with controllable microstructures and location in the mineral solution. Patterned organic films serve as a simple analog of insoluble matrix or spatially constrained microenvironments for crystallization of minerals. Polymers and small organic molecules are used to control the morphology and microstructures of crystals. Our experiments provide a facile, low-cost method to yield large-area arrays of NWs with different morphology, spatial distribution and growth orientations. This approach for the synthesis and organization of uniform fibrous building blocks on specific sites may be helpful for patterning of other functional materials.

2. Experimental

2.1. Materials

All chemicals were of analytical grade and used without further purification. Octadecyltrichlorosilane (OTS, 96%) was purchased from

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Alfa Aesar; Sylgard 184 and its curing agent were bought from Dow Corning Company; Polyethyleneglycol-b-[(2-[4-dihydroxyphosphoryl]-2-oxabutyl) acrylate ethyl ester] ($M_w=135\,000$ g/mol) was synthesized as literature (Scheme S1) [13].

2.2. Surface modifications

All glassware were cleaned and sonicated in ethanol for 5 min, after being rinsed with distilled water and further soaked with a $\text{H}_2\text{O}-\text{HNO}_3$ (65%)– H_2O_2 (1:1:1, V/V/V) solution, then ultrapure water (Barnstead Esayppure UV, $\rho=18.2$ M Ω cm), and finally dried in air with acetone. Polydimethylsiloxane (PDMS) stamps with convex stripes, square patterns and grids (Fig. S1) were utilized to make patterned surfaces. A solution of octadecyltrichlorosilane (OTS) in n-hexane (1 mM) was used as the “ink” for μ -CP. After applying the “ink” by cotton Q-tip, the PDMS stamp was dried in a stream of nitrogen gas for 1 min and then brought it to contact with the surface of hydrophilic glass or silicon slide for an interval of 30 s. Then the substrate was heated to 80 °C for 45 min.

2.3. Mineralization

Typically, a 5 mM BaCl_2 solution was freshly prepared and transferred into a glass bottle (10 mL). The aniline blue (AB) (0.8 mg) (Scheme S2) and polymer (0.5 mg) were dissolved in it. Then several modified glass slides were placed at the bottom of the bottle. The initial pH values were adjusted by HCl or NaOH. Finally, the bottle was covered with Parafilm with three needle holes and placed in a desiccator. The desiccator contains bottles filled with crushed ammonium carbonate, which provides the gas of NH_3 and CO_2 . After different reaction intervals, the glass slides covered with the crystals were taken out, rinsed with doubly distilled water and ethanol and then dried at room temperature.

2.4. Characterization

X-ray diffraction patterns were obtained by means of a Rigaku DMax- γ A with Cu-K α radiation ($\lambda=1.54178$ Å). SEM images were taken on a field emission scanning electron microscope (JEOL JSM-6700F, 15 kV). TEM, HRTEM photographs were performed on a JEOL JEM 2011 microscope at an accelerating voltage of 200 kV. Energy-dispersive X-ray (EDX) analysis was obtained with an EDAX detector installed on the same HRTEM. FTIR spectra were measured on a Nicolet 6700 FT-IR spectrometer from 400 to 4000 cm^{-1} at room temperature. Photoluminescence (PL) spectra were performed on a Fluorolog3-TAU-P at room temperature. The emission images were acquired on a fluorescence microscope (Olympus B202) with a spot-enhanced charge-coupled device (CCD, Olympus DP70). The wavelength of UV light ranges from 340 to 380 nm.

3. Results and discussion

3.1. Growth of NWs in bulk solution

Control experiments were performed to study the roles that different additives played in the mineralization. When AB was utilized in the mineralization, mixtures of wires and large microspheres were synthesized in the mineral solution (Fig. S1a). If simple copolymer was applied, helixlike nanofibers were observed (Fig. S1b).[10] To obtain pure luminescent NWs in the mineralization, mixed additives of the polymer and organic dye were necessary. The mineral solution turned light blue after 4 h (inset in Fig. S3a). TEM analysis revealed that nanoparticles (NPs, 2–5 nm) coated with organic additives first formed in the solution (Fig. S2). The electron diffraction (ED) pattern indicated that they were amorphous barium carbonate (inset in Fig. S3b). These amorphous particles were heavily aggregated together in the bulk

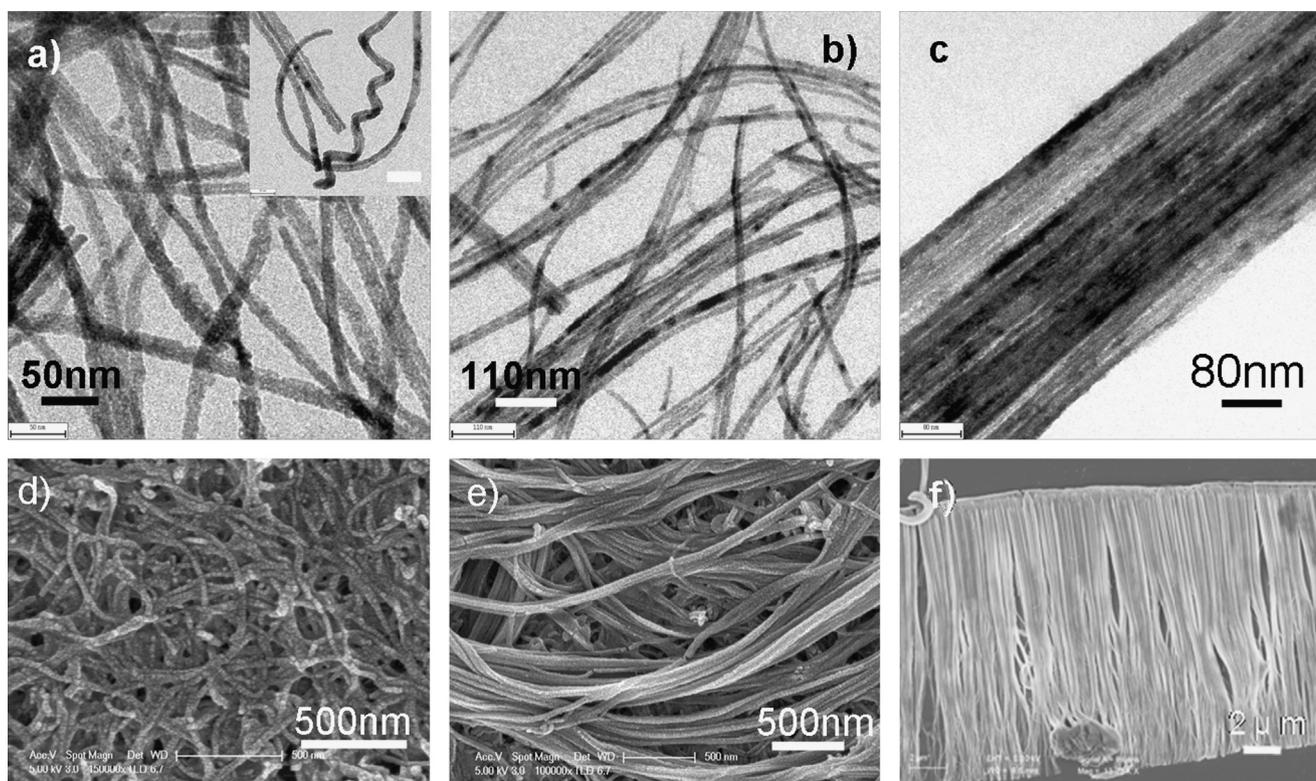


Fig. 1. TEM images of NWs obtained at different times: (a) 6 h, inset shows some helices, scale bar is 50 nm; (b) 8 h; (c) 12 h; SEM images of (d) unattached NWs, after 6 h; (e) bundles, after 12 h; and (f) raft-like crystal slices, after 24 h.

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