Responsive Periodic Mesoporous Polydiacetylene/Silica Nanocomposites

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Many fascinating biological systems, such as abalone shells and lotus leaves, are only composed of ordinary materials. Their superior properties, however, arise from the meticulous control of structures and functionalities over multiple length scales.[1] Drawing from nature, recent research has witnessed rapid advances in bio-inspired materials and has recognized self-assembly, the spontaneous organization of pre-programmed building blocks via noncovalent interactions, as the most promising approach.[2] By deliberately controlling the assembly and programming the functionalities of building blocks, it is possible to construct hierarchically biomimetic systems with spatially defined structure and functionality.[3]

The introduction of organic functional components into hierarchically porous inorganic scaffolds represents an important endeavor toward bio-inspired hybrid materials.[4] Synthesis approaches involve either grafting organic moieties onto preformed porous scaffolds or using functional organosilanes as building blocks.[4–6] The use of organosilanes containing bridged functional groups, in particular, allows the formation of periodic mesoporous organosilica (PMO) with an integral hybrid pore wall.[7,8] These PMO materials often contain high-loading organic groups with better accessibility, which is important for catalysis and environmental remediation.[6–8] Moreover, subtle chemical and/or physical changes of the organic components may be amplified macroscopically, providing novel responsive materials for device applications.[7] To date, a number of PMO materials have been synthesized;[6] however, the embedded organic components are mainly limited to passive functional groups, such as methylene,[9] ethane,[8] ethylene,[5] dodecane,[10] and benzene.[11]

Here we report the first example of responsive PMO synthesized through cooperative assembly of surfactant molecules (e.g., cetyltrimethylammonium bromide, CTAB) and silsesquioxanes containing a bridged diacetylenic group. As illustrated in Scheme 1, the diacetylenic molecules spontaneously organize around the surfactant liquid crystalline structure, forming a mesoscopically ordered composite with molecularly aligned diacetylenic units. Subsequent surfactant removal followed by topo-polymerization creates the responsive PMO embedded with polydiacetylene (PDA), a polymer that chromatically responds (e.g., blue to red) to a wide range of external stimuli.[12] Such a hierarchical molecular design endows the PDA−PMO with thermochromic reversibility, mechanical robustness, enhanced thermal stability, and rapid chemochromic response.

Figure 1a displays X-ray diffraction (XRD) patterns of the PMO. The intensive peak, indexed as the (100) diffraction of a 2D hexagonal mesostructure (*p*6mm), slightly shifts from 5.2 to 4.9 nm after surfactant removal, suggesting the well-retained mesostructure. Transmission electron microscopy (TEM) image (Figure
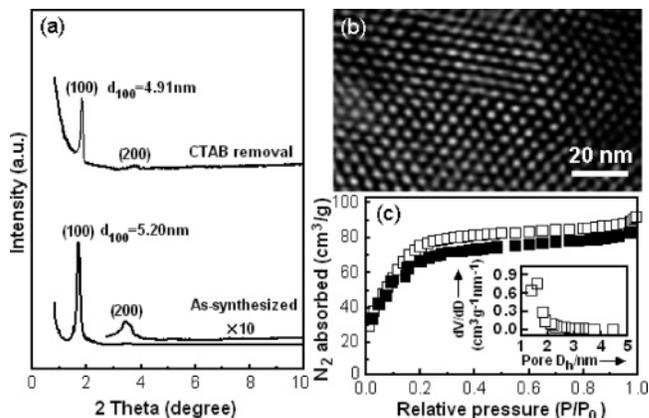
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Figure 1. (a) XRD patterns (before and after CTAB removal), (b) TEM image, and (c) nitrogen adsorption/desorption isotherms and BJH pore diameter distribution (inset, from the desorption branch) of the PDA−PMO.

Scheme 1. Molecular Structure of a Diacetylene-Bridged Silsesquioxane and Schematic of the Formation of the Responsive PMO
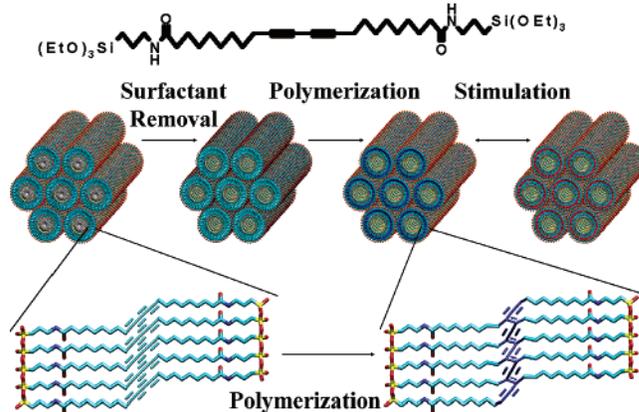
1b) further reveals the hexagonal pattern with a lattice constant of 5.7 nm, agreeing well with the XRD results. The nitrogen adsorption−desorption isotherms (Figure 1c) show a significant nitrogen uptake mainly below 0.2 relative pressure with a negligible hysteresis, indicating a uniform pore-size distribution (see inset).[5]

The reversible chromatic responses to external stimuli were demonstrated by subjecting a PDA−PMO to thermal cycles between 20 and 103 °C. As the photographs show in Figure 2a, the PDA−PMO rapidly changes its color reversibly between blue and red. The chromatic response can be quantitatively defined using colorimetric response (CR), which is defined as the percentage of blue-to-red transition calculated from the corresponding UV−vis spectra.[13] As shown in Figure 2b, consistent chromatic responses
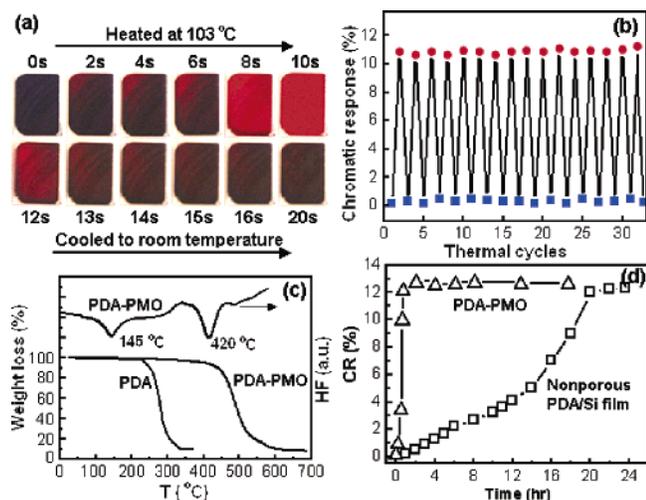
Figure 2. (a) Photographs of rapid thermochromic reversibility for the PDA−PMO nanocomposite film. (b) CR values of a PDA−PMO at 25 and 103 °C during thermal cycles. (c) DSC and TGA analysis of the PDA−PMO. TGA of the corresponding polydiacetylenic acid is also shown. (d) CR of the PDA−PMO before and after CTAB removal when exposed to a mixture of 10 M HCl and methanol (v/v = 7/1).

(14% at 103 °C and 0.2% at 20 °C) are achieved over 15 thermal cycles (see Supporting Information for the corresponding UV−vis spectra). While the high CR value at high temperatures may provide fine thermochromatic sensing ability, the near-zero CR values at low temperatures imply a complete red-to-blue reversibility and a potential reusable device.

It is known that diacetylenic derivatives undergo topo-polymerization forming chromatically responsive PDA only when the diacetylenic units are strictly aligned in certain molecular scale.[14] The observed chromatic transition verifies the diacetylenic molecular alignment within the PDA−PMO framework (see Scheme 1). Besides, the diacetylenic units are covalently linked to the ethoxysilane groups, leading to a robust hybrid scaffold after hydrolysis and condensation reactions of the diacetylenic silsesquioxane molecules. The novel reversible chromatic response is a direct result from this relatively strong molecular configuration that helps the restoration of the PDA side chain conformation when released from external stimuli.[15]

The robust framework also provides the PDA−PMO with enhanced thermal stability. Figure 2c represents a typical differential scanning calorimetry (DSC) trace of the PDA−PMO. The DSC transition at 145 °C is attributed to the side chain disordering of the PDA. The PDA−PMO shows reversible color transitions only below this temperature. Note that this temperature is a much higher critical value than any reported results (e.g., 90 °C for the noncovalent interaction-based PDA assemblies).[16] The higher DSC transition temperature at 420 °C may be associated with the melting of the main chain structure. Thermogravimetric analysis (TGA) curves of a pure PDA prepared by polymerizing the corresponding diacetylenic acid (10,12-docosadiyndioic acid) and of the PDA−PMO are compared in Figure 2c. The pure PDA decomposes at 290 °C, while the PDA/silica nanocomposite decomposes at a much higher temperature of ~500 °C, further indicating an improved thermal stability.

The unique mesoporous structure of the PDA/silica composite promotes faster mass transport and more rapid responses to chemical stimuli. The blue PDA changes its color to red when exposed to chemicals, such as methanol.[3a] The response rate, however, is often limited by the slow diffusion of chemicals into the solid PDA.[15] Figure 2d compares the chromatic responses of the PDA composites before (nonporous) and after surfactant removal to a methanol/HCl mixture. The chromatic response of the PDA−PMO rapidly reaches its maximum in minutes compared with that of the nonporous PDA in hours. The fast response is of great interest for sensing applications. In addition, the capability of tuning pore diameter of the PDA−PMO by selecting appropriate surfactants may provide size-selective applications.

In summary, we have demonstrated the synthesis of responsive PMO materials through co-assembly of bridged diacetylenic silsesquioxane and surfactant. The spatially defined functional component, the mesoporous network, and the covalent proximity of PDA to silica endow the PMO with mechanical robustness, reversible chromatic responses, improved thermal stability, and faster responses to chemical stimuli. This research also provides an efficient molecular design and assembly paradigm to fabricate a family of conjugated optoelectronic materials, creating novel platforms for sensors, actuators, and other device applications.

Supporting Information Available: Detailed synthesis and thermochromatic characterizations of the PDA/silica materials, and complete ref 3a. This material is available free of charge via the Internet at http://pubs.acs.org.

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