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Reversible Photoswitchable Fluorescence in Thin Films of Inorganic Nanoparticle and Polyoxometalate Assemblies

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Nanostructures with reversible photoswitchable fluorescence have received much scientific and technical interest due to their potential applications in the fields of both optical information recording and bioimaging.[1] Such nanostructures are normally composed of photochromic dyads and luminescent dyads/inorganic nanoparticles (NPs).[2,3] Under photostimulation, the geometrical or electronic structures of the photochromic dyads are changed, which activate/deactivate the electron or energy transfer between the photochromic and luminescent components, leading to fluorescence switching of the nanostructures. Although much progress has been made, the nanostructures with reversible photoswitchable fluorescence need to be further improved before getting into the practical applications. For example, the possible photodegradation of organic photochromic dyads under photoirradiation may prevent repetitive use of the nanostructures.[4]

In this communication, we report a novel type of hybridized nanostructure, in which both active components are inorganic nanomaterials: photochromic Preyssler-type polyoxometalates $K_{14}[Na(H_2O)P_5W_{30}O_{110}]$ (Na-POMs) and luminescent core−shell CdSe@CdS NPs. As shown in Figure 1A, the layer-by-layer (LbL) technique, which has been recognized as a general and versatile method to prepare the nanostructured thin film on different substrates,[5−7] is adopted to construct the inorganic hybridized nanostructures based on the alternative adsorption of negative-charged Na-POMs or CdSe@CdS NPs and the positive-charged polyelectrolyte (poly(ethyleneimine), PEI) pair. Na-POM components in the nanostructured films are well-known to exhibit reversible, high contrast photo- and electrochromic characteristics upon photo- or electrochemical stimulation.[8,9] Such a reversible photochromic phenomenon is also observed for the multilayer of Na-POMs and PEI. The multilayer only containing single inorganic component nanostructures, $(PEI/Na\text{-}POMs)_{10}$ (here and below, the subscript 10 denotes the number of the layers), is rather transparent under room light (curve 1 in Figure 1B) and contrastively has strong adsorption in the region 550−800 nm after exposure to UV light (curve 2 of Figure 1B). On the other hand, the LbL film only containing CdSe@CdS NPs, $(PEI/CdSe@CdS)_{10}$, shows a strong fluorescence feature in the region 550−650 nm (curve 3 in Figure 1B), which exactly covers the wavelength range of photochromic switching of Na-POMs. Therefore, if both CdSe@CdS NPs and Na-POMs are in the same nanostructures and the interdistances between CdSe@CdS NPs and Na-POMs are less than 10 nm, the fluorescence resonance energy transfer (FRET) between luminescent NPs and photochromic Na-POMs will be expected to occur, leading to the switching of fluorescence of CdSe@CdS NPs.

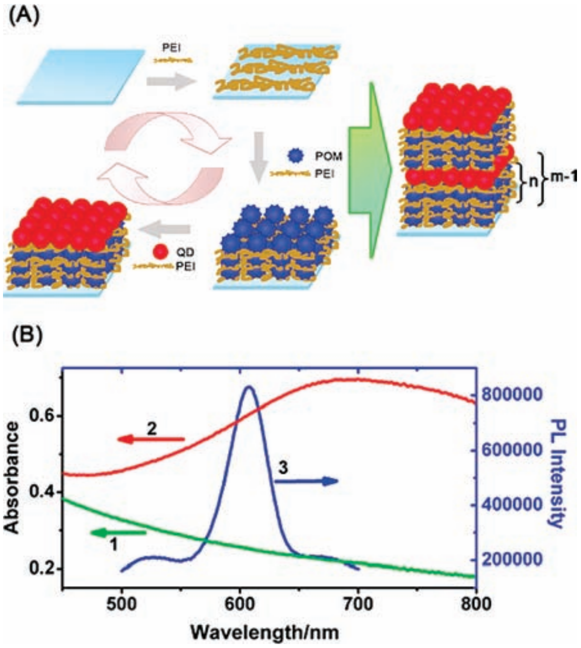

Figure 1. (A) Scheme of preparation of $[(PEI/Na\text{-}POM)_n/PEI/CdSe@CdS)]_m$ LbL films on the glass substrates (not scaled). (B) Absorption spectra of $(PEI/Na\text{-}POMs)_{10}$ film under room light (curve 1) and after exposure to UV light (curve 2); fluorescence spectrum of $(PEI/CdSe@CdS)_{10}$ film (curve 3).

The hybridized nanostructured films of $[(PEI/Na\text{-}POM)_n/PEI/CdSe@CdS)]_m$ on the glass substrates are fabricated by the LbL method (Figure 1A). To optimize the efficiency of photoswitching fluorescence, the relative concentration of Na-POMs and NPs in the same nanostructures are changed by controlling the number of Na-POM layers (n) in one composite layer of $(PEI/Na\text{-}POM)_n/PEI/CdSe@CdS$ (Figure S8 in Supporting Information). Meanwhile, the whole fluorescence intensity of the nanostructured film is manipulated by altering the number of composite layers (m) (Figure S3). Finally, the nanostructured films of $[(PEI/Na\text{-}POM)_9/PEI/CdSe@CdS)]_{10}$ are chosen for the following study, and different types of spectra prove involvement of both Na-POM and CdSe@CdS components in the prepared films (part S2 in Supporting Information). Figure 2A shows fluorescence switching of the $[(PEI/Na\text{-}POM)_9/PEI/CdSe@CdS)]_{10}$ film on the glass substrate under exposure to UV light and subsequent to room light. The as-prepared nanostructured film under ambient conditions exhibits a strong fluorescence peak centered at 600 nm (curve 1 in Figure 2A). After

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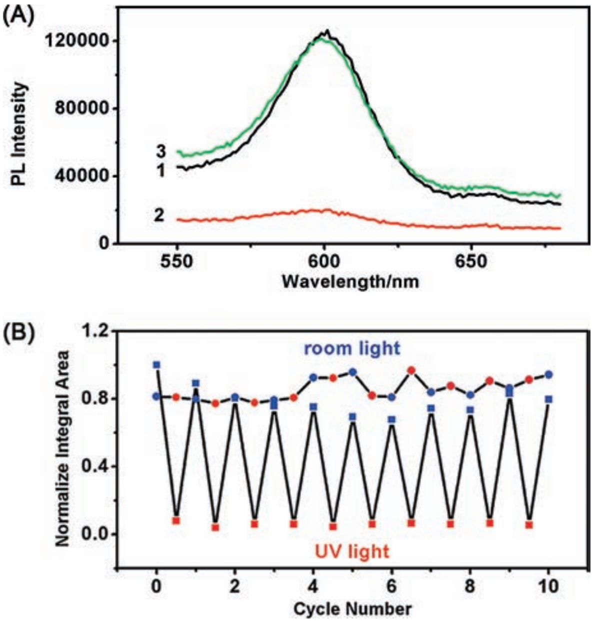

Figure 2. (A) Fluorescence switching of [(PEI/Na-POM)$_9$/PEI/CdSe@CdS]$_{10}$ film from the as-prepared state (curve 1), to UV exposure (curve 2), to room light exposure (curve 3). (B) Normalized integral fluorescence area of [(PEI/Na-POM)$_9$/PEI/CdSe@CdS)]$_{10}$ film in the UV−vis cycles as a function of cycle number (square dotted curve). Round dotted curve represents the contrast experiment of [PEI/CdSe@CdS)]$_{10}$ film. All the blue dots were detected after the film was kept under room light, and all the red dots were measured after the film was irradiated by UV light. No obvious fluorescence switching highlights the importance of photochromic Na-POMs in the nanostructures.

exposure to UV light of intensity of 396 mW/cm^2 for 30 s, the fluorescence of the nanostructured film is dramatically quenched; i.e., the integral fluorescence area decreases to only 8% (the integral fluorescence area is $\sim$2.70 $\times$ 10^5) of that before UV irradiation (the integral fluorescence area is $\sim$3.32 $\times$ 10^6) (curve 2 in Figure 2A). Further, when the UV-irradiated film is kept under room light (intensity: 0.5 mW/cm^2) in air for 24 h, the fluorescence of the nanostructured film is recovered and the integral fluorescence area reaches 90% (the integral fluorescence area is $\sim$2.96 $\times$ 10^6) of the original value (curve 2 in Figure 2A). It should be noted that the long fluorescence recovery time of the nanostructured film results from the low intensity of room light; for example, the recovery time shortens to 1 h in air when the film is exposed to the visible light of intensity of 985 mW/cm^2.

Two prominent features can be observed for the photoswitchable fluorescence of the [(PEI/Na-POM)$_9$/PEI/CdSe@CdS)]$_{10}$ film. (1) Reversibility. As shown in Figure 2B (square dotted curve), the changes in both “on” and “off” fluorescence intensities of the nanostructured film are less than 20% in 10 cycles of UV and visible exposures. Such high reversibility should be ascribed to the inorganic nature of both Na-POMs and CdSe@CdS NPs in the nanostructured film, which have good resistance toward photoirradiation. (2) Stability. For applications of the nanostructures, it is highly desirable for the long-term stability of both the “on” and “off” state of fluorescence against thermal relaxation.[10] Generally, the geometrical or electronic structures of the organic photochromic dyads are easily changed under thermal agitation,[11] possibly leading to the spontaneous transformation of fluorescence of the nanostructures. As a comparison, the photochromism of inorganic Na-POMs mainly originates from the conversion of their redox state (see below for detailed discussion), which is insensitive to thermal relaxation.[12,13] The stability of the [(PEI/Na-POM)$_9$/PEI/CdSe@CdS)]$_{10}$ film is explored by experiments which showed almost no change in the “on” fluorescence intensity of the nanostructured film for at least 1 month when placed in air under room light (Figure S6A in Supporting Information) and the “off” florescence intensity to be also stable for at least 1 month when kept in darkness with oxygen isolation (Figure S6B in Supporting Information).

The size of Na-POMs, the diameter of CdSe@CdS NPs, and the width of PEI molecules are approximately 1.1 nm, 6.0 nm, and 0.3 nm, respectively.[14,15] Although the exact interdistances between CdSe@CdS NPs and Na-POMs in one layer of (PEI/Na-POM)$_9$/PEI/CdSe@CdS is difficult to accurately calculate, most of them are estimated to be in the range 1−10 nm, which falls into the effective length of either energy transfer or charge transfer.[16−20] Detailed analyses reveal that the reversible photoswitchable fluorescence of the [(PEI/Na-POM)$_9$/PEI/CdSe@CdS)]$_{10}$ film is mainly attributed to the tunable FRET between luminescent NPs and photochromic Na-POMs (part S4 in Supporting Information). Upon irradiation with UV light, electrons in Na-POMs are promoted from the low-energy electronic states, which are mainly comprised of oxygen 2p orbitals, to the high-energy electronic states that are mainly comprised of metal d orbitals. The d^1 electrons in the ligand-to-metal (oxygen-to-metal, O→M) charge transfer (LMCT) states facilitate the absorption of visible light via intervalence charge transfer among metal centers and d−d transitions, which gives rise to a strong absorption feature of the nanostructured film in the region 550−800 nm (Figure S7 in Supporting Information).[21] Because the fluorescence characteristic of CdSe@CdS NPs is located in the same absorption region of the reduced Na-POMs, the resonance energy transfer from NPs to Na-POMs occurs and thus the fluorescence of the nanostructured films is quenched (curve 2 in Figure 2A). When placed in the presence of oxygen under room light, the colored Na-POMs return to their original colorless state and the nanostructured film becomes relatively transparent in the region 550−800 nm (Figure S7 in the Supporting Information). As a result, the resonance energy transfer from NPs to Na-POMs is interrupted and therefore the fluorescence of the nanostructured films is recovered (curve 3 in Figure 2A). The FRET mechanism can also be confirmed by contrast experiments that show no obvious fluorescence switching for the nanostructure film only containing luminescent NPs (round dotted curve in Figure 2B). Furthermore, the FRET may be quantified by recording the fluorescence decay dynamics of [(PEI/Na-POM)$_9$/PEI/CdSe@CdS)]$_{10}$ film under room light or after UV irradiation (Figure S12 in the Supporting Information). The average fluorescence lifetime of the nanostructured film is found to be 2.15 ns (τ_{rm}) under room light while decreasing to 1.85 ns (τ_{uv}) after exposure to UV light. So the FRET rate (K_{ET}) in the nanostructured film can be estimated to be 0.08 ns^{-1} from the below equations: $K_{\mathrm{ET}} = (1/\langle\tau_{\mathrm{uv}}\rangle - 1/\langle\tau_{\mathrm{rm}}\rangle)$.[22]

Finally, the [(PEI/Na-POM)$_9$/PEI/CdSe@CdS)]$_{10}$ nanostructured film on the silicon substrate is examined for its possible application in the field of optical information recording. First, a 400 mesh copper grid with square pores is used as the mask and placed on the surface of the nanostructured film. After irradiation by UV light for 30 s, an image of negative patterns is clearly observed by the confocal fluorescence microscopy (Figure 3A). The pattern formation is easily understood to be FRET between QDs and Na-POMs taking place only within the UV-exposed square areas, resulting in the fluorescence quenching of the nanostructured film in the designated area. Impressively, the square patterns are totally erased after the nanostructured film is placed under room light for 1 day (Figure 3B). As discussed above, FRET between QDs and Na-POMs in the films is deactivated after exposure to room light, and thus the fluorescence is recovered in the quenching areas. Subsequently, another type of mask, a 400 mesh copper grid with

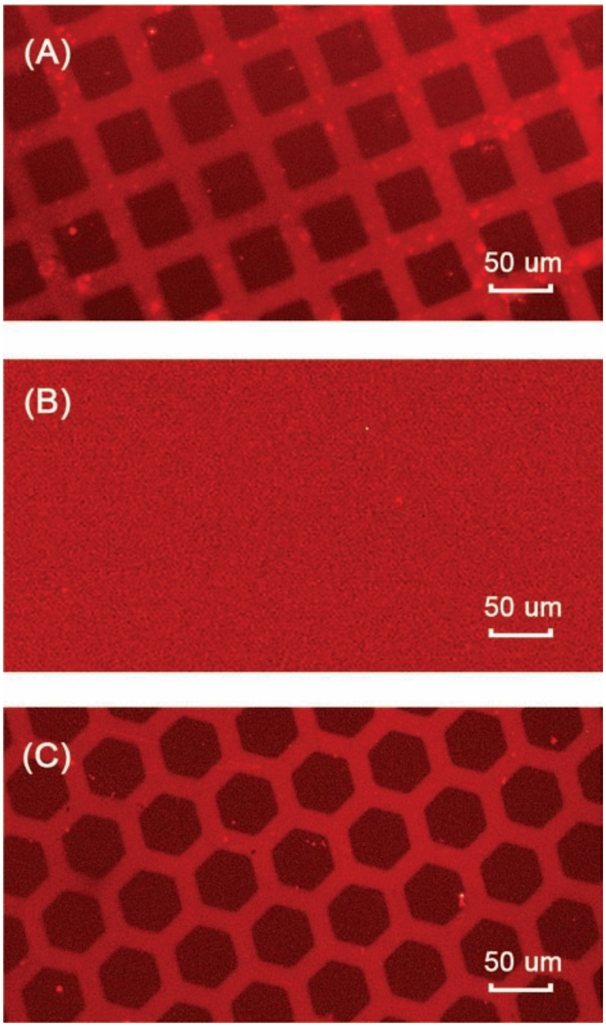

Figure 3. Confocal fluorescence microscopy images of [(PEI/Na-POM)$_9$/PEI/CdSe@CdS)]$_{10}$ multilayer film on silicon substrate via the process of writing (A) − erasing (B) − writing (C) in the pattern experiment.

honeycomb pores, is placed on the surface of the pattern-erased nanostructured film. The fluorescence image demonstrates that the nanostructured film maintains the capability of recording the patterns (Figure 3C). Recent studies have shown that the inorganic hybridized nanostructures can be used for the next generation of solar cells and field effect transistors because of their unique optical/electrical properties and high thermal/optical stability.[23,24] Such a writing/erasing experiment exemplifies that the inorganic hybridized nanostructures may have new application potential in photonic storage devices.

In conclusion, we fabricated the inorganic hybridized nanostructures of CdSe@CdS QDs and Na-POMs on the solid substrates by using the LbL assembly technique. The nanostructured films exhibit remarkably reversible and stable optical writing/erasing behavior under the control of UV light/visible light irradiation. It is also noted that, in current work, the recovery time of the film under visible light is rather long (1 h, 985 mW/cm^2) compared to the switching time under UV light (30 s, 396 mW/cm^2). To realize possible application of the device in the field of high-speed information storage, higher power visible light or other chromism techniques (for example, the response time for electrochromic process of Na-POMs/polycations multilayers is short at 4 s[8]) will be performed in future work.

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Supporting Information Available: All the materials including the synthesis of Na-POM and CdSe@CdS NPs, the fabrication of hybridized nanostructured films by LbL technology, and the optical property and the fluorescence quenching and recovery mechanism of the hybridized nanostructured films. This material is available free of charge via the Internet at http://pubs.acs.org.

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