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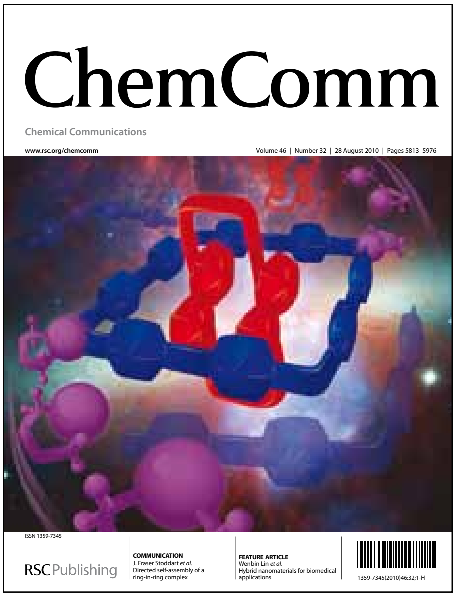

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ARTICLE TYPE

Multifunctional Polyoxometalates-Modified Upconversion Nanoparticles: Integration of Electrochromic Devices and Antioxidants Detection†

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We report a novel design, based on a combination of lanthanide-doped upconversion nanoparticles and polyoxometalates, for electrically controlled fluorescence switches and sensitive detection of antioxidants in aqueous solution.

Recently, lanthanide ion (Ln^{3+}, such as Er^{3+}, Tm^{3+}, Ho^{3+})-doped upconversion nanoparticles (UCNPs), which can emit higher-energy visible photons after being excited by lower-energy near-infrared (NIR) photons via a two-photon or multiphoton mechanism, have attracted a tremendous amount of attention.[1] They have become promising alternatives to organic fluorophores and quantum dots. Compared with conventional down-conversion fluorescent labels, which require ultraviolet or blue excitation wavelength, upconversion fluorescent materials have many conceivable advantages, including higher photostability and thermal stability, very weak auto-fluorescence background, greater tissue penetration, and high signal-to-noise ratio. Various host materials such as fluorides, oxides, chlorides, bromides, oxysulfides, and oxyhalides were selected to synthesize the lanthanide-doped nanomaterials with high upconversion efficiency and controllable emission profile.[1] Among them, $NaYF_4$ with low phonon energy has been demonstrated to be the most efficient host material.[2] Therefore, the design and development of new materials functionalized with upconversion luminescence property is undoubtedly of great importance in future.

Electrochemical devices are under intense study for electrical energy storage, transduction and information processing, and many electrochromic systems involving switchable chromophores included, or grafted on polymers have been already described.[3] In terms of possible components for electrochromic devices, polyoxometalates (POMs) are promising candidates due to their ability to act as an electron reservoir,[4] and some luminescence devices based on POMs have also been fabricated because of an extensive range of structures and stable redox states.[5] Spectroelectrochemistry, the combination of electrochemistry and spectroscopy, has been proved to be an effective approach for studying the redox chemistry of inorganic, organic, and biological molecules, and has attracted much scientific and technical interest because of the possible applications like electrochromic displays, electro-optical switches or optical sensors.[6] Until now, a large number of electricity-dependent luminescence-controllable systems have been designed and studied.[7] However, no examples of upconversion luminescence modulations were carried out. To better exert the advantages of upconversion materials, upconversion fluorescence stimuli-responsive systems need to be further exploited. Therefore, the core-shell structured hybrid nanocomposites combining the electricity-responsive POMs and UCNPs into one unit is predicted to be attractive candidates in fields of electronic devices, detection, and cell imaging.

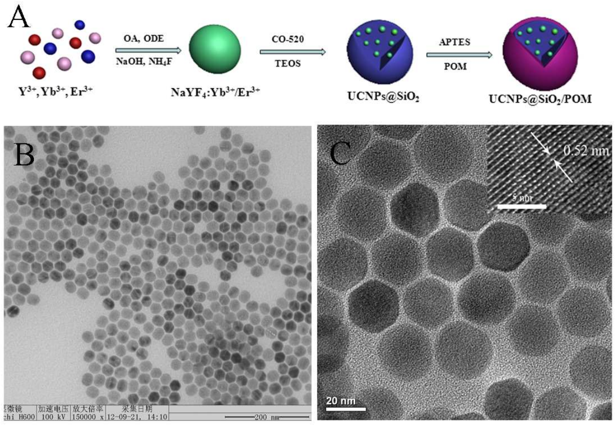

Fig. 1 (A) Schematic illustration of the synthesis and surface modification of OA-stabilized upconversion nanoparticles (UCNPs); TEM (B) and high-resolution TEM (C) images of UCNPs. The insets show the corresponding high-resolution TEM images and arrows highlight d spacing.

Herein, we present the first example of reversible upconversion fluorescence switching system, and the strategy is schematically illustrated in Fig. 1A. Firstly, highly monodisperse UCNPs (Fig. 1B) in organic solvents were synthesized according to a reported method.[8] The high-resolution TEM images revealed uniform hexagonal-phase UCNPs with size of (20±0.5) nm in diameter (Fig. 1C), and lattice fringes with a spacing of about 0.52 nm were highly consistent with (100) phases of the hexagonal $NaYbF_4$ crystalline structures. The oleic acid (OA)-doped UCNPs were then transformed to hydrophilic nanoparticles by silica layer capped (Fig. S1A), and the peak at 1088 cm^{-1} in FTIR spectra is attributed to the vibration bands of Si-O-Si (Fig. S1B).[5]

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After silica coating, the nanocrystals were dispersible in water with good chemical and photochemical stability, and a clear colloidal solution was formed. The SiO_2 shell was also used to passivate the surfaces of UCNPs.[9] Finally, the prepared Na-POMs layers were formed on the surface of the synthesized UCNPs@SiO_2 nanoparticles via electrostatic interaction.[10] By comparison, hydrophilic UCNPs were also synthesized through a facile hydrothermal method.[2] The as-synthesized UCNPs consist of spherical microspheres with an average diameter of 150 nm (Fig. S2A, B). However, the luminescence intensity of hydrophilic UCNPs (Fig. S2C) was much weaker than that of OA-UCNPs (Fig. S2D), which is not favorable for further use. Therefore, OA-UCNPs are employed in our study.

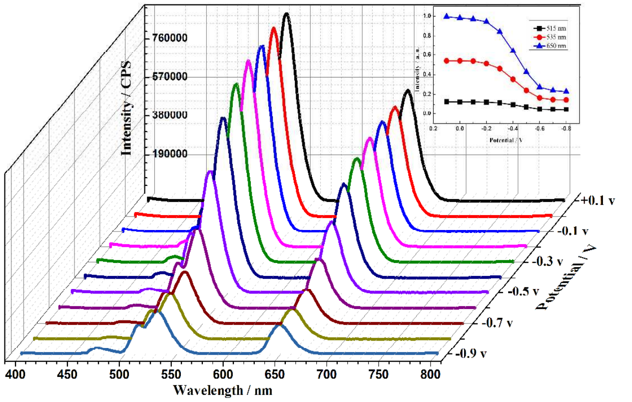

Fig. 2 Spooled fluorescence spectra of hybrid film during the applied potential from 0.1 to -0.9 V.

Electrochemical techniques were used to characterize UCNPs@Na-POMs hybrids films. The cyclic voltammograms of ITO/PAH/UCNPs@Na-POMs/PDDA electrode at different scan rates indicated the redox reaction of Na-POMs belongs to a surface confined process (Fig. S3A),[11] and the hybrids films possess good stability in aqueous solution while no sign of losing redox current intensity was observed upon performing 100 consecutive potential cycles (Fig. S3B). All these results suggested the great potential of Na-POMs to construct reversible and extremely stable switches. The spectroelectrochemical experiments were all conducted in a spectroelectrochemical cell shown in Fig. S4. The effect of applied potentials on the upconversion fluorescence quenching was investigated (Fig. 2). It was found that fluorescence emission of UCNPs decreased slowly with potential decreasing from 0.1 to -0.2 V, and then decreased rapidly with potential decreasing from -0.2 to -0.7. However, as the applied potential became even more negative, the luminescence intensity basically remained unchanged. The variations of three characteristic peaks all showed the same tendency (inset in Fig. 2).

The mechanism of upconversion fluorescence excitation and quenching was given in Fig. 3A. Firstly, under the 980 nm NIR light, double band at 523 and 541 nm, and single emission band at 653 nm were observed, which can be assigned to $^2H_{11/2}\rightarrow{}^4I_{15/2}$, $^4S_{3/2}\rightarrow{}^4I_{15/2}$, and $^4F_{9/2}\rightarrow{}^4I_{15/2}$ transitions of Er^{3+}, respectively.[12] In the present system, potential-induced absorbance change of Na-POMs was considered to be a key factor for the luminescence switching process. Because the absorption band of reduced Na-POMs (500-800 nm) overlaps greatly with the emission band of UCNPs (not shown here), fluorescence quenching could happen via either inner filter effect (IFE) or energy transfer effect.[13] When UCNPs were excited, the emission travelled through the hybrids film, and the emitted light located at 523, 541 and 653 nm would be absorbed severely via the corresponding quenching mechanism[12, 14], resulting in the light reached to the detector rarely. But the above quenching process can be reversed easily under electrical stimulus. Fig. 3B showed the electrical-controlled "on" and "off" luminescence switching of UCNPs@Na-POMs nanostructure. In oxidized state I (black line), UCNPs could emit its characteristic fluorescence. After a potential of -0.7 V was applied, the detected emission intensity of the three peaks from as-prepared multilayer structure were all rather weak (blue line), which was assigned to the upconversion fluorescence emission was overwhelmingly absorbed by reduced Na-POMs. When an oxidation potential 0 V was further applied, the fluorescence was recovered to its original state completely (red line), because the fluorescence quenching mechanism was insufficient. The contrast luminescence ratio of the system at -0.7 and 0 V was calculated to be about 0.8. Moreover, the fluorescence switching operation was quite reversible, and can be repeated several times without noticeable fluorescence changes between "on" and "off" states (inset in Fig. 3B).

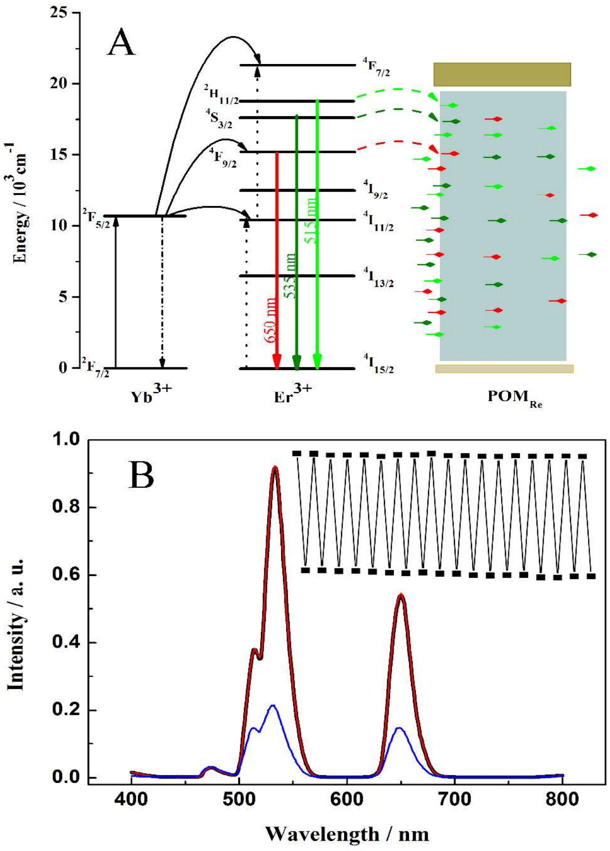

Fig. 3 (A) Schematic energy level diagrams and fluorescence quenching progress in the UCNPs@Na-POMs systems; (B) Fluorescence switching of hybrid film from 0 V (black line), to applied potential of -0.7 V (blue line), and to applied potential of 0 V

(red line); and (inset) reversible fluorescence (541 nm) on–off cycles under alternating applied potential with -0.7 V (bottom lines) and 0 V (top lines).

Antioxidants play a central role in cellular defense against toxins and free radicals, and their levels are implicated in many diseases.[15] Thus, it is important to be able to monitor the change of antioxidants concentration in real time. Herein, the developed UCNPs@Na-POMs can also be used for sensing antixidants, such as BAS, glucose, glutathione (GSH), and so on. We employed GSH as a model molecule and detect it in aqueous solution. GSH can be oxidized by Na-POMs$_{Ox}$, generating glutathione disulfide (GSSG) based on the equation,

$$\text{Na-POMs}_{\text{Ox}} + \text{GSH} \rightarrow \text{Na-POMs}_{\text{Re}} + \text{GSSG}$$

As anticipated, upconversion luminescence was gradually decreased with increasing GSH concentration (Fig. 4). Because of the low background signal by NIR excitation, this method has a low detection limit of 0.02 μM, and a good linear relationship from 5 to 50 μM. In addition, a sensitive detection towards glucose was also given in Fig. S5, the detection limit was 0.01 mM, and a linear relationship from 1 to 20 mM was obtained. This investigation revealed universal antioxidants can be sensitively detected in this system.

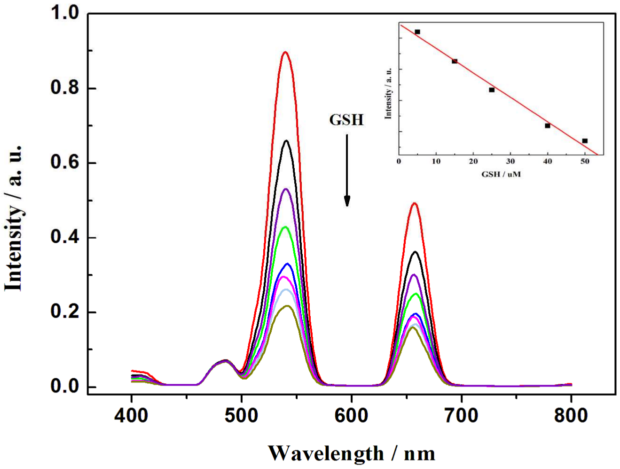

Fig. 4 Photoluminescence response of POM-modified NaYF$_4$:Yb/Er@SiO$_2$ as a function of GSH concentration (0, 5, 15, 25, 40, 50, 75, 100 μM) in an aqueous solution.

In summary, a UCNPs-based electricity-stimuli fluorescence switch device has been developed. Under electricity trigger, Na-POMs transformed between oxidation and reduction states, resulting in reversible and high contrast upconversion fluorescence switching between "on" and "off". Furthermore, by taking advantage of the highly sensitive redox reaction of Na-POMs and the nonautofluorescent assays offered by the UCNPs, we have demonstrated the monitoring of antixidants levels in aqueous solution. These findings are important not only for enabling promising applications of UCNPs in the photoelectric field but also for providing a sensor platform useful for detection of antioxidants in living cells.

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Notes and references

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