



Temperature-responsive multifunctional switchable nanoreactors of poly (N-isopropylacrylamide)/SiO₂/lanthanide-polyoxometalates/Au: Controlled on/off catalytic and luminescent system



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ABSTRACT

A method was developed for the preparation of temperature-responsive multifunctional nanoreactor by coating the poly (N-isopropylacrylamide) (PNIPAM) on the external surface of silica/lanthanide-POMs/Au spheres. The nanoreactor showed the repeated on/off catalytic activity and switchable luminescence by temperature stimuli. For example, the nanocomplexes showed strong red luminescence in solution and excellent catalytic activity in the reduction of 4-nitrophenol at 25 °C. However, when the temperature was 40 °C, the red luminescence almost disappeared in solution and catalytic activity was sharply decreased. Moreover, in solutions of K₄Fe(CN)₆ containing Na₂SO₄ at 25 °C, it demonstrated the well-defined cyclic voltammograms (CV) peaks with large peak currents, showing the “on” state; at 40 °C, the CV response was significantly suppressed, showing the “off” state. The smart nanoreactors have great potential for applications in many fields, such as bio-materials, controlled labeling catalysis, switches and so on.

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1. Introduction

The production of smart switchable materials that are able to respond to external stimuli is one of the most active fields in material chemistry. They are very attractive in catalysis, biomedical imaging, microelectronic devices and smart nanoreactors, as the properties of materials can be controlled by applying appropriate stimuli [1–4]. For the catalytic reaction, it would be much more significant if the catalytic activity of the catalyst can be tuned. Recently, the gold nanoparticles functionalized with a responsive polymeric coating that is sensitive to external temperature stimuli, have gained considerable interest for applications in a diverse range of areas embracing catalysis, diagnostics, and therapeutic purposes. And a lot of temperature-responsive switches of temperature-responsive polymer/Au composites were reported [5–9]. In the studies cited above, the noble metal catalyst particles were directly deposited onto the polymer body. Direct contact between the catalyst and temperature-responsive polymer allowed the polymer to directly control the access to the catalyst and affect its activity.

However, some luminescence materials are sometimes needed to be grafted on these smart gold/polymer switches. The controlled luminescent switches will be useful for us to investigate the catalytic mechanism, label and monitor the catalytic reactions. Moreover, owing to the noninvasive character and high sensitivity of luminescence detection, the smart luminescent switches responding to external stimuli have emerged as an important area of research with application in (bio) chemical sensing, diagnostics, imaging, controlled release of drugs, and smart nanoreactors [10,11]. Therefore, it is interesting for us to fabricate the multifunctional switches whose luminescence and catalysis could be controlled by temperature. In our previous research, it is found that some lanthanide-polyoxometalates (Ln-POMs) show fine red luminescence [12–14]. Compared with the semiconductor quantum dots and organic dyes which are traditionally used as fluorescent probes for biomedical imaging, materials of lanthanide have obvious advantages, such as long-lived excited states, long emission lifetimes, sharp line like emission bands, higher photochemical stability, low toxicity, and little background auto-luminescence [15,16]. Due to their photoluminescent properties, unique molecular structure, electronic versatility and easy obtainability, Ln-POMs would have various applications in smart luminescent nanoreactors, labeling, biological imaging and sensing.

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As a typical temperature-sensitive hydrogel, poly (N-isopropylacrylamide) (PNIPAM) hydrogel undergoes a dramatic volume change at lower critical solution temperature (LCST, about 32 °C). Below the LCST, the amide functionality binds water molecules via hydrogen bonding, thus imparting both water solubility and surface activity. However, moving above the transition temperature breaks these hydrogen bonds, and the polymer expels water molecules and undergoes a coil-to-globule transition. The PNIPAM could be used in the fabrications of smart switches because of the unique properties. The multifunctional switchable nanoreactors have potential applications in many fields, such as drug delivery, luminescent sensors, catalysis. Therefore, it is significant to fabricate multifunctional switchable nanoreactors based on luminescent Ln-POM and Au/PNIPAM. However, until now, the study of the multifunctional on-off switches of Ln-POM/Au/PNIPAM controlled by temperature has not been reported. The reversible modulation of the multifunctional switchable nanoreactors remains a challenge.

In previous research, many cross-linkers, such as [3-(methacryloyloxy)propyl]trimethoxysilane (MPS) were used in order to coat temperature-responsive polymer on composite spheres [5,17]. However, MPS is very expensive. Moreover, few literatures reported that the luminescence of lanthanide and catalytic properties of composites could be controlled by temperature simultaneously. In this paper, a simple method was devised to fabricate the temperature-responsive multifunctional switches. This method is simple and it can be operated easily. However, a very small amount of the composite we prepared in this research showed high performance in catalytic reduction of 4-nitrophenol and strong luminescence at room temperature. Moreover, the resulting multifunctional “smart” nanoreactors exhibited sharply different catalytic activity and luminescence at temperatures below and above the LCST of PNIPAM. These nanoreactors showed excellent red luminescence and catalytic activity in 4-nitrophenol (4-NP) reduction at 25 °C (below LCST of PNIPAM). However, they show almost no luminescence and very low catalytic activity at 40 °C (above LCST).

2. Experimental

2.1. Materials and reagents

Tetraethyl orthosilicate, ammonia solution (25 wt%), HAuCl₄ were purchased from Beijing Chemical Reagent Co. N-isopropylacrylamide (99%) were obtained from Tianjin Kemiou Chemical Reagent Co. Polyethyleneimine (PEI, MW. 10,000, 30%) was purchased from Sinopharm Chemical Reagent Co. Eu₂O₃ was purchased from Shanghai Yuelong Chemical Reagent Co.

2.2. Synthesis of SiO₂/EuW₁₀/Au nanoparticles

SiO₂ particles (80 nm) were prepared according to Stöber method [18]. Na₉[EuW₁₀O₃₆] (EuW₁₀) were synthesized according to the literature [19]. SiO₂/EuW₁₀/Au particles were synthesized according to the literature with some modifications [12]. Briefly, 1.5 g silica particles and 0.5 g PEI were dispersed in 70 ml 0.1 M KCl aqueous solution, and the pH was adjusted to 7.0 with dilute HCl. The SiO₂/PEI suspension was stirred vigorously at room temperature for 24 h, and then the products were recovered by centrifugation and washed with water three times. 30 ml of EuW₁₀ (50 mg) solution was added in the 100 ml suspension of SiO₂/PEI and stirred for 12 h at room temperature. The SiO₂/EuW₁₀ suspension was centrifuged and washed three times. Au nanoparticles were prepared by the literature method [20]. 1 g SiO₂/EuW₁₀ particles were dispersed in 100 ml aqueous solution. Then 100 ml of

Au nanoparticles solution was added to the above SiO₂/EuW₁₀ suspension and stirred for 12 h at room temperature. Finally, the suspension was centrifuged, washed with water and dried. The EuW₁₀ and Au particles could be absorbed on PEI. The purple SiO₂/EuW₁₀/Au particles were obtained. The percentage of Au nanoparticles is 1 wt%.

2.3 Synthesis of PNIPAM/SiO₂/EuW₁₀/Au hydrogel

Poly-N-isopropylacrylamide (PNIPAM, MW 10,000) was synthesized according to literature [21]. Then 0.3 g of PEI were added in 30 ml of PNIPAM (1.0 g) hydrogel and stirred for 24 h. The PNIPAM/PEI mixture was heated to 70 °C and white PNIPAM/PEI was precipitated to remove the supernatant. Then the PNIPAM/PEI precipitation was redissolved in aqueous solution (25 °C). The precipitation/dissolving process was repeated three times to remove unabsorbed PEI in supernatant. Finally, the PNIPAM/PEI precipitation was redissolved in aqueous solution. 100 ml of SiO₂/EuW₁₀/Au colloids (0.2 g) solution were mixed with 100 ml of PNIPAM/PEI (0.5 g) hydrogel. The mixtures were stirred for 24 h and collected by centrifugation at 10,000 rpm to removal unabsorbed PNIPAM hydrogel. The precipitate was collected and redispersed in aqueous solution. The procedure of precipitate/redispersed was repeated three times. Finally, the purple PNIPAM/SiO₂/EuW₁₀/Au hydrogels were obtained.

2.4. Preparation of PNIPAM /SiO₂/EuW₁₀/Au particles modified electrode

The glassy carbon electrode (GCE) was polished with gamma alumina powders, then washed with ethanol and distilled water in an ultrasonic bath, and finally dried with N₂ gas. 15 microliters of PNIPAM/SiO₂/EuW₁₀/Au suspension (25 °C or 40 °C) in nafion/ethanol (V: V = 1:20) was dropped on the pretreated bare GCE and dried in air.

2.5. Reduction of 4-Nitrophenol (4-NP)

0.10 mL of 4-nitrophenol aqueous solution (5.0 mmol/L), 0.1 mL of the colloidal dispersion containing 0.25 mg of PNIPAM/SiO₂/EuW₁₀/Au and 2.5 mL of ultrapure water for UV-vis spectroscopy were mixed in a quartz cell at the desired temperature (25 or 40 °C). 0.5 mL of fresh NaBH₄ (0.2 mol/L) solution was heated to the same temperature and was added to the quartz cell. UV-vis absorption spectra were recorded immediately after mixing and then subsequently after given time intervals.

2.6. Characterization of the nanoparticles

Dynamic laser scattering (DLS) measurements were performed on a laser light scattering spectrometer ZEN 3690, Malvern Instruments. Transmission electron microscopy (TEM) measurements were conducted by using a Philips T20 G2 electron microscopy, whereby a small drop of micelle/composite solution was deposited onto a carbon-coated copper TEM grid and dried at room temperature. Scanning electron microscope (SEM) images were observed by a JEOL 6700-F apparatus. UV-vis spectra were recorded on a UV2550 UV-visible spectrophotometer. FT-IR was measured on a Nicolet Nexus 470 FT/IR infrared spectrophotometer. The crystalline structure was investigated by X-ray power diffraction (XRD) with a Bruker D8 Advance X-ray diffractometer. Thermogravimetric analysis (TGA) was performed in a nitrogen atmosphere at a heating rate of 10 °C/min on STA409 PC Luxx. Luminescence spectra were obtained on a Spex spectrofluorometer using xenon lamp as excitation source.

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