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Short communication

Reversible modulation of gold nanoclusters photoluminescence based on electrochromic poly(methylene blue)

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ABSTRACT

Reversible photoluminescence (PL) switches based on a complex of gold nanoclusters and electrochromic poly(methylene blue) (PMB) were realized. The gold nanoclusters PL of hybrid device can be modulated reversibly under electrochemical stimulation. Such an electrochromic device presents several advantages, such as large fluorescence contrast under reduction and oxidation potentials, good reversibility and excellent long-time stability. This simple protocol is anticipated to offer important hints for other nanoclusters and electrochromic materials in the field of photoelectric devices.

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1. Introduction

Considerable attention has been paid to a new class of fluorescent metal nanoclusters, e.g., gold and silver [1]. Metal nanoclusters, whose size is further reduced to 2 nm or less, provide the missing link between atomic and nanoparticle behavior in metals because they are usually composed of a few to a hundred atoms [2]. These nanoclusters present dramatically different optical and electronic properties [3]. Gold nanoclusters have attracted, and are still attracting considerable attention, particularly for applications in bioimage [4], sensors [5] and catalysis [6]. Despite extensive efforts to synthesize fluorescent gold nanoclusters with enhanced quantum yield, little attention is paid to modulate gold nanoclusters photoluminescence (PL) for potential applications in optical information storage. It is especially important to modulate gold nanoclusters PL located on surface rather than in solution, because immobilized PL devices can be more easily manipulated for device incorporation.

Hybrid devices consisting of fluorescent and electrochromic elements have evoked substantial research efforts because electrochromic [7,8] elements can modulate PL through inner filter effect (IFE) or fluorescence resonance energy transfer (FRET), which present quick response [9], good cycling performance [10]

and high fluorescence contrast [11] within a narrow potential range. Electrochromic poly(methylene blue) (PMB) is suitable for these devices because it exhibits outstanding electrochromic performance in terms of stability, reversibility, and optical contrast. Herein, we immobilized gold nanoclusters on the surface of PMB, and utilized the PMB electrochromic properties to modulate gold nanoclusters PL.

2. Experimental

2.1. Materials and reagents

Bovine serum albumin (BSA, fraction V) and chitosan (low molecular weight) were purchased from Sigma. H₂AuCl₄ · 3H₂O and methylene blue (MB) were bought from Beijing Reagent Company. The single-sided indium tin oxide (ITO) electrodes (30–60 Ω/cm², ~1.0 cm × 5.5 cm) were bought from Nanbo Display Technology Co., Ltd., China. Ultrapure water from Water Purifier (Sichuan Water Purifier Co., Ltd., China) was used in all the experiments.

2.2. Synthesis of gold nanoclusters

We synthesized gold nanoclusters as described in reference [12]. 5 mL H₂AuCl₄ solution (10 nM, 37 °C) was added to BSA solution (5 mL, 50 mg/mL, 37 °C) under stirring. NaOH solution (0.5 mL, 1 M) was introduced after two minutes. Then the mixture

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was incubated at 37 °C for 12 h. Finally the mixture was dialyzed in water for 24 h to remove the unreacted reagents.

2.3. Preparation of the ITO/PMB electrode

We cleaned and activated ITO electrode [13]. After that the ITO electrode was immersed in phosphate buffer solution (PBS, 0.05 M, pH 7.0) containing 0.25 mM methylene blue (MB), which was electropolymerized at 0.1 V/s in the potential range from -0.60 to 1.10 V for 100 cycles using a CHI 660 electrochemical workstation. Finally the ITO/PMB electrode was rinsed to remove the physically adsorbed MB. We chose a lower MB concentration to form PMB film more densely.

2.4. Preparation of the ITO/PMB/Au₂₅ electrode

Gold nanoclusters were immobilized on the ITO/PMB electrode by spin-coating [7]. Acetic acid (10 mL, 1%) containing 0.1 g chitosan was mixed with gold nanoclusters solution (10 mL). The obtained solution (80 μL) was immobilized on the ITO/PMB electrode by spin-coating at 500 rpm for two minutes.

2.5. Spectroelectrochemical experiments

Photoluminescence measurements were performed using a Fluoromax-4 spectrofluorometer. The cuvette was capped with a Teflon plate to support electrodes as described [14]. The ITO electrode was served as the working electrode in the cuvette consisting of a Pt wire counter electrode and an Ag/AgCl reference electrode. The aqueous solution containing 0.1 M KH₂PO₄ and 0.1 M KCl (pH 6) was used as electrolyte. The potential was held for 50 s before the spectra were recorded. Absorption measurements were performed using a Cary 500 UV-vis-NIR spectrometer. The position of ITO electrode for absorption measurements (Fig. S1a) was different from that for PL measurements (Fig. S1b).

3. Results and discussion

Our electrochemically controlled PL switching devices are based on optical coupling between the selected gold nanoclusters and PMB. We chose gold nanoclusters stabilized by bovine serum albumin because these nanoclusters are stable not only in solution but also in solid form. In addition, these nanoclusters are easy to synthesize and can achieve high quantum yields [12]. The absorption band of oxidized PMB overlaps greatly with the emission band of gold nanoclusters (Fig. 1), which is particularly favorable for the occurrence of highly inner filter effect (IFE) that would ensure the successful luminescence switching in our system [4].

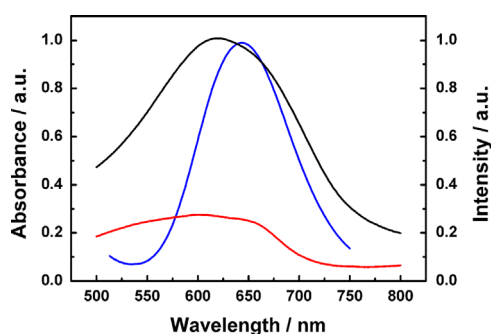
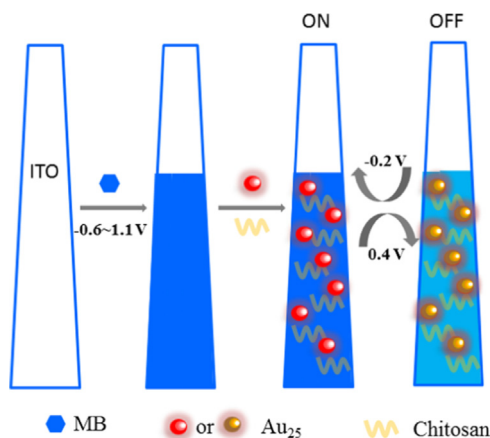


Fig. 1. Absorption spectra of the ITO/PMB electrode at -0.2 V (black curve) and 0.4 V (red curve). Emission spectra of gold nanoclusters (blue curve); sample was excited at 390 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In addition, the short distance between PMB and gold nanoclusters may facilitate fluorescence resonance energy transfer (FRET) to occur [15], which was also expected to be responsible for the luminescence quenching. When gold nanoclusters were excited, the emission traveled through the oxidized PMB. Due to the strong absorbance of the oxidized PMB, the emitted light located at 640 nm would be absorbed severely via the corresponding quenching mechanism. If the emission traveled through the reduced PMB, the emitted light was maintained high because of the weak absorbance of the reduced PMB.

Scheme 1 presents the scheme of fabricating the ITO/PMB/Au₂₅ electrode. Briefly, electrochromic PMB was electropolymerized on the indium tin oxide (ITO) electrode [8,16]. The ITO/PMB electrode was incorporated into the electrochemical cell as a working electrode after gold nanoclusters were immobilized on the surface of PMB. A cuvette was used as an electrochemical cell. Fig. S2 shows the cyclic voltammograms (CVs) of PMB electropolymerized on ITO. A new oxidation peak at 0.29 V appears while the initial oxidation peak at -0.14 V disappears. The new oxidation peak shifts toward positive potentials and its currents increase with cyclic potential scanning, indicating PMB is formed successfully [17]. The gold nanoclusters were synthesized according to previous reports [12], and the typical transmission electron microscopy (TEM) image is shown in Fig. S3. The size of the prepared gold nanoclusters is about 2–3 nm. The excitation and emission of gold nanoclusters in aqueous solution are located at 390 and 640 nm, respectively (Fig. S4), which is evident that gold nanoclusters are synthesized successfully [12]. The emission peak remains approximately the same when gold nanoclusters were immobilized on the surface of PMB (Fig. S5). This result demonstrates that gold nanoclusters are stable when they turn into solid form. Absorption spectra are also used to monitor the preparation process of the ITO/PMB/Au₂₅ electrode. No difference of absorbance between the ITO/PMB and ITO/PMB/Au₂₅ electrodes is observed (Fig. S6). Immobilizing gold nanoclusters on the surface of PMB does not affect the absorbance of PMB.

Next, several influencing factors were optimized. (1) Fig. S7 shows PL response of gold nanoclusters at various pH values. It is evident that gold nanoclusters are stable in solutions of a broad pH range just as a previous study [12]. However, the PL intensity enhances slightly at pH 6. So aqueous solution containing 0.1 M KH₂PO₄ and 0.1 M KCl (pH 6) is selected as the electrolyte. (2) We choose -0.2 V and 0.4 V as the optimal potential range because absorption spectra of the ITO/PMB electrode do not change much when potentials exceed the range (Fig. S8). (3) Fig. 2 shows the PL response of the ITO/PMB/Au₂₅ electrode to the potential. It is



Scheme 1. The scheme of ITO/PMB/Au₂₅ electrode fabrication.

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