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Short communication

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

Hui Zhang [a,b,1], Yanling Zhai [a,b,1], Shaojun Dong [a,*]

[a] State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China
[b] University of Chinese Academy of Sciences, Beijing 100039, China

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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.

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. $HAuCl_4 \cdot 3H_2O$ and methylene blue (MB) were bought from Beijing Reagent Company. The single-sided indium tin oxide (ITO) electrodes (30–60 Ω/cm^2, ~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 $HAuCl_4$ 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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* Corresponding author. Tel.: +86 431 85692886; fax: +86 431 85689711.
E-mail address: dongsj@ciac.ac.cn (S. Dong).

[1] These authors contributed equally to this work.

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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/Au$_{25}$ 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 KH_2PO_4 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]. 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.

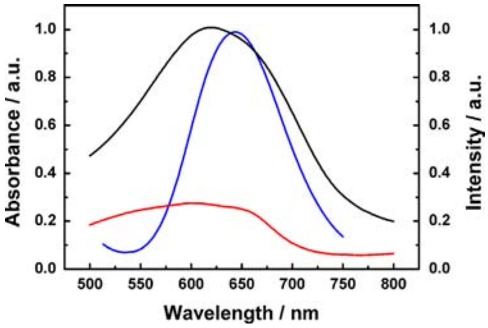
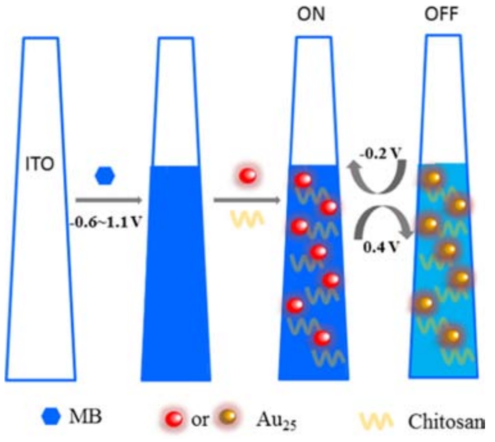


Fig. 1. Absorption spectra of the ITO/PMB electrode at −0.2 V (black curve) and 0.4 V (red curve). Emission spectra of gold nanoclusters (blue curve); sample was excited at 390 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this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

Scheme 1 presents the scheme of fabricating the ITO/PMB/Au$_{25}$ 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/Au$_{25}$ electrode. No difference of absorbance between the ITO/PMB and ITO/PMB/Au$_{25}$ 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 KH_2PO_4 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/Au$_{25}$ electrode to the potential. It is



Scheme 1. The scheme of ITO/PMB/Au$_{25}$ electrode fabrication.

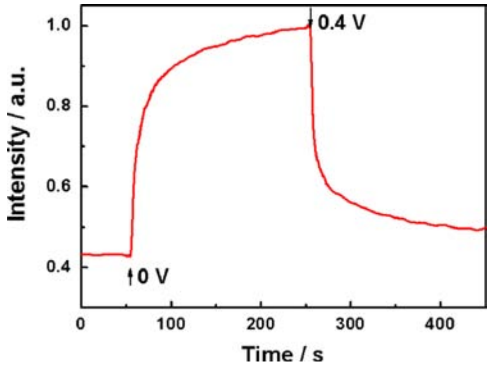


Fig. 2. Fluorescence at 640 nm of the ITO/PMB/Au_{25} electrode as a function of time upon application of 0 V and 0.5 V.

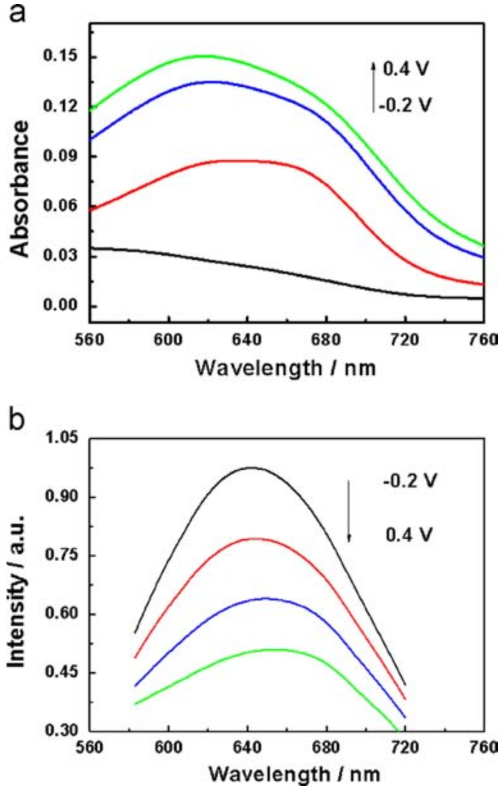


Fig. 3. (a) Absorption and (b) emission spectra of the ITO/PMB/Au_{25} electrode at −0.2 V (black curve), 0 V (red curve), 0.2 V (blue curve), 0.4 V (green curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

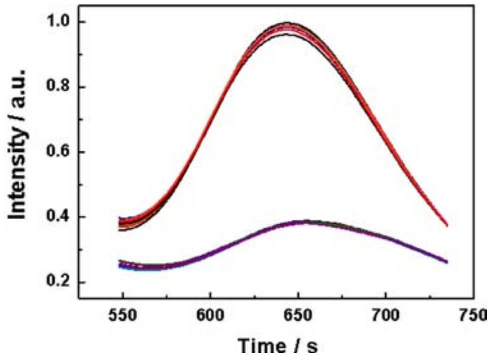


Fig. 4. Emission spectra of the ITO/PMB/Au_{25} electrode at −0.2 V (top curves) and 0.4 V (bottom curves).

demonstrated that only 50 s is required to restore 90% of the maximum PL change.

At optimum conditions, the absorption (Fig. 3a) and emission spectra (Fig. 3b) of the ITO/PMB/Au_{25} electrode under electrochemical stimulation were recorded. The broad absorption peak increases with increase of the applied potentials, while the emission peak is drastically reduced. The variation of the emission peak at 640 nm shares just the opposite trend as the absorption changes. These all show that the design is feasible.

PL of the ITO/PMB/Au_{25} electrode before and after the electrochemical reduction of PMB was investigated (Fig. 4). In reduced state (top curves, −0.2 V), gold nanoclusters exhibit their original PL due to the weak absorbance of reduced PMB. In oxidized state (bottom curves, 0.4 V), PMB is converted to its oxidized form with the strong absorbance, and PL of gold nanoclusters reduces through IFE or FRET. The PL then returns to its original value when the potential returns to −0.2 V. The fluorescence contrast keeps 63% for eight cycles. In a

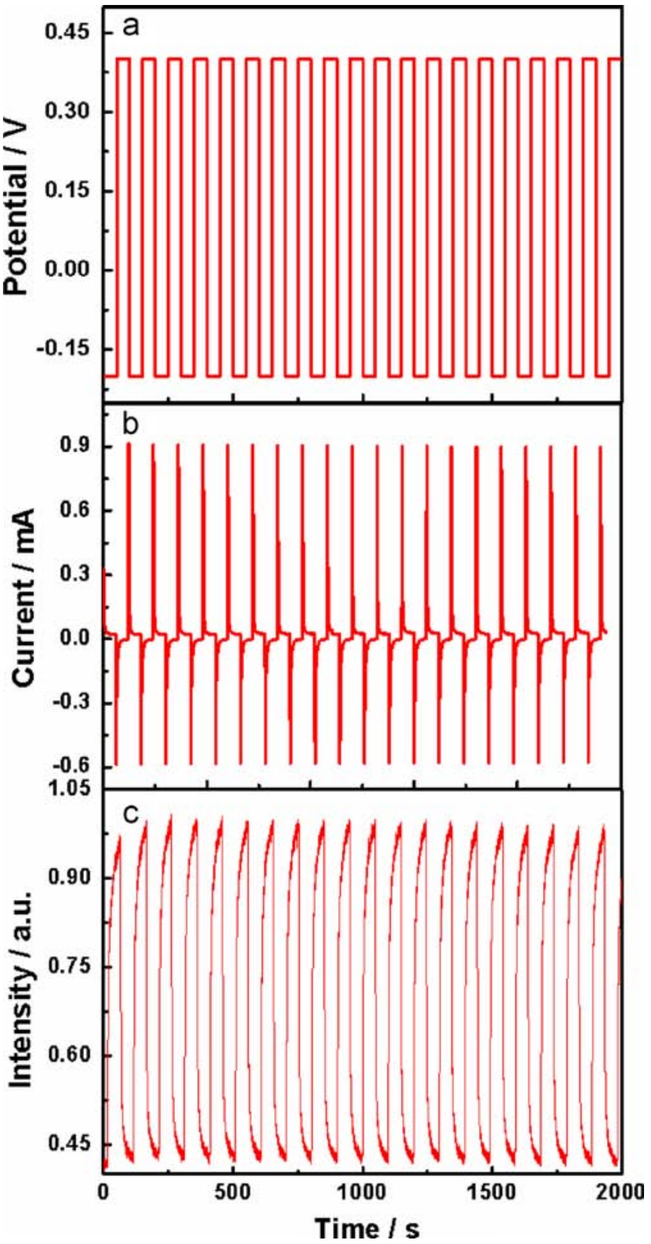


Fig. 5. (a) Potential, (b) current, and (c) fluorescence at 640 nm of the ITO/PMB/Au25 electrode during subsequent double-potential steps between −0.2 V and 0.4 V. 50 s for each step.

parallel test, the fluorescence contrast can be as high as 76%, but drops to 68% after 20 cycles (Fig. S9). On the other hand, the emission spectra of the ITO/Au_{25} electrode at −0.2 and 0.4 V are recorded for comparison (Fig. S10). The emission spectra remain almost the same at different potentials.

Fig. 5 shows emission spectra of the ITO/PMB/Au_{25} electrode subjected to repeated cyclic electroconversion. A loss of ~0.3–2% PL is observed after the hybrid device is operated up to 20 switching cycles, indicating the electrochemical controlled device is reversible. As shown in Table S1, the reproducibility of our proposed method has been discussed in comparison with the reported methods.

Compared with the previous photoelectric devices, our proposed methodology presents several advantages, such as quick response, large fluorescence contrast under reduction and oxidation potentials, good reversibility, excellent long-time stability and low power consumption [18,19]. However, our hybrid device is a little more complicated than those photoswitches. On the other hand, the proposed methodology presents high fluorescence contrast within a quite narrow potential range (−0.2–0.4 V, 68%) compared to the electroswitches reported before (−0.9–0.4 V, 91% [10]; −0.9–0.9 V, 77% [20]; −1.8–1.8 V, 60% [21]; −2–2 V, 75% [22]).

4. Conclusions

In conclusion, we have demonstrated reversible modulation of gold nanoclusters PL using electrochromic elements attached to gold nanoclusters. The level of modulation efficiency may be adjusted by applying different potentials on PMB based on IFE or FRET. The hybrid device exhibits good reversibility and excellent stability, and no obvious degradation was observed in both “on” and “off” luminescence intensities after 20 switching cycles. We anticipate that electrochromically switched devices would provide important hints for the promising applications of metal clusters in the field of fluorescent imaging, sensors, photoelectric devices, security document and nonvolatile memory system. Development of devices integrated on-chip for application in security document is now in progress. In addition, the current protocol for the hybrid film fabrication can be easily extended from PMB and clusters to other novel stimulus-responsive matched nanostructures in future.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.05.044.

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