Electronic Supplementary Information

In Situ Reversible Color Variation of a Ready-Made Upconversion Material with the Designed Component on a Three-State Fluorescence Switching System

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Experimental

1. Materials.

 Y_2O_3 , Yb_2O_3 , Er_2O_3 , and $TmCl_3 \cdot 6H_2O$ were bought from Aladdin. NaF, KCl, HCl, $K_3[Fe(CN)_6]$, FeCl₃, NaOH and dehydrated trisodium citrate were bought from Tianjing Reagent Company (Tianjing, China). All chemicals were of analytical grade, and all the water used during the experiments was ultrapure water (>18 M Ω). Phosphate buffer solution (PBS) consisting of 0.1 M K_2 HPO₄ and 0.1 M KH₂PO₄ (pH 6.0) acted as the electrolyte throughout the experiments.

2. Instrumentation.

All the electrochemical experiments were operated on a CHI832C electrochemical workstation (Shanghai Chenhua Instrument Corporation, China). Fluorescence luminescence measurements were carried out on a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon Inc., France); the emission slit width was 2.5 nm and a 980-nm laser served as the excitation light source (Hi-Tech Optoelectronics Co. Ltd.). The TEM images were gained with a TECNAI G2 high-resolution TEM with the potential of 200 kV. Absorption measurements were operated on a Cary 500 UV-vis-NIR spectrometer (Varian). The SEM images were conducted with a Philips XL-30 ESEM. Spectroelectrochemical measurements were carried out on the modified fluorescence cell according to the previous reports (1 cm-length quartz cell).^{1, 2} Platinum wire, ITO electrode, and Ag/AgCl (saturated KCl) acted as the counter electrode, the working electrode, and the reference electrode, respectively. The ITO chips (geometric area: ~ 1 cm * 5 cm) with surface resistance of 30-60 Ω /cm² were brought from Nanbo Display Technology Co., Ltd. (Shenzhen, China).

3. Synthesis of monodispersed β -NaYF₄:Er³⁺, Yb³⁺, Tm³⁺, hexagonal crystals.

The multicolor NaYF4:Er3+, Yb3+, Tm3+ hexagonal UC materials were prepared by a mild hydrothermal method according to a previous literature with some modifications [67]. In order to obtain multicolor UC materials, we slightly changed the doping proportion of the rare earth elements. 5 mL Yb(NO₃)₃, Y(NO₃)₃, TmCl₃ and Er(NO₃)₃ aqueous solution (the total lanthanide ion molar was 1 mmol, and the molar ratio of Y/Yb/Er/Tm was kept at 79.5/18/2/0.5) was added into 10 mL sodium citrate (3.0 g) aqueous solution and stirred for 2 h to obtain a homogeneous solution. Then, 0.52 g NaF in 20 mL water was added with magnetic stirring for 2 h. The lanthanide/sodium citrate/NaF molar ratio was kept at 1/10/12. Subsequently, by adding sufficient HNO3, the pH of the solution was adjusted to 3. After that, the solution was treated with ultrasound for 10 min and transferred into two 50 mL autoclaves. The autoclaves were treated for 3 h under 180 °C. Finally, the autoclaves were cooled to room temperature and the obtained solution was separated by centrifugation. After washed with deionized water and ethanol for several times to remove the excess reactant, the white precipitates were dried for 12 h at 80 °C. For multicolor UC materials, just repeated the above synthetic procedures while kept the doping proportions as the following ones: Y/Yb/Er/Tm=80/18/2/0; 79.5/18/2/0.5; 78.5/18/2/1.5; 77.5/18/2/2.5; 75/18/2/5; 81.5/18/0/0.5 (mole ratio) respectively.

4. Preparation of the ECFS.

Before modification, the ITO chips were washed several times with acetone, ethanol, and water under an ultrasonic bath for 20 minutes sequentially. Subsequently, in order to get the activated electrodes, the chips were immersed in a solution consisting of 1:1 (v/v) ethanol/NaOH (1 M) for 15 min. Then, the ITO chips were washed with pure water for several times and dried under N2 flow. Afterwards, the ITO electrodes were electrodeposited with PB by a freshly prepared solution containing 0.1 M HCl, 0.1 M KCl, 2.5 mM FeCl₃, and 2.5 mM K₃[Fe(CN)₆] under a controlled potential of 0.4 V for 100 s. Then, the ITO chips were washed with pure water for several times and dried under N₂ flow. After that, the chosen UC materials were dripped on the ITO electrodes with the infrared lamp as the dry source. The UC layer was repeated for another two times. A layer of Nafion protective solution was integrated afterwards. The above cycle was repeated for 6 times. Lastly, we obtained the integrated LLDEA-ECFS system. Note that to guarantee the successful assembly of the LLDEA-ECFS, one should make sure each step of assembly smooth and stable.



Figure S1 The photos of different doped proportions UC materials under 980-nm diode laser. From left to right, the corresponding doped proportions are Y/Yb/Er/Tm=80/18/2/0; Y/Yb/Er/Tm=79.5/18/2/0.5; Y/Yb/Er/Tm=78.5/18/2/1.5; Y/Yb/Er/Tm=77.5/18/2/2.5; Y/Yb/Er/Tm=81.5/18/0/0.5 (mole ratio) respectively.



Figure S2 The proposed energy-transfer mechanisms of the UC materials under 980-nm diode laser.



Figure S3 The TEM images of the UC materials. From a to f, the doping proportions are Y/Yb/Er/Tm=80/18/2/0; Y/Yb/Er/Tm=79.5/18/2/0.5; Y/Yb/Er/Tm=78.5/18/2/1.5; Y/Yb/Er/Tm=77.5/18/2/2.5; Y/Yb/Er/Tm=81.5/18/0/0.5; Y/Yb/Er/Tm=75/18/2/5 (mole ratio) respectively. (g) From top to bottom, the corresponding XRD patterns for the above UC materials. The last one is the XRD standard card for the hexagonal NaYF₄ crystal.

The UC materials have an average diameter of 400 nm with the length of 2 μ M from the TEM data. Considering the TEM and XRD data simultaneously, the multicolor UC materials shared the same structure as the hexagonal NaYF₄ host crystal, which is in agreement with our design. Although those UC materials were not so uniform with some cubic phase still existed, the proposed UC materials synthesized in aqueous phase are just enough for the ECFS. Generally, the UC materials synthesized in oil phase would be more homogeneous than in aqueous phase. However, synthesis in oil phase needs high temperature heating (> 300 °C), resulting in expensive instrument and high risk of the experiments. Here, a hydrothermal method with milder experimental conditions was selected. The synthesis process was much safer. More importantly, the synthesized UC materials had a good hydrophilicity and conductivity, and could be modified easily. Those merits made the present UC materials conform to the requirement of the proposed system.



Figure S4 The SEM (a), HRTEM (b) and SAED (c) images of the UC materials (Y/Yb/Er/Tm=75/18/2/5).

As all the UC materials shared the same crystal structure, we chose one of the UC materials (Y/Yb/Er/Tm=75/18/2/5) for the following HRTEM, SAED and SEM characterization. The HRTEM showed the lattice distance was around 0.29 nm, which was matched well with the d(110) of the β -NaYF₄.



Figure S5 SEM image and the corresponding elemental mapping images of the UC materials (Y/Yb/Er/Tm=79.5/18/2/0.5).

The percentage of Tm and Er in reactants were very small (~2%), then it will be even smaller in the products. Such a tiny amount of Tm and Er could not be distinguished from elemental mapping. So we only chose one of the UC materials (Y/Yb/Er/Tm=79.5/18/2/0.5) for the elemental mapping. The element distributions of the UC material were analyzed by SEM elemental mapping. F, Na, Y, Yb elements were uniformly distributed throughout the UC material, except that Er and Tm elements were too few to distinguish.



Figure S6 SEM-EDS spectra and the corresponding element content of the as prepared UC materials (Y/Yb/Er/Tm=79.5/18/2/0.5).

EDS showed the percentage of Er and Tm were 0.22% and 0.15%, which was in accordance with the former assumption (much less than 2%). F/Na atomic ratio was about 4.16 (69.11/16.61). This was similar to the 4 of NaYF₄, which also proofed that the UC material possessed a NaYF₄ host crystals.



Figure S7 The photos of the LLDEA-ECFS during the step by step assembly process.



Figure S8 The i-t curve obtained during PB formation.



Figure S9 (a) Potential, (b) current and (c) fluorescence at 475 nm of the ITO/UC materials electrode (without PB) under different applied potentials. At the time of 140 s, the potential began to be applied on the electrode. Twenty seconds for each step. P_0 stood for the fluorescence intensity before the potential was applied.



Figure S10 Absorption spectra of the LLDEA-ECFS under alternating applied potential with -0.4 V (bottom lines) and 0.4 V (top lines).



Figure S11 The absorbance variation of PB under different applied potentials.

References

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- 2. Y. Zhai, H. Zhang, L. Zhang and S. J. Dong, *Nanoscale*, 2016, **8 (18)**, 9493-9497.