

Supporting Information

CdS modified TiO₂ film showing multicolor switching and enhanced optical contrast

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1. XRD pattern of pure CdS film

Fig. S1 shows the XRD pattern of pure CdS film. It can be seen three peaks located

at 26.71° , 43.91° and 52.19° that are corresponding to the crystallographic planes of (111), (220) and (311) of cubic CdS (JCPDS NO. 80-0019), respectively.

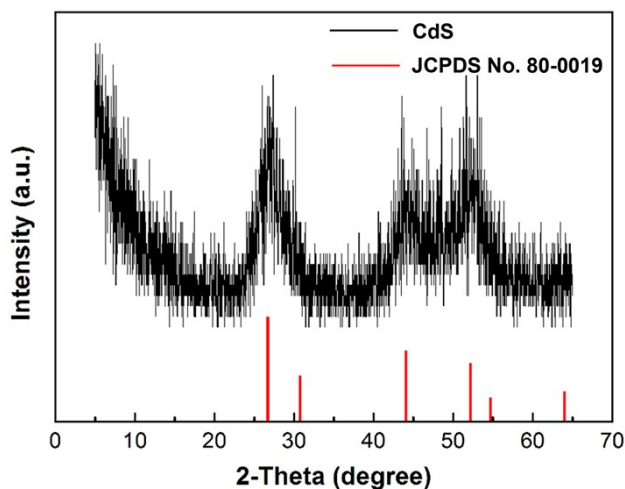


Fig. S1. XRD pattern of pure CdS film

2. SEM and TEM graphs of pure CdS film

The surface morphology of pure CdS film was also investigated by using SEM graphs, as shown in Fig. S2. It can be seen CdS film is composed of stacked nanoparticles. But these CdS particles tend to be aggregated, resulting in a denser surface than that of CdS quantum dot grown on TiO_2 nanoparticles. For further investigation, FETEM graphs were also collected, as shown in Fig. S2b. It can be seen that CdS nanoparticles for depositing pure CdS film show poor mono-disperse property. The size of CdS particles is about 4 nm, demonstrating its quantum dot structure. The measured lattice space of 0.33 nm shown in Fig. 2Sb can be assigned to the (111) plane of CdS (JCPDS No.80-0019, cubic).

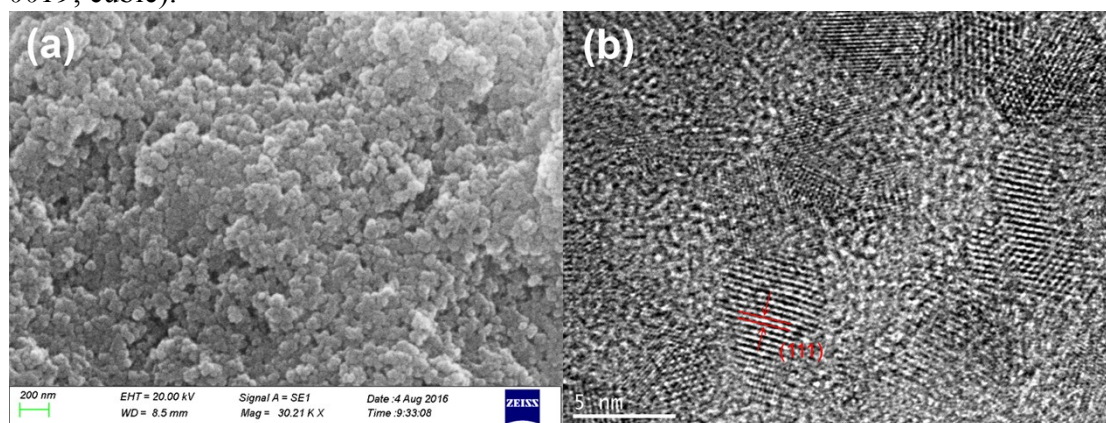


Fig. S2. (a) SEM image of pure CdS film and (b) FETEM image of CdS quantum dots showing detailed crystal lattice fringes.

3. Electrochemical impedance spectra of pure CdS. Fig. S3 shows the Nyquist plots of pure CdS film. The high frequency semicircle corresponds to the charge-transfer impedance on electrode/electrolyte interface, and the inclined line in low frequency

region is assigned to the ion diffusion process within electrodes.¹ By fitting to the equivalent circuit, the pure CdS shows much higher electrochemical resistance of 2936 Ω (R_{ct}), comparing to that of TiO_2/CdS film. It proves that the porous TiO_2 substrate significantly reduces the charge-transfer impedance on CdS electrode/electrolyte interface, which improves the insertion/extraction of Li^+ in/out CdS lattice.

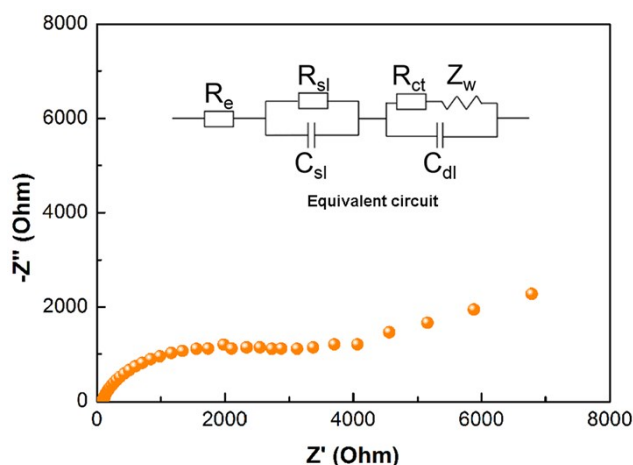


Fig. S3. Electrochemical impedance spectra of CdS film in 1 M $\text{LiClO}_4\text{-PC}$ with corresponding equivalent circuit.

4. Absorption spectra of electrodes. Typical absorption spectra of TiO_2 particles before and after modified with CdS quantum dots are shown in Fig. S4. The color change of TiO_2 film from colorless to yellow demonstrates the successive deposition of CdS on TiO_2 particles. After modifying the TiO_2 film with CdS quantum dots, the absorption edge onset moves from ultraviolet region to visible region, showing a yellow color.

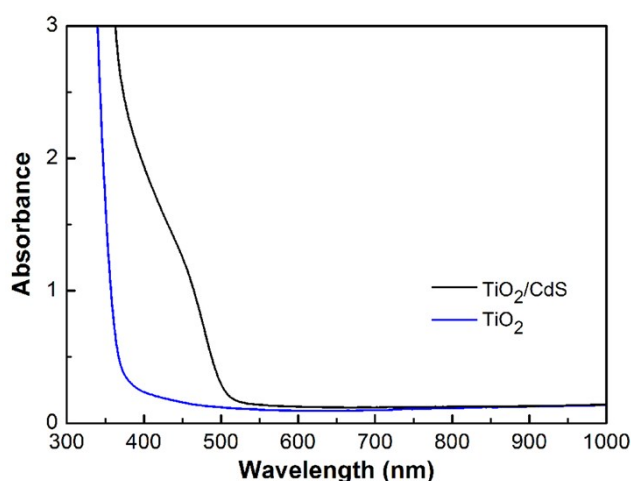


Fig. S4. Absorbance spectra of TiO_2 and TiO_2/CdS films as a function of wavelength from 300 nm to 1000 nm.

5. Transmittance spectra of pure CdS. Pure CdS film were colored at -2 V for 20 s and discolored at 1 V for 20 s. Fig. S5a shows that CdS film changes from yellow to black under -2 V with a transmittance about 15% in the whole visible region. After

discolored at 1 V for 20s, the optical transmittance of CdS does not change obviously. In Fig. S5b, photos of colored CdS, discolored CdS by external potentials and discolored CdS by oxygen are all shown in Fig. S3b. It can be seen that pure CdS is failed to recover to its original state by being applied with an external potentials.

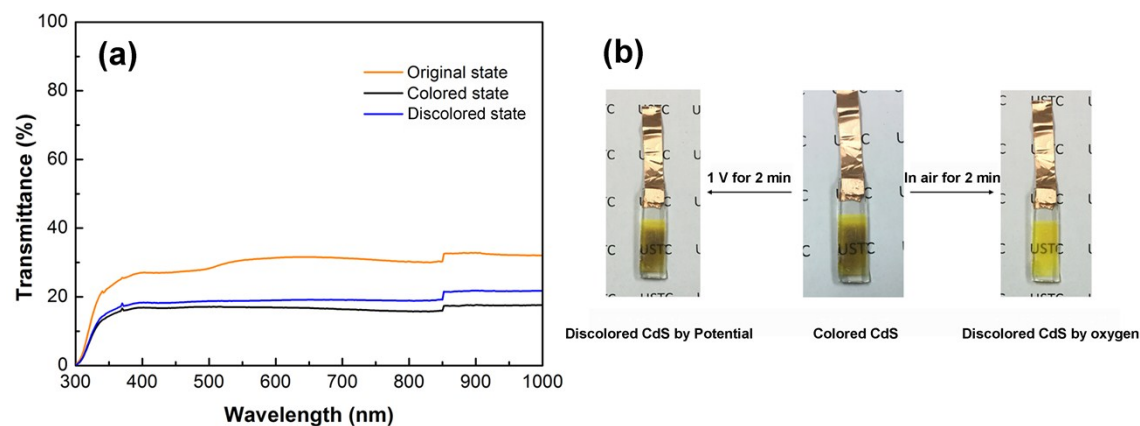


Fig. S5. (a) Transmittance spectra of pure CdS film in original state, colored state and discolored state. (b) Direct graphs of CdS in colored state and discolored state.

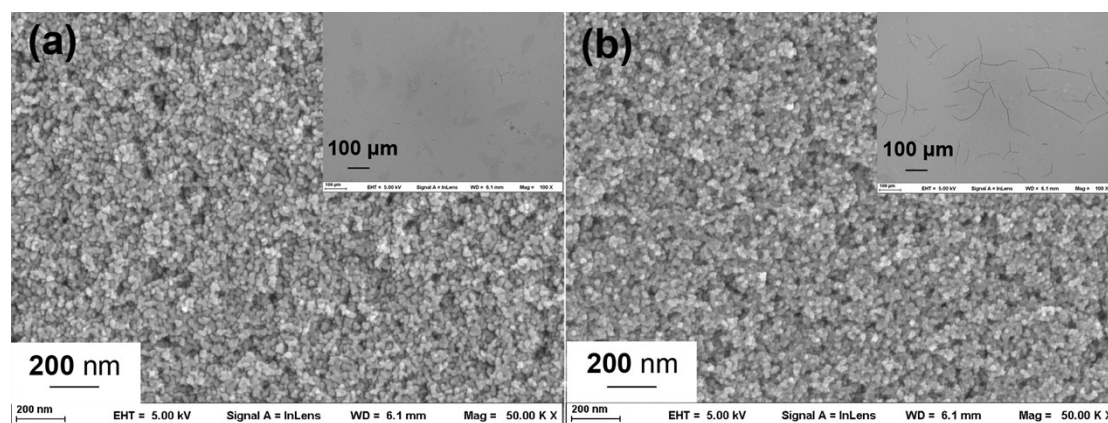


Fig. S6. SEM graphs of (a) TiO_2 and (b) TiO_2/CdS films after running for 200 CV cycles. Graphs in low magnification are inserted.

6. SEM graphs of electrodes after running for 200 cycles. The morphologies of TiO_2 and TiO_2/CdS films after running 200 cyclic voltammetry cycles in 1 M PC- LiClO_4 were collected by using SEM, as shown in Fig.S6. It can be seen that TiO_2 film after running for 200 cycles shows negligible difference in morphology when compared with that of as-prepared TiO_2 film, which indicates a good cycle life. However, TiO_2/CdS film after running 200 cycles shows more regular grain boundaries when compared with that of as-prepared TiO_2/CdS film and thus may arise from the desorption of CdS quantum dots. Especially, the desorption of CdS quantum dots and the appearance of cracks could be ascribed to the volume change during the Li ions intercalation/de-intercalation process.

Reference

1. G. Cai, J. Tu, D. Zhou, J. Zhang, Q. Xiong, X. Zhao, X. Wang and C. Gu, *J. Phys. Chem. C*, 2013, **117**, 15967-15975.