

Supporting Information

Enhancing photoelectrochemical activity of CdS quantum dots sensitized WO₃ photoelectrodes by Mn-doped

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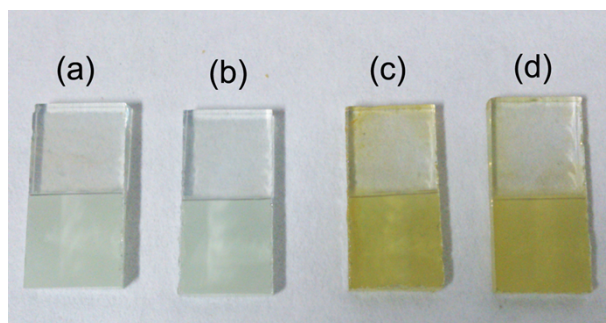


Fig. S1 Photographs of the film samples.

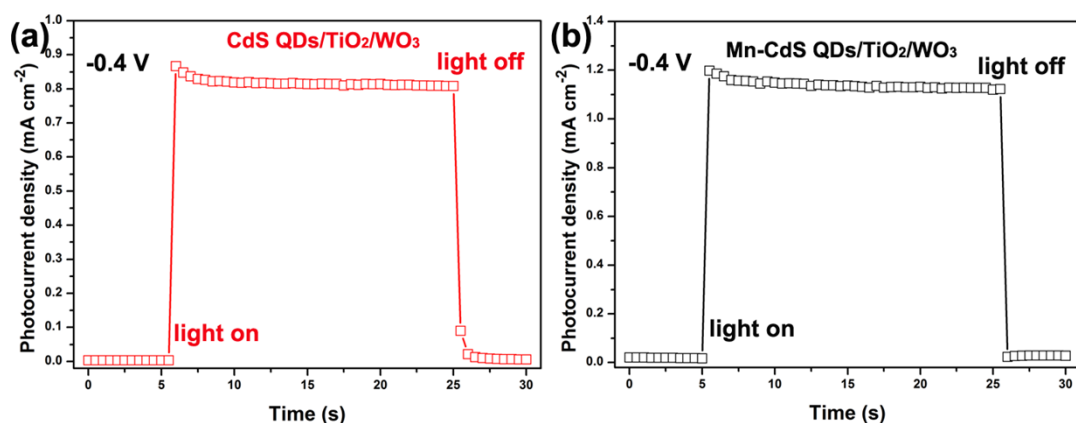


Fig. S2 Transient photocurrent spectra of the photoelectrodes at -0.4 V vs. Ag/AgCl.

Transient photocurrent of the prepared electrode was measured at constant voltage to evaluate the recombination lifetime of photogenerated carriers. The shape of the transient photocurrent response to the switching on and off of the visible light illumination, and the rise and decay times of the signal, depend on the photogeneration of charge carriers and the relaxation mechanism¹. Fig.7 shows the transient photocurrent curve of the undoped and doped electrode at the applied potential of -0.4 V vs. Ag/AgCl. A large photocurrent appears immediately after switching on the light, and the photocurrent gradually decays with the illumination time, which may be described in terms of the two competitive processes: generation of pairs electron-hole and their recombination^{1, 2}. The initial photocurrent spike (I_i) is caused by separation of photogenerated electron-hole pairs at the semiconductor/electrolyte interface: the electrons are move to the back contact (FTO), while holes are captured or trapped by reduced species in the electrolyte. Soon, a continuous decrease of the photocurrent with time is showed until a steady state photocurrent (I_f) is reached. The photocurrent decay means that recombination processes are occurring. Instead of capturing electrons from the electrolyte, the holes that reach the semiconductor surface may accumulate at the surface and recombine with photogenerated electrons. The process of recombination is commanded by the following kinetic equation:

$$D = \exp\left(-\frac{t}{\tau}\right), \quad (1)$$

Where D is defined as

$$D = \frac{I_i - I_f}{I_i - I_f}, \quad (2)$$

Where t denotes time, I is the current, and i and f are related to the initial and final steady states, respectively. The transient time constant, τ , can be defined as the time at $\ln D = -1$. The transient time may be treated as a lifetime of the photogenerated electron-hole pairs³. The determined average transient time constant in Mn-CdS QDs/TiO₂/WO₃ photoelectrodes are ca. 5.05 s at -0.4 V vs. Ag/AgCl, respectively. They are longer value than that in undoped CdS QDs/TiO₂/WO₃ photoelectrodes (2.41 s). This means that the addition of Mn²⁺ into a crystal lattice of CdS QDs prolongs the lifetime of the photogenerated electron-hole pairs and reduces the recombination processes.

Reference

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