Supporting information

Electrochemical synthesis of CdS/ZnO nanotube arrays with excellent photoelectrochemical properties

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Effect of CdS thickness over the photoelectrochemical properties

In this communication, we employed an electrochemical method to sensitize the ZnO nanotubes with CdS. Using this method, the thickness of the CdS sensitizer could be simply controlled by adjusting the time for CdS electrodeposition. Figure S1 show the SEM images of the CdS/ZNT samples with different CdS electrodeposition time varying from 150s to 600s. The photoelectrochemical properties of CdS/ZNT the samples with different CdS thickness were investigated. It was found that as the thickness increased, the photocurrents increased initially and then reached an maximum value of 10.64 mA/cm^2 (at 0 V vs SCE), corresponding to CdS electrodeposition time of 300s, which resulting a CdS thickness of 40(±15) nm. It is easy to understand the initial increase of the photocurrent is because of the enhanced light absorption, caused by the increasing amount of the CdS sensitizer. However, further prolonging the CdS electrodeposition time to 450s and 600s caused a decay of the photocurrent to 10.40 mA/cm^2 and 9.62 mA/cm^2 respectively.

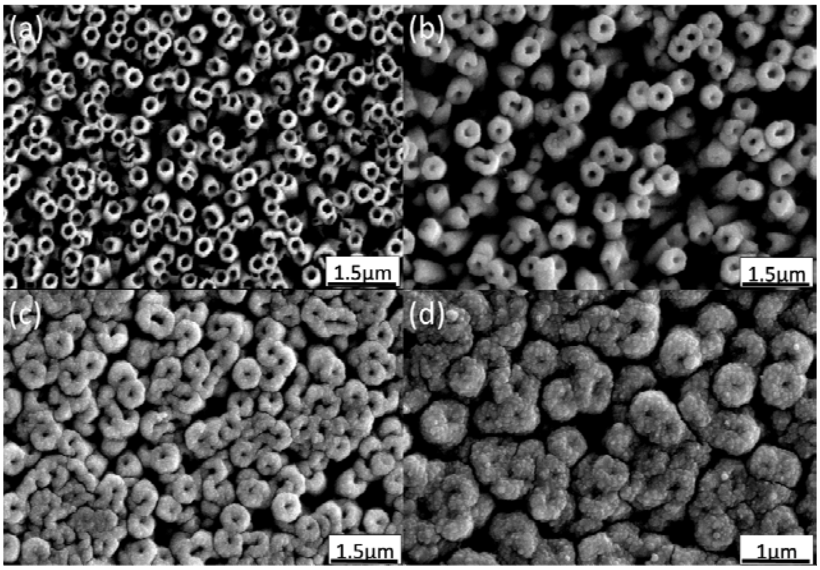

Fig. S1 The SEM images of CdS/ZNT samples with different CdS electrodeposition time: (a) 150s, (b) 300s, (c) 450s, (d) 600s.

It is believed the decay of the photocurrent was because of the increased recombination of the charge carriers caused by the increased collection length. For a semiconductor photoelectrode, there are two critical factors (but not limited to) influencing its photoelectrochemical performance, the absorption of the incident photons and the collection of the photoinduced charge carriers. In the space charge layer of the semiconductor at the interface of the semiconductor/electrolyte, the built-in field would help to separate and transfer the photoinduced charge carriers. In the field-free region, it is the diffusion accounting for the transportation of the charge carriers. Theoretically, for a collection length longer than $L_p + L_{sc}$ (where the L_p is the diffusion length of the minority carrier and the L_{sc} is the thickness of the space charge layer), there would be large recombination loss of the photoinduced charge carriers during the collection. In practice, the optimized collection length (or the “thickness”) is largely influenced by the material properties. An increased thickness of the sensitizer would undoubtedly enhance the absorption ability of the photoelectrode. However, the collection length for the photoinduced charge carriers would be simultaneously longer, which is harmful to the performance of the photoelectrode. For our CdS/ZNT photoelectrode, it was finally found the optimized time to electrodeposit the CdS is 5min, resulting a CdS thickness of 40(±15) nm.

Stability test

A demerit of metal sulfide photocatalysts is the stability against photocorrosion. CdS is an excellent photocatalyst for H_2 evolution under visible light irradiation if a hole scavenger exists, otherwise, the photo-induced holes accumulated in the CdS/solution interface would oxidize the S^{2-} in the CdS, which is the so-called photocorrosion. The S^{2-} in the electrolyte (1M Na_2S) in our photoelectrochemical tests, is an commonly used sacrificial scavenger to reduce the photo-induced holes.

We have conducted the stability test for the CdS/ZNTs with a CdS electrodeposition time of 300s. The test was performed in a three electrode configuration with the CdS/ZNTs as the working electrode, and a Pt foil and a standard saturated calomel electrode (SCE) used as the counter electrode and the reference electrode, respectively. The sample was tested by monitoring the photocurrent evolution with time at a fixed potential (o v vs SCE), and the results was shown in figure S2. As can be seen in figure S2, little reduction of the photocurrent was observed within 300s. The SEM image of the CdS/ZNT after 30 min stability test is shown in figure S3. From the SEM image, no obvious changes in the morphology of the CdS/ZNTs were observed, indicating the photocorrosion of the CdS is not prominent.

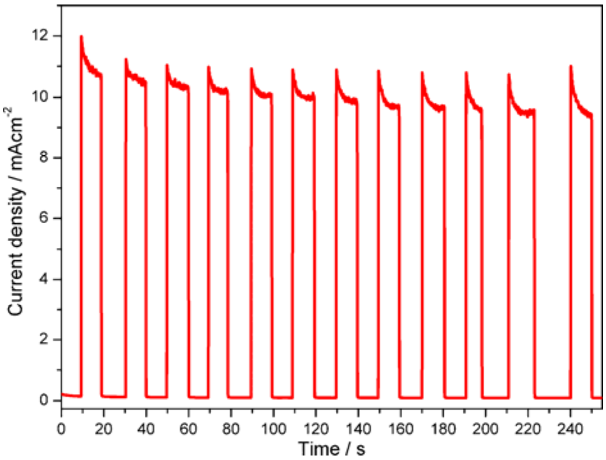

Figure S2 Stability test by performing photocurrent evolution with time at a fixed working electrode potential of 0 v vs SCE.

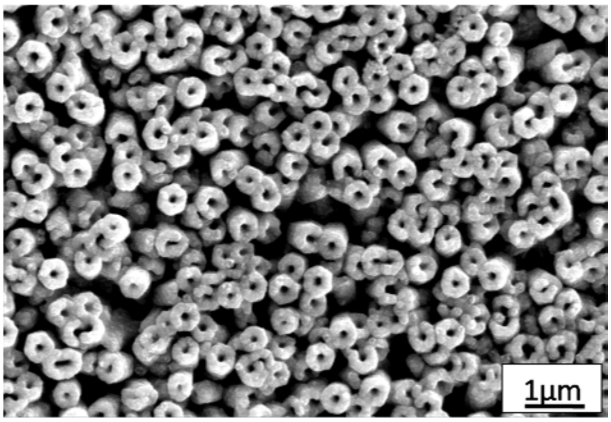

Figure S3 SEM image of the CdS/ZNT arrays after 30 min stability test at a fixed working electrode potential of 0 v vs SCE.