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Quantum Dots Sensitized ZnO Nanowires-array Photoelectrodes for Water Splitting

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Abstract

We demonstrated that QDs (eg. CdTe and InP) and ZnO nanowires fabricated photoelectrode could improve the conversion efficiency of water splitting reaction to 1.83%. For the concerning of the stability, the longtime measurement showed the photocurrent only slightly decreased after 50 cycles. We also decorated the ZnO nanowires with the gold nanoparticles for photoelectrochemical water splitting. The systematic measurement demonstrated that the coupled plasmonic induced effects could enhance the photoelectrochemical water splitting significantly.

1. Introduction

Over the past decade, owing to the increasing need for clean energy production, significant effort has been made to exploit the properties of materials for applications in photovoltaic and related solar-harvesting devices.[1] Hydrogen generated by splitting of the water is one of the most potential forms of energy production, solar-harvesting devices can be an important source of sustainable energy and essential to decrease the consumption of fossil fuels. Metal oxides such as TiO_2, ZnO, and WO_3 have been investigated for water splitting with various morphologies.[2] Nevertheless, most of the metal oxides have large bandgap, leading to limited light absorption in the visible region, which impose a fundamental limitation on overall efficiency. One of methods is the use of semiconductor nanocrystals, known as quantum dots (QDs). QDs provide the more matches the solar spectrum better due to their absorption spectrum can be tuned with particle size. Additionally, it has been recently shown that QDs can generate multiple electron-hole pairs per photon, which could enhance the efficiency of the device.[3]

In order to address this fundamental issue, we examine the combination of CdTe and InP QDs with ZnO nanowires for photoelectrochemical water splitting. Employment of CdTe QDs in water splitting system could be exactly measured the efficiency for water splitting reaction in aqueous system, which is never demonstrated in literature.

The water splitting reaction was measured with the gold nanoparticles modified ZnO nanowires. Recently, the plasmon induced effects, such as “hot” electrons injection and the induced electromagnetic field, were demonstrated could improve the photovoltaic and the photoelectrochemical water splitting reaction.[4] Systematically investigation were designed for distinguishing the effects of the plasmon induced effects.

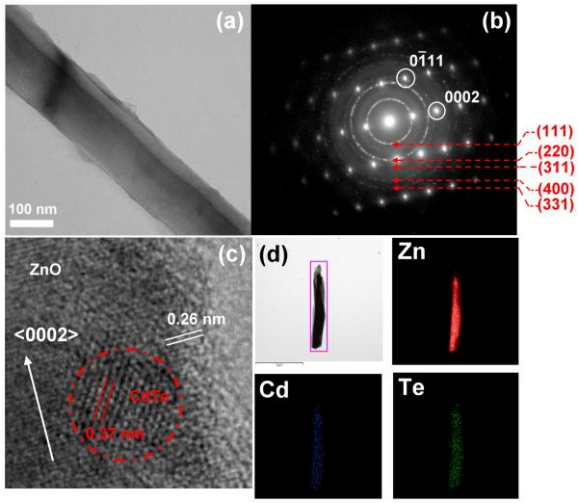
2. Results and Discussion

Transmission electron microscopy (TEM) image (Fig 1(a)) of ZnO nanowires decorated with an ensemble of CdTe QDs (24 hr) reveals that they are uniform in diameter (~150 nm). Most interestingly, the selected electron diffraction pattern (Fig 1(b)) is characteristic of the two component crystalline nature. The set of spot pattern can be indexed to the ZnO wurtzite structure along the $[2\bar{1}\bar{1}0]$ zone axis, which shows a single crystalline nature (white circle). The Set of rings reveal a typical face-centered-cubic polycrystalline structure corresponding to bulk CdTe, and probably associated with the large amount of CdTe QDs on the surface of the ZnO nanowires. These results indicate that QDs were successfully attached to the surface of ZnO nanowires. High-resolution TEM image of the edge of a nanowire (Fig 1(c)) provides more compelling evidence that QDs are attached to the nanowire surface. The lattice fringes with d-spacing of 0.26 nm match the interspacing of the (0002) planes of the wurtzite ZnO, which demonstrate that the ZnO nanowires grew along the [0002] direction. An abrupt transition is observed. The lattice spacing between the (111) planes, 0.37 nm, is also in agreement with that of the CdTe bulk crystal (JCPDS no. 89-3053). Fig 1(d) shows a TEM image of a CdTe/ZnO nanowires heterostructure and corresponding elemental mapping of Zn, Cd, and Te, respectively. It is noticed that Zn is uniformly distributed along the nanowires, while Cd and Te elements are found on the same spots corresponding to the position of nanoparticles.

To examine the photoresponse of this structure over time, I-t curve collected from the ZnO nanowires with loading of CdTe QDs (24 hr) at +0.5 V is shown in Fig 2(a). These results further confirm that photogenerated electrons quickly transport from CdTe QDs to ZnO nanowires. In the long term, the chemical stability issue of this structure could be addressed by depositing a monolayer on the ZnO nanowires. Fig 2(b) demonstrated that the photocurrent response was almost identical over 50 cycles, demonstrating the stability of this structure and used as photoanodes were relatively stable in the photo-oxidation process in aqueous solution. The achieved high efficiency and stability may be attributed to major improvement. Monolayer deposition of CdTe QDs allow a fast and efficient transfer

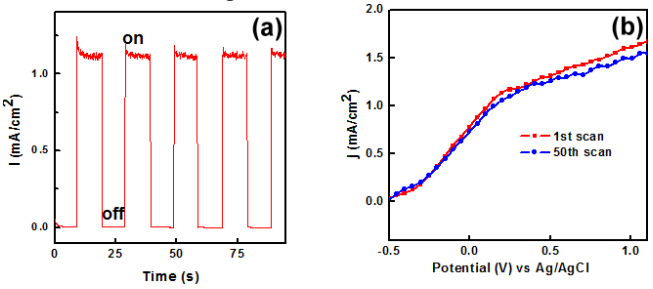
of the photogenerated electrons from CdTe to the ZnO nanowires, which lead to a much reduced the anodic decomposition/corrosion and much improved the stability of photodevices.

Fig 1. (a) TEM micrograph of a ZnO nanowires decorated



with CdTe QDs. (b) Corresponding electron diffraction pattern of (a). (c) HR-TEM micrograph of a ZnO nanowire decorated with CdTe QDs. (d) Elemental mapping images of the Zn, Cd, and Te, respectively.[5]

Fig 2. (a) Amperometric I-t curves of the ZnO nanowires with/without loading of CdTe QDs at 100 mW/cm^2 with



on/off cycles. (b) Stability of PEC performance after 50 scans.[5]

The gold nanoparitlces modified ZnO nanowires photoelectrodes were measured the photoelectrochemical water splitting in the same condition as the CdTe decorated ZnO nanowires photoelectrode. The TEM image of the photoelectrode were shown in the Fig. 3(a). The photocurrents of the gold modified ZnO nanowires show the enhancement than the pristine ZnO photoelectrode, as shown in Fig. 3(b). The X-ray absorption spectroscopy of the gold nanoparitcles modified ZnO were measured for the investigation of the vacancies in the conduction band of the ZnO nanowires, demonstrating that the plasmon induced electromagnetic field would collect the vacancies, which will enhance the probability of the electrons excitation and thus enhanced the water splitting reaction. The "hot" electrons measurement was carried with the photoelectrode illuminated under 530 nm light (surface plasma peak of the gold nanoparticles), as shown in Fig. 3(d). The stable and quick response of the photocurrent was investigated, indicating that the gold nanoparticles could inject electrons to the conduction band of the ZnO nanowires to generate the photocurrent.

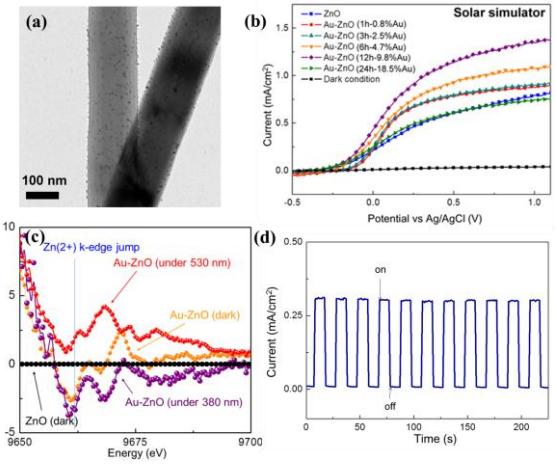


Fig. 3 (a) TEM image of the gold nanoparticles modified ZnO nanowires. (b) I-V curves of the ZnO nanowires with/without loading of gold nanoparticles at 100 mW/cm^2. (c) XAS measurement and (d) I-t curves of the ZnO nanowires with/without loading of gold nanoparticles at 530 nm monochromatic light.[6]

3. Conclusions

We demonstrated the QDs and gold nanoparticles could enhance the photoelectrochemical water splitting. The QDs could absorb the visible light and generated photocurrent and thus enhance the water splitting reaction. The gold nanoparticles coupled the surface plasma resonance induced effects, explaining why the coupling of hot electrons that were formed by plasmons with the electromagnetic field effectively increases the probability of the photochemical reaction in the splitting of water.

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