Plasmon-enhanced near-infrared-active materials in photoelectrochemical water splitting†

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We report the near-infrared-driven photoelectrochemical water splitting using a ZnO nanorod-array decorated with CdTe quantum dots and plasmon-enhanced upconversion nanoparticles. The plasmon enhanced the intensity of the upconversion emission, which improved the photocurrent and the gas evolution rate of the photoelectrochemical reaction greatly.

Hydrogen has been hailed as the clean energy form of the future because of its reaction with oxygen without producing pollutants and greenhouse gases, only water. Photoelectrochemical (PEC) and photocatalytic water splitting, which directly convert solar energy into hydrogen and oxygen, have become two of the most promising methods in renewable energy research since Fujishima and Honda’s first demonstration in 1972.1 The use of metal oxide electrode materials, such as TiO2, ZnO, Fe2O3, and WO3, in water splitting has been progressing because of their unique nanostructure-derived properties and effectiveness.2–7 However, some of the semiconductors have large band gaps (>3 eV, except Fe2O3 and WO3), which limits the absorption of visible light and thus the improvement of solar energy conversion efficiency.6 Numerous methods, such as doping heteratoms2 and the use of photosensitive dyes9 or quantum dots (QDs),10,11 have been adopted to harvest visible light. Currently, sensitizers do not use near-infrared (NIR) and infrared (IR) light active materials because the NIR and IR active sensitizers commonly absorb sub-band gap energy, which indicates that irradiation with energy below 1.8 eV (~688 nm) cannot provide sufficient energy potential to excite electron–hole pairs with enough energy to drive the overall water splitting reaction.4 Using upconversion nanoparticles (UCNs) is an alternative method of converting NIR and IR into usable energy and improving the overall energy conversion efficiency. UCNs have attracted significant attention in biological imaging, data storage, and solar energy conversion.7,12 Previously, gold nanoparticle (Au NP)-modified UCNs have been found to enhance the upconversion emission through plasmonic modulation.13,14 Few reports have suggested the use of UCNs to convert NIR light to visible light in solar cells, PEC, or photoelectrochemical applications.15

In the present work, we constructed a PEC cell that could up-convert the NIR light into visible light and further generate chemical fuels through light-driven water splitting. For this purpose, we attempted to embed UCNs, Er3+/Yb3+ co-doped NaYF4, in the CdTe QD-sensitized ZnO nanorod array to compose a NIR-driven PEC cell (Fig. 1a). UCNs were employed to harvest and convert NIR light to high-energy photons. The high-energy photons excited the CdTe QDs to generate high-energy electron–hole pairs. These excited electrons transferred to the conduction band (CB) of ZnO nanorods, and then conducted to the Pt foil through the external circuit and reacted with water to generate hydrogen, thereby producing the photocurrent. The photogenerated holes oxidized water to produce oxygen (Fig. 1b). When appropriate amounts of Au NPs were modified on the UCN surface, the induced surface plasma resonance (SPR) enhanced the intensity of upconversion emission, which improved the photocurrent and the gas evolution rate of the photoelectrochemical reaction.

In a typical procedure, the ZnO nanorod-array was grown on fluorine-doped tin oxide (F–SnO2) substrates via a modified...
hydrothermal reaction (experiment details are provided in the ESI†). The one-dimensional ZnO nanorods facilitated the charge transportation to reduce the possibility of recombination. The synthesized ZnO nanorods were about 5 μm in length and about 150 nm in diameter with a high surface density, as shown in Fig. S1 (ESI†). The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images of the ZnO nanorods decorated with CdTe QDs (Fig. 2a and b) provide evidence that QDs are directly attached to the ZnO nanorod surface. An abrupt transition was found between the (0002) lattice planes of the ZnO nanorod and the (311) lattice planes of the CdTe QDs. The lattice spacing between the (311) planes is 0.20 nm, which is also in agreement with that of the CdTe bulk crystal (JCPDS No. 89-3053). The structural properties of the ZnO were examined by X-ray diffraction (XRD) pattern studies as shown in Fig. S2a (ESI†).

In the present study UCNs (Er<sup>3+</sup>/Yb<sup>3+</sup> co-doped NaYF<sub>4</sub>) were synthesized via a facile wet chemical technology (ESI†). The water soluble UCNs were modified with the desired weight percent (0.2, 0.4, 1 and 2 wt%) of Au NPs, in which the controlled UCN concentration was 10 mg mL<sup>−1</sup>. The UCNs typically have a cubic structure with a uniform size of approximately 30 nm to 35 nm (Fig. S3, ESI†). The (111) lattice planes of UCNs are clearly illustrated in the HRTEM image. The (111) lattice planes of CdTe QDs. The lattice spacing between the (111) planes is 0.20 nm, which is also in agreement with that of the CdTe bulk crystal (JCPDS No. 89-3053). The structural properties of the ZnO were examined by X-ray diffraction (XRD) pattern studies as shown in Fig. S2a (ESI†).

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The electron transfer between the Au NPs and UCNs decreased the electron transfer between the Au NPs and UCNs.16 The electron transfer between the Au NPs and UCNs decreased the electron density on the Au NPs, thereby broadening the SPR peak.17 To absorb the high-energy photons and generate electron–hole pairs for the PEC reaction, the overlap of the upconversion emission peak of UCNs and the excitation peak of the CdTe QDs is essential. The first excitonic peak of the CdTe QDs was at 690 nm (Fig. 3b), which could overlap the emission spectra of the UCNs (Fig. 3c). Thus, the upconversion emission could be absorbed by the CdTe QDs and generated the high-energy electron–hole pairs. The upconversion emission intensity of the Au-x-UCNs was enhanced most significantly in the case of x=1.0 wt%. The enhancement of the emission intensity at 650 nm and 530 nm was more than threefold and double that of the pure UCNs, respectively. The electric field generated by plasmonic resonance might cause local field enhancement or surface plasmon-coupled emission (SPCE) to enhance the upconversion emission intensity.13,18 The SPCE could enhance the emission rate at 530 nm, which overlapped with the SPR peak, hence, enhancing the upconversion emission, even absorbed by the Au NPs. The enhancement of the upconversion emission at 650 nm is attributed to the local field enhancement. The plasmonic field influenced the local electric field of the UCNs, which consequently generated more electrons in the upconversion progress and thus enhanced the emission intensity. By contrast, the emission spectra intensity decreased when the weight percentage of Au NPs increased to 2.0 wt%, which revealed that the NIR light was scattered by the Au NPs and thus quenched the upconversion emission. Owing to the emission at 530 nm being absorbed by the Au NPs, the enhancement of the upconversion emission intensity at 650 nm was greater than that at 530 nm of the Au-UCNs. To discuss further about the plasmon enhanced upconversion emission, the quantum yields of the Au-x-UCNs suspended in water (x = 0, 0.2, 0.4, 1.0 and 2.0 wt%) were calculated and are listed in Table S1 (ESI†).19 The quantum yield of the Au-1.0 wt%-UCNs (0.40%) was enhanced by plasmon more than twofold compared to the pure UCNs (0.15%).
To prevent the electron transfer between the Au, ZnO and CdTe QD interface, the prepared Au-UCNs were deposited on the ZnO nanorod surface after coating with a thin layer of ZnS as shown in Fig. S5 (ESI†). After coating with ZnS, the Au-UCN surface was investigated with an amorphous ZnS layer. The TEM image (Fig. 2g) shows that the Au-1.0%-UCNs–CdTe–ZnO structure provides more compelling evidence that the Au-UCNs have attached onto the ZnO nanorod surface as expected. As a proof of concept, we performed a set of linear-sweep voltammetry measurements (Fig. 4a) for the PEC, which was composed of an Au-UCNs–CdTe–ZnO nanocomposite as the photoanode, a platinum plate as the counter electrode, and Ag/AgCl as the reference electrode under 980 nm laser illumination with a power density of 50 mW cm$^{-2}$ (experiment details are provided in the ESI†). The generated photocurrent demonstrated that via the up-conversion process the UCNs converting the 980 nm light to the visible light were absorbed by the CdTe QDs to excite electron–hole pairs to drive the photoelectrochemical reaction. For the other sets, the photocurrent intensity of the Au-UCNs increased as the Au NP weight percentage increased to the appropriate Au NP concentration (1.0 wt%) but it decreased at high Au NP concentrations, a trend similar to that observed for the upconversion emission spectrum. The quenching of the upconversion emission under high Au NP concentration caused the lower photo-response. The UCNs–ZnO, Au-UCNs–ZnO and Au–CdTe–ZnO photoelectrode showed negligible photocurrent intensity (Fig. S6, ESI†), confirming that the enhancement of the photocurrent was from the NIR up-conversion mechanism, neither from the plasmonic effect of the Au nanoparticle nor the CdTe QDs modification. The photocurrent density of the Au-1.0%-UCNs–CdTe–ZnO photoelectrode can reach up to 0.036 mA cm$^{-2}$ at 1.0 V. Fig. S6 (ESI†) shows plots of the photocurrent that was generated by the Au-1.0%-UCNs–CdTe–ZnO photoelectrode. This result verifies the rapid transportation of the electrons and the stability of the photoelectrode. The enhancement ratio is almost 40-fold of the pristine ZnO nanorod photoelectrode, and threefold greater than the UCNs–CdTe–ZnO photoelectrode. To demonstrate the water splitting the reaction was conducted under NIR illumination, and the gas evolution (Fig. 4b) of the PEC was measured with 0.5 V bias under 980 nm laser illumination with a power density of 100 mW cm$^{-2}$. The Au-1.0%-UCNs–CdTe–ZnO and UCNs–CdTe–ZnO photoelectrodes show that about 0.18 and 0.045 μmol h$^{-1}$ of H$_2$ were produced (0.08 and 0.017 μmol h$^{-1}$ of O$_2$), indicating that water had been split under NIR illumination. The slight decrease in the oxygen evolution after two hours of measurement might contribute to the lower faradaic efficiency. We estimated the highest overall conversion efficiency from the NIR to chemical fuel to be around 0.006%.

These findings show that the Au NP-modified UCNPs can enhance the upconversion emission intensity, thereby increasing NIR light conversion into high-energy photons, which are then absorbed by the CdTe QDs to generate sufficient potential electron–hole pairs to drive the photoelectrochemical water splitting.

The band positions of the samples were determined by the electrochemical methods as shown in Fig. S7 (ESI†). In summary, we have demonstrated a process of utilizing NIR to drive the photoelectrochemical water splitting reaction. The Au-UCNs can significantly enhance the upconversion emission intensity by a plasmonic effect. Thus, the enhancement of photocurrent and gas evolution was achieved. The results offer a convincing demonstration that energy can be converted from NIR to chemical fuel. We believe that our strategy is fundamental to the design of solar energy devices and should become an accepted technique for solar energy utilization in the NIR and IR regions.

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Notes and references