TiO_2 Branched Nanorods-Modified ZnO Nanorods Decorated with Au Nanoparticles for Plasmon-Enhanced Photoelectrochemical Water Splitting

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1. Introduction

Nowadays, with the rise of environmental awareness and energy crisis, sustainable energy has been widely studied. Photoelectrochemical (PEC) water splitting is one of the most environment friendly ways in which the process of converting solar energy into fuels only produces hydrogen and oxygen. Semiconductor metal oxides such as ZnO and TiO_2 have been generally explored for PEC water splitting because they possess high chemical stability, low cost, and proper band gap. In addition, the gold nanoparticles exhibiting distinctive localized surface plasmon resonance (LSPR) cause optical scattering and near-field enhancement to trap the incident light in the semiconductor and to improve the light absorption and effective optical path length [1].

In this study, we used atomic layer deposition (ALD) to grow ZnO and TiO_2 seed layer and then used hydrothermal synthesis method to obtain ZnO nanorods (NRs) arrays and anatase-TiO_2 branched nanorods (b-NRs) arrays. Finally, a layer of 5 nm-thick Au film was deposited by e-beam evaporator to form agglomerated Au nanoparticles on b-NRs TiO_2@ZnO to complete the Au-NPs@b-NRs TiO_2@ZnO system.

2. Results and discussion

The schematic diagram of the heterostructure Au-NPs@b-NRs TiO_2@ZnO is shown in Figure 1(a). We designed the uniform growth of anatase-TiO_2 b-NRs on ZnO NRs arrays, which was followed by depositing Au-NPs on both b-NRs TiO_2 and ZnO NRs surfaces. Furthermore, we proposed the electrons transfer mechanism between Au-NPs and b-NRs TiO_2@ZnO as shown in Figure 1(b). Based on the heterogeneous semiconductors assembly, the electrons can transport via the bending band at the interface of heterostructure [2]. Therefore, when photoanode is illuminated, the photogenerated electrons are transferred through conduction bands, FTO glass and finally moved to the external circuit. After that, the other electrode receives electrons to form a reduction site, and then these electrons reduce H_2O to form hydrogen by reacting with hydrogen ions in the electrolyte. On the other hand, photogenerated holes in the valence band of ZnO NRs are transported to the valence band of TiO_2 and form an oxidation site, such that H_2O is oxidized to produce oxygen and hydrogen ions. According to the mechanism, it can efficiently prevent the recombination of photogenerated electron-hole pairs and increase the life-time of charge carriers.

In addition, another mechanism is enhancement of electromagnetic field arising from LSPR of free electrons of Au-NPs. Meanwhile, we utilized finite-difference time-domain (FDTD) simulations (Figure 1(c)) to prove the enhancement of electric field at the interface between Au-NPs and b-NRs TiO_2. Because of plasmon-induced electric field, it can increase hot-electrons injection and improve visible light absorption. With these plasmon-induced effects, the efficiency of solar water splitting can be markedly enhanced.

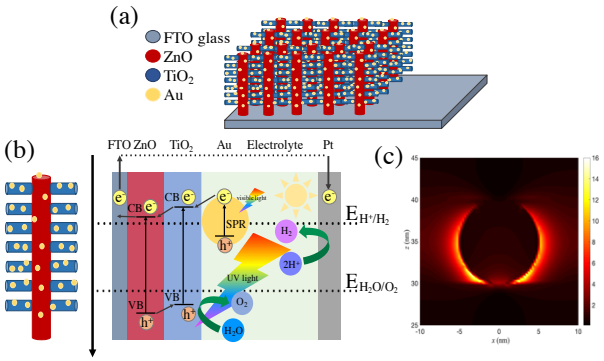

Figure 1. (a) The schematic diagram of Au-NPs@b-NRs TiO_2@ZnO. (b) Schematic representation of the possible mechanism of photogenerated charge separation at the interface of Au-NPs@b-NRs TiO_2@ZnO with their corresponding energy band diagram during PEC water splitting. (c) Simulated spatial distribution of electric field on the *x*–*z* plane for Au-NPs on b-NRs TiO_2 under incident light of 570 nm wavelength.

3. Conclusion

Au-NPs@b-NRs TiO_2@ZnO system exhibits outstanding photoactivity. This high performance PEC water splitting application is attributed to the synergistic effects of the enhanced visible light absorption, resulting from LSPR of Au-NPs, and the increased separation of photogenerated electron-hole pairs.

Acknowledgements

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References

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[2] Zhang X., et al., ACS Appl. Mater. Interfaces., **6** (2014) 4480–4489.

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