Au@Cu_2Se Yolk@Shell Nanocrystals for Photoelectrochemical Water Splitting and Photocatalytic Hydrogen Production

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Abstract: The combination of metal and semiconductor has been a useful strategy to enhance the charge separation efficiency and thereby improve the photocatalytic activity.[1,2] This work reported the use of Au@Cu_2Se yolk@shell nanocrystals as the photocathode for photoelectrochemical water splitting. Results showed that Au@Cu_2Se nanocrystals exhibited substantially larger photocurrent generation of water reduction than the counterpart samples did. The superior activity of Au@Cu_2Se toward photocatalytic hydrogen production was also demonstrated, which can be attributed to the pronounced charge separation caused by the Au core as well as the abundant active sites endowed by the yolk@shell structures.

Keywords: Yolk-Shell, Water splitting, Hydrogen production.

1. Introduction

Cu_2Se is a p-type semiconductor with a relatively narrow direct bandgap between 2.0 to 2.3 eV,[3] which is beneficial to visible photons harvesting. However, the high recombination probability of charge carriers reduces the carrier utilization efficiency, thereby limiting the photoconversion performance.[4] The combination of semiconductor nanostructures with metal has proven as a useful approach to enhance the charge separation efficiency and thereby improve the photocatalytic activity.[5] On the other hand, yolk@shell nanocrystals with interior, void space can provide large surface area and homogeneous environment for reactant molecules, both of which are favorable for catalytic applications. Here we demonstrated the use of Au@Cu_2Se yolk@shell nanocrystals as the photocathode for efficient photoelectrochemical water splitting as well as the photocatalyst for practical photocatalytic hydrogen evolution.

2. Experimental

For the experimental section, we first obtained Au nanoparticles from the typical citrate reduction method. And then a chemical reduction method was used to deposit Cu_2O on the surface of Au, forming the core@shell nanocrystals. Au@Cu_2Se yolk@shell nanocrystals were prepared by using Au@Cu_2O core@shell nanocrystals as the growth template. The growth of yolk@shell nanocrystals was achieved by performing the selenization treatment on Au@Cu_2O. By reacting with Na_2Se, the Cu_2O shell can be further transformed into Cu_2Se. Since the outward diffusion of Cu^+ was faster than the inward diffusion of Se^{2-}, Kirkendall voids were generated and coalesced into a single hollow space, which resulted in the formation of Au@Cu_2Se yolk@shell nanocrystals.

3. Results and discussion

The dimensions and morphology of the samples were analyzed with SEM and TEM. Both of the core@shell and yolk@shell structural features can be confirmed from the evident image contrast difference between the inner core and the outer shell. For the core@shell nanocrystals, the shell thickness of Cu_2O was around 20 to 30 nm. As to the yolk@shell nanocrystals, the shell thickness of Cu_2Se was reduced to 8 to 10 nm. On the other hand, for the pure Cu_2O and pure Cu_2Se, they had structural characteristics similar to the core@shell and yolk@shell nanocrystals. With this outcome, a direct and fair comparison between Au@Cu_2O core@shell and pure Cu_2O can be made and the effect of the Au core can then be demonstrated.

The optical properties of the samples were determined with absorption and PL spectroscopy. All the spectra exhibited remarkable visible absorption that can be attributed to the excitonic absorption of Cu_2O and Cu_2Se. Additional absorption peak at 660 nm was recorded on the Au@Cu_2O nanocrystals, which was assigned to the SPR effect of the Au core. However, such SPR peak was not identified on Au@Cu_2Se

nanocrystals. This was due to the overlap of the absorption of Cu_2Se and the SPR of Au. For the steady-state PL spectra,both core@shell and yolk@shell nanocrystals displayed substantially depressed PL emissions, suggesting the occurrence of pronounced charge separation at the interface.

To further elucidate the mechanism of the PL depression for core@shell and yolk@shell nanocrystals, we performed time-resolved PL measurement. For pure Cu_2O, an emission lifetime of 0.77 ns was recorded. As to the Au@Cu_2O, a shortened emission lifetime was observed, indicating the emergence of a nonradiative pathway from the electronic interaction between Cu_2O and Au. The electron transfer rate constant for yolk@shell nanocrystals was substantially higher than the value for core@shell samples. This outcome further illustrates that Au@Cu_2Se yolk@shell nanocrystals may exhibit higher photoconversion efficiency than Au@Cu_2O core@shell nanocrystals.

The samples were then used as photocathode for practical application in photoelectrochemical and photocatalytic hydrogen production systems. Results showed that Au@Cu_2Se nanocrystals exhibited substantially higher photocurrent of water reduction (-42.2 μA cm^{-2}) and much higher photocatalytic hydrogen evolution rate (48.3 μmol hr^{-1} g^{-1}) than the counterpart core@shell nanocrystals (-27.5 μA/cm^2, 23.9 μmol hr^{-1} g^{-1}) and pure Cu_2Se samples did (-31.0 μA/cm^2, 34.8 μmol hr^{-1} g^{-1}). Besides, among all the samples tested, yolk@shell nanocrystals showed the highest photocurrent generation and hydrogen production, which can be attributed to the abundant active sites endowed by the yolk@shell structures as well as the superior interfacial charge dynamics revealed in the time-resolved PL data.

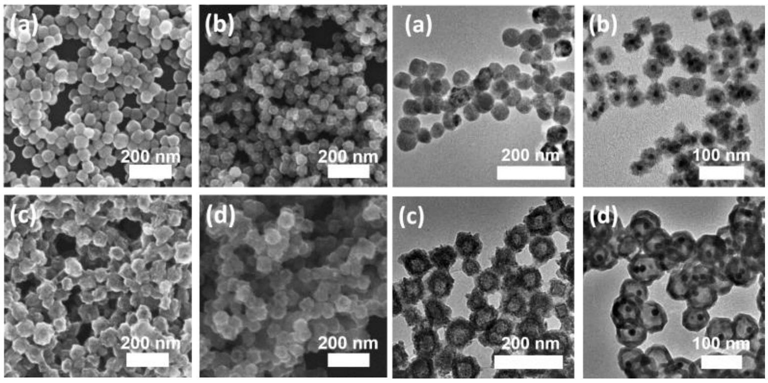

Figure 1. SEM and TEM images for all samples. (a)pure Cu_2O, (b)Au@Cu_2O, (c)pure Cu_2Se, (d)Au@Cu_2Se

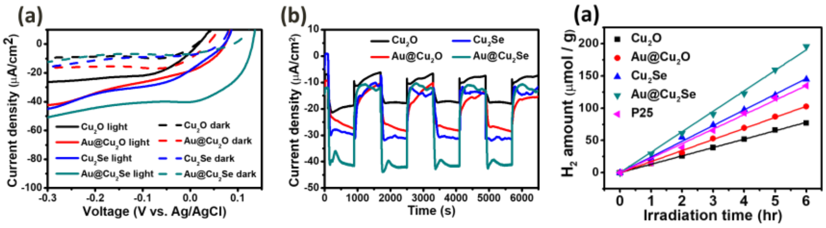

Figure 2. PEC measurements and hydrogen production for all samples.

4. Conclusions

In conclusion, we successfully demonstrated the use of Au@Cu2Se yolk-shell nanocrystals for practical PEC water splitting. And The beneficial effect of Au decoration in enhancing the PEC performance and photocatalytic hydrogen production were studied and realized.

References

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