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Plasmon-Enhanced Hydrogen Evolution on Au-InVO₄ Hybrid Microspheres

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We demonstrate the plasmon-enhanced hydrogen evolution from photocatalytic water reduction by using Au-InVO₄ hybrid microspheres. The surface plasmons of gold nanoparticles enhance the sub-band gap excitation of InVO₄ and promote charge separation on its surfaces through plasmon-exciton coupling, thereby significantly improve their photocatalytic efficiency.

Solar-to-fuels conversion through photocatalytic water splitting has been recognized as highly important energy sources for the sustainable future.¹ Researchers have made tremendous efforts to develop various visible-light-active metal oxide photocatalysts, such as BiVO₄,^{2,3} Fe₂O₃,^{4,5} and Cu₂O.^{6,7} for water oxidation or reduction. Ye and co-workers have reported a new type of metal oxide InVO₄ which is capable of producing H₂ through visible-light driven photocatalytic water reduction.^{8,9} Recent studies revealed that the actual band-to-band energy gap of InVO₄ could be more than 3 eV, while its visible-light activities were attributed to sub-band gap transitions from impurity states.¹⁰⁻¹² Though it is certainly beneficial from extended absorption in the visible range, the impurity states will also promote undesirable recombination of photogenerated electrons and holes, which may reduce the photocatalytic activities. Consistently, some researchers also found that their prepared InVO₄ structures are unviable to show visible-light-driven hydrogen production due to inefficient charge separation from visible-light-induced sub-band gap transition.¹²⁻¹⁴

In order to achieve high photocatalytic activities, efficient charge separation is crucial for all photocatalysts. To date, researchers have developed many different methods to enhance the separation of photogenerated electrons and holes. One promising approach is depositing plasmonic particles of noble metals (e.g. Au and Ag) onto the photocatalysts.¹⁵⁻¹⁷ As well known, gold and silver nanoparticles exhibit strong surface plasmon resonance (SPR) in the visible range.^{18,19} It has been demonstrated that the SPR of metal nanoparticles would greatly promote the photocatalytic efficiencies of metal oxide photocatalysts because the SPR-enhanced localized electric field can improve the charge separation near the metal-semiconductor interfaces.^{20,21}

Herein, we report a new strategy to utilize gold SPR to enhance visible-light-driven hydrogen evolution through photocatalytic water reduction by using Au-InVO₄ hybrid microspheres prepared by growing gold nanoparticles on pre-synthesized InVO₄ hollow microspheres. We demonstrate that the gold nanoparticle SPR can significantly enhance the sub-band gap transition of InVO₄ microspheres and thereby their photocatalytic efficiencies. The detailed plasmonic effect on charge separation is also discussed in-depth.

Fig. 1 (a) UV-vis spectrum of InVO₄ microspheres, inset is the plot of $(ah\nu)^{1/2}$ vs photon energy ($h\nu$) to calculate the band gap; (b, c) SEM images and (d, e) TEM images of InVO₄ microspheres.

The prepared InVO_4 sample is identified as orthorhombic phase through XRD analyses (Fig. S1). The absorption spectrum (Fig. 1a) shows that the InVO_4 sample exhibits obvious absorption in the visible light range with a band gap estimated as 2.16 eV. The analyses by SEM and TEM (Fig. 1b-d) reveal that the sample consists of hollow microspheres that are built by assembly of many InVO_4 nanocrystals. The high-resolution TEM image (Fig. 1e) of the nanocrystal indicates a fringe spacing of 0.477 nm in accordance with the lattice spacing of the (110) plane of orthorhombic InVO_4 .

Three Au- InVO_4 hybrid samples with different Au content were prepared by reducing HAuCl_4 with L-ascorbic acid in the presence of InVO_4 microspheres and L-cysteine that can bind to the InVO_4 surface through its carboxylate group and captured gold onto InVO_4 surfaces via the Au-S bonding.^{22,23} SEM and TEM images (Fig. 2a, S2, S3, S4) indicate that gold nanoparticles were successfully grown onto the InVO_4 microspheres and the original microsphere morphology did not change during the gold nanoparticle growth process. The gold contents in these three samples were estimated as ~2 wt%, 4 wt%, and 7.5 wt%, respectively, according to the analyses by energy-dispersive X-ray (EDX) spectroscopy. The high-magnification TEM images (Fig. S2-S4) reveal that the sizes of gold nanoparticles in these samples are 3.7 (± 0.9) nm, 6.7 (± 1.5) nm, and 13.0 (± 1.9) nm, respectively. The SPR feature of gold nanoparticles can be clearly observed at ~540 nm for the 4 wt% and 7.5 wt% Au- InVO_4 samples (Fig. 2b). The absence of SPR feature for the 2 wt% Au- InVO_4 sample may be due to the low concentration of gold nanoparticles. In addition, the SPR of small gold particles (<5 nm) is usually very weak,^[24] and may be overwhelmed by InVO_4 absorption.

Fig. 2 (a) SEM and TEM image (inset) of 4 wt% Au- InVO_4 microspheres; (b) UV-vis spectra of 2, 4, 7.5 wt% Au- InVO_4 samples.

The prepared Au- InVO_4 hybrid microspheres were then tested for photocatalytic H_2 evolution under visible-light ($\lambda > 420$ nm) irradiation. L-ascorbic acid (0.1 M, pH=4.0) was used as the electron donor. Fig. 3a shows the H_2 evolution plots by different samples as a function of irradiation time. In comparison to pure InVO_4 microspheres that showed no H_2 evolution, all Au- InVO_4 hybrid microspheres exhibit obvious visible-light-driven photocatalytic activity for H_2 evolution. Among them, the 4 wt% Au- InVO_4 sample showed the highest H_2 evolution rate of $116.7 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ which then dropped to $15.9 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ after 90 min and became quite stable thereafter (Fig. S5). The stable H_2 evolution rate (after 90 min) of the 2 wt% and 7.5 wt% Au- InVO_4 samples were $12.5 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ and $8.6 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, respectively.

As well known, semiconductor photocatalysts can have improved efficiencies after loaded with nanoparticles of noble metals such as Pt, Pd and Au.^{25,26} The metal nanoparticles can act as electron sinks to hold the excited electrons from the semiconductor band-gap excitation, which retard the charge recombination process and thereby increases its photocatalytic efficiency.²⁷ In order to clarify whether the electron-sink effect dominates in the Au- InVO_4 samples, we prepared Pt- InVO_4 hybrid microspheres with 4 wt% Pt by using similar methods (Fig. S6). The XPS analyses (Fig. S7) reveal the binding energy of Au 4f (84.1 and 87.8 eV) and Pt 4f (71.2 and 74.6 eV), indicating the zero-valent nature of the deposited gold and platinum. However, after visible-light irradiation for 3 hours, the photocatalytic H_2 evolution amount of this Pt- InVO_4 sample (5.0 $\mu\text{mol/g}$) is much lower than that of the 4 wt% Au- InVO_4 sample (167.1 $\mu\text{mol/g}$) (Fig. 3b). The Pt- InVO_4 samples with less Pt loading (1 wt% and 2 wt%) showed even smaller H_2 evolution amount (Fig. S8). This comparison result suggests that the pure electron-sink effect only play a minor role for the metal- InVO_4 hybrids as it's well known that Pt is usually more active than Au for H_2 evolution due to the lower H_2 evolution overpotential on Pt surfaces.²⁸

Fig. 3 (a) Plots of photocatalytic H₂ evolution amount versus irradiation ($\lambda > 420$ nm) time for different samples; (b) Comparison of H₂ evolution amount of for Au-InVO₄ and Pt-InVO₄ samples after 3h irradiation; (c) Photocatalytic H₂ evolution for 4 wt% Au-InVO₄ and 4 wt% Pt-InVO₄ under irradiation at 460±20 nm and 500±20 nm; (d) Schematic illustration of the plasmon-enhanced photocatalytic process for H₂ evolution on the Au-InVO₄ hybrid structure, in which H₂A and HA• refers to ascorbic acid and ascorbate radical, respectively.

To strengthen the above conclusion, we carry out further comparison tests by controlling the irradiation wavelengths at 460±20 nm and 500±20 nm, respectively. Fig. 3c indicate that in both wavelength ranges, the 4 wt% Pt-InVO₄ sample does not show observable H₂ evolution, while the 4 wt% Au-InVO₄ sample is still quite active. This means that even though InVO₄ microspheres absorb photons in these two ranges through sub-band gap transition, the majority of photogenerated electrons would recombine rapidly with the holes rather than transfer to the contacted Pt nanoparticles for water reduction. Note that small Pt nanoparticles do not exhibit SPR absorption in the visible light range. So the SPR-absorption from the Au nanoparticles grown on the InVO₄ microspheres should play important roles in the enhanced efficiency of Au-InVO₄ samples.

It is known that the SPR-excitation of metal nanostructures can generate strongly enhanced localized electric fields with magnitudes up to 10⁵ times of the incident energy.²⁹ By this way, the metal nanostructures act like optical antenna to concentrate the light energy at the near surfaces. Therefore the InVO₄ nanocrystals near the Au-InVO₄ interfaces would encounter much more intense sub-band gap excitation by this SPR-enhanced electric field, which can generate more photo-excited electrons for water reduction. Moreover, the visible-light absorption of InVO₄ induced by the sub-bandgap transition has been ascribed to impurities or defects in the crystal structure. But these impurities and defects can also act as recombination sites of photogenerated electrons and holes. However, the wide overlap between Au-plasmon band and InVO₄ absorption in the visible light range enables intensive plasmon-exciton coupling that significantly increases the exciton dissociation efficiency,^{20,21} and thereby promote the photocatalytic efficiency. As a result, the photogenerated holes can oxidize L-ascorbic acid (H₂A) on the InVO₄ surface; meanwhile the separated electrons will have relatively longer time to reduce H⁺ to H₂ on the gold nanoparticle surface. This SPR-enhanced photocatalytic process is illustrated in Fig. 3d.

It is also noted that for the Au-InVO₄ sample, the 460±20 nm irradiation results in higher H₂ evolution efficiency than the 500±20 nm irradiation (Fig. 3c) even though the gold nanoparticles have stronger SPR at the latter irradiation range. This means that the major contribution of the photocatalytic activity still comes from the InVO₄ excitation. Certainly the excitation at 460±20 nm creates more excitons than the excitation at 500±20 nm since the InVO₄ microspheres have stronger absorption at 460±20 nm. Even if the gold plasmon at 460 nm is relative weak, it still can provide sufficient enhancement to achieve desirable exciton dissociation yield on InVO₄. While under excitation at 500 nm, the stronger excitation of gold SPR at 500 nm does not show further improvement due to weaker excitation of InVO₄ with less available photogenerated electrons for water reduction. Nevertheless, in order to achieve good photocatalytic performance, the gold surface plasmon is still indispensable to enhance the exciton dissociation on InVO₄ since the Pt-InVO₄ sample shows no activity for H₂ evolution under the irradiation at the same wavelength range.

However, when the gold loading amount is too high, the excessive gold nanoparticles would serve as the centers to promote electron-hole recombination and thereby reduce the photocatalytic activity. That's why the 7.5 wt% Au-InVO₄ showed less H₂ evolution activity as comparing with the other two Au-InVO₄ samples. In addition, the decreased activities of the Au-InVO₄ samples after 90 min (Fig. 3a) are attributed to increased size of the gold nanoparticles on InVO₄ during the photocatalytic reaction. As shown in Fig. S9, the gold particle size changes to above 15 nm, which may be ascribed to the structure re-construction of small Au nanoparticles induced by ascorbic acid.³⁰ While larger gold particles have higher resistance to the etching by ascorbic acid, thus the photocatalytic activity becomes stable thereafter. Since the EDX

analysis indicates no change in the gold percentage (Fig. S9e), the conversion of gold nanoparticles from small to large size causes decrease of Au-InVO₄ interfaces. Therefore, the effective area of SPR enhancement is also reduced, leading to lower photocatalytic efficiency of Au-InVO₄ samples.

In summary, we have demonstrated the plasmon-enhanced H₂ evolution from photocatalytic water splitting by using Au-InVO₄ hybrid microspheres. The surface plasmons of gold nanoparticles that were grown on InVO₄ microspheres substantially improve the separation of photogenerated electrons and holes on InVO₄ through plasmon-exciton coupling. In comparison, the Pt-InVO₄ sample showed very little activity on H₂ evolution due to the lack of visible light SPR from Pt nanoparticles. We believe that our studies will have considerable impact on future development of more efficient plasmonic metal-semiconductor photocatalysts for visible-light-driven water splitting.

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Notes and references

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