

Au Multimer@MoS₂ hybrid structures for efficient photocatalytical hydrogen production via strongly plasmonic coupling effect

Xuanhua Li^{a,*}, Shaohui Guo^a, Caixia Kan^c, Jinneng Zhu^a, Tengting Tong^a, Shanlin Ke^c, Wallace C.H. Choy^d, Bingqing Wei^{a,b,*}

^a State Key Laboratory of Solidification Processing, Center for Nano Energy Materials, School of Materials Science and Engineering, Northwestern Polytechnical University and Shaanxi Joint Lab of Graphene (NPU), Xi'an 710072, China

^b Department of Mechanical Engineering, University of Delaware, Newark, DE 19716, USA

^c College of Science, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China

^d Department of Electrical and Electronic Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, China

ARTICLE INFO

Keywords:

MoS₂
Plasmonic coupling
Photocatalytical hydrogen production
SERS
Near-field enhancement

ABSTRACT

Photocatalytical water splitting of MoS₂ nanomaterials based on plasmonic nanoparticles (NPs) has been limited because of the insufficient utilization of plasmonic hot spots, which is an important strategy for efficient light harvesting. Here, we design a high-performance photocatalyst Au multimer@MoS₂ core-shell hybrid structures to address this issue. The Au NP's multimer with 5–10 nm inter-particle distance realized by a pre-decoration is employed as a plasmonic component. As expected, rationally structural arrangement provides a strong near-field coupling at their inter-particle gaps of Au NPs and then gives rise to strong absorption enhancement, which leads to the significant improvement of exciton generation and dissociation in the Au-MoS₂ junctions. Theoretical modeling and surface enhanced Raman scattering (SERS) have been used to demonstrate the enhanced optical effect; and the photoluminescence (PL) and electrochemical measurements are adopted to clarify the improved electrical effect. As a result, a 240.2% increment in hydrogen gas production amount (2997.2 μmol/g) is achieved as compared to that of the pure MoS₂ spheres (881.6 μmol/g). The hydrogen gas production amount of Au multimer@MoS₂ spheres is among the highest values reported in the plasmon-enhanced photocatalytic hydrogen production.

1. Introduction

The designing of functional materials with excellent photoelectrical and photoelectrochemical properties provides a promising approach to transforming solar energy into hydrogen fuel. Up to date, many semiconductors have been explored for the photocatalytic process of producing hydrogen gas from the water splitting reaction [1–9]. Recently, MoS₂ nanostructures have attracted a lot of attentions due to their anomalous electronic and catalytic properties [10–15]. Hinnemann et al. have found that the S atoms on exposed edges of MoS₂ have strong bonds with H⁺ ions in a solution, which are easily reduced to H₂ [16]. However, the limited utilization of the visible light and the high exciton recombination ratio of MoS₂ restrict its performance and the development of the MoS₂-based photocatalysis systems for water splitting under the visible light irradiation. Thus, it is a critical issue to enhance the light absorption of MoS₂ efficiently for satisfying the requirements of applications.

Recently, the introduction of plasmonic metal NPs to semiconductors as hybrid nanostructures has attracted much interest [1,11,17–24]. The

metal NPs can enhance optical absorption of their adjacent semiconductors through the plasmonic effect for high-performance photocatalysts [17,25–34]. The preparation of metal/MoS₂ material hybrid nanostructures is the foundation for studying the optical properties and their photocatalytic application [35–40]. For example, Ag/MoS₂ nanocomposites catalysts have been reported by a simple combination of Ag NPs and MoS₂ nanomaterials [41] or by the straightforward introduction of Au NPs on top of MoS₂ surface [42]. Our groups have also reported Au NPs-enhanced MoS₂/ZnO hybrid nanostructures for hydrogen gas evolution [34]. Although all of the hybrid nanostructures boost the photocatalytic performance of water splitting, the efficiency is still low. One of the main reasons is that the previous report is mainly focused on the random and single metal NPs hardly exploiting the localized plasmonic electromagnetic enhancement from the inter-particle coupling hot spots for hydrogen production [17,43–49]. The stronger plasmonic electromagnetic enhancements can give rise to more absorption cross-section; and more plasmonic energy can facilitate dissociation of photo-induced hole-electron pairs, both of which will help for an efficient hydrogen production in the photocatalytic water splitting.

* Corresponding author.

E-mail addresses: lixh32@nwpu.edu.cn (X. Li), weib@udel.edu (B. Wei).

Thus, how to take advantage of the hot spots is one of the crucial challenges currently in the plasmon-enhanced water splitting.

Here, the uniform and monodispersed Au multimer@MoS₂ core-shell structures have been prepared for the first time, which show a strong performance enhancement for the hydrogen gas evolution, compared to the pure MoS₂ and Au monomer@MoS₂. The Au multimers with 5–10 nm inter-particle distance realized via a pre-decoration are integrated with MoS₂, to produce very strong near-field enhancement and then drastically promote the light absorption and exciton generation of MoS₂. The effects of the Au multimers on the light absorption, photoluminescence property, and photocatalytic activity are investigated, and the possible mechanisms that contribute to the improvement of visible-light-driven photocatalytic performance for the as-prepared structures are also discussed in detail.

2. Experiments

2.1. Synthesis of the photocatalysts

2.1.1. Synthesis of the Au nanoparticles

High-quality Au nanoparticles can be synthesized via a previously published protocol based on a seed-mediated method with slight modification [50]. This synthesis is based on the repeated growth of seed particles in the presence of HAuCl₄ and citrate until the desired size is achieved. For the growth of seed particles, sodium citrate solution (2 mL, 60 mM) was dispersed in 50 mL ultrapure water, and the mixed solution was boiled with vigorous stirring. Then, HAuCl₄·3H₂O solution (165 μ L, 50 mM) was dropped into the boiling solution. After 10 min reaction, the solution exhibited a light red-wine color as the seed particles were formed. For further growth of the seed particles, the reaction was diluted by adding sodium citrate (2 mL, 60 mM) and 50 mL of water. Then, HAuCl₄·3H₂O solution (335 μ L, 50 mM) was injected into the boiling reaction system. This process was repeated for three times.

2.1.2. Synthesis of the MoS₂ submicron spheres

2.0 mmol Na₂MoO₅ and 4.0 mmol L-cysteine (HSCH₂CH(NH₂)COOH) solutions were prepared, respectively, and then transferred into a Teflon-lined stainless steel autoclave. The autoclave was heated in the oven at 200 °C for 12 h and cooled to room temperature naturally. The as-obtained product was precipitated by centrifuge with a speed of 5500 rpm. The supernatant was decanted after centrifugation and the MoS₂ spheres in the form of precipitate were re-dispersed in ethanol. The precipitation and re-dispersion process were repeated twice. Finally, the resultant precipitate was MoS₂ sphere solution.

2.1.3. Synthesis of the Au monomer@MoS₂ nanocomposites

The Au monomer@MoS₂ spheres as a control sample have been obtained based on our previous report [34]. Typically, 2.0 mmol Na₂MoO₅ and 4.0 mmol L-cysteine (Cys) solutions were prepared, respectively; and the as-synthesized Au nanoparticles dispersed in 20.0 mL distilled water were added dropwise to the above mix solution. After 20 min sonication, the solution was transferred into a Teflon-lined stainless steel autoclave. The autoclave was heated at 200 °C for 12 h and cooled to room temperature naturally. The as-obtained product was precipitated by the centrifuge with a speed of 5500 rpm. The supernatant was decanted after centrifugation and the Au monomer@MoS₂ nanocomposites in the form of precipitate were re-dispersed in ethanol. The precipitation and re-dispersion process were repeated twice. Finally, the resultant precipitate was the Au monomer@MoS₂ solution.

2.1.4. Synthesis of the Au multimer@MoS₂ nanocomposites

For the synthesis of Au NPs multimers, the 10 mL as-prepared Au nanoparticles were mixed with Dithiol Poly(ethylene glycol) (HS-PEG-SH) solution (500 μ L, 10 μ M). In addition, a NaCl solution (100 μ L,

1 mM) was added into the solution for further aggregation of Au NPs. The rest process to the Au multimer@MoS₂ core-shell nanocomposites is similar to the above synthesis process.

2.2. Characterization of the photocatalysts

2.2.1. Morphology and structural characterization

The morphology of the samples was characterized using a scanning electron microscope (SEM) (Quanta 600 FEG) and transmission electron microscope (TEM) (FEI Tecnai F30G2). The absorption was measured using the ultraviolet-visible (UV-vis) spectrophotometer (Perkin-Elmer Lambda 35 UV-vis-NIR). The Raman spectrum was measured using a Raman spectrometer (Renishaw inVia). The photoluminescence (PL) was measured using the PL spectrometer (FLS 980). Photoelectrochemical measurements were performed in a homemade three-electrode quartz cell with a PAR VMP3Multi Potentiostat apparatus. A Pt plate was used as the reference electrode, and an Ag/AgCl electrode was used as the reference electrode, and a fluorine-doped tin oxide (FTO) glass was as the working electrode. The exposed area of the working electrode was 0.7 cm². The electrolyte was 0.1 M aqueous Na₂SO₄ solution without an additive.

2.2.2. Photocatalytic activity

The reaction was conducted by mixing 0.05 g of photocatalysts with 100 mL of deionized water in a quartz cell, which had been loaded with 0.3 M Na₂S and 0.3 M Na₂SO₃ as hole scavengers. A 300 W Xe arc lamp as a light source was mounted with a beam turner (Newport 66245) and was equipped with a fin-like heat sink for dissipating excessive heat effectively. The average power was determined to be 0.310 W cm⁻² for the visible-light that fell in the wavelengths between 420 and 800 nm. The selected wavelengths were realized through the optical filters. The quartz cell was placed 5.0 cm away from the edge of the filter holder. During the photocatalytic reaction, the gasses evolved were transferred into a sample loop by a peristaltic pump and were further quantified using gas chromatography (Shimadzu GC-2014c), equipped with a thermal conductivity detector (TCD). The amount of hydrogen gas produced every 30 min was quantified by integrating with a calibration curve. The same experimental parameters were employed for the pure MoS₂, Au monomer@MoS₂ nanocomposite, and Au multimer@MoS₂ nanocomposites.

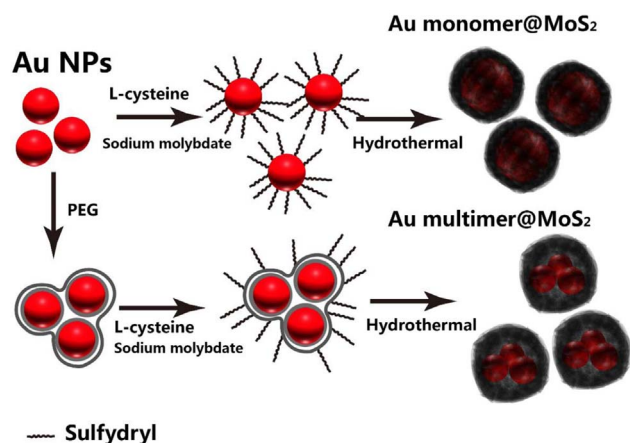
2.3. Theoretical modeling

Maxwell's equations are rigorously solved by three-dimensional (3D) finite-element method [51]. The dielectric constant of the Au NP is adopted from references [52,53]. The size of the Au NP in the model is 55 nm. The distance between the dimer Au NPs is 5 nm. For the multimer case, the distance between the center NP and surrounding NPs is 5 nm. The used mesh grid is 1 nm, and the Au NPs can be well depicted in the simulation. In addition, the perfect matched layer (PML) is adopted for truncating the simulation domain and absorbing the reflected wave. The polarization of the incident light is along the axis of the dimer, i.e. vertical direction as shown in Fig. 2(c). For better clarification, the intensity of electrical field distribution is visualized in a logarithm scale.

3. Results and discussion

3.1. The strategies for obtaining monodispersed, well-controlled Au multimer@MoS₂ core-shell hybrid nanostructures with a broadband absorption enhancement

The Au multimer@MoS₂ hybrid structures could be accomplished in a two-step synthetic process, as shown in Schematic 1 and Experimental Section. The Au multimers are firstly obtained by adding the Dithiol Poly(ethylene glycol) (PEG) molecules with sulphydryl



Schematic 1. Scheme of the fabrication process of the Au multimer@MoS₂ spheres.

groups to the solution of Au monomers. Several Au NPs can be linked together by the PEG molecules. After that, L-cysteine (Cys)/Mo complexes, initially attached to the surfaces of the Au multimers via the S-Au bonds decompose to yield MoS₂ on Au multimer surface, resulting in the formation of Au multimer@MoS₂ hybrid nanostructures. In addition, the pure MoS₂ sphere and Au monomer@MoS₂ spheres (control samples) are also prepared for comparison.

The morphology characterization of the Au multimer@MoS₂ spheres are performed using scanning electron microscope (SEM) and transmission electron microscope (TEM) (Fig. 1). For comparison, the pure MoS₂ spheres and Au monomer@MoS₂ spheres are also investigated. As shown in Fig. 1(a), the pure MoS₂ spheres of about 430 nm are uniform and well dispersed. TEM images show that many nanosheets intertwine together in the spheres (Fig. 1(b) and Fig. S1). The energy dispersive X-ray analysis (EDXA) was conducted to estimate the chemical composition and only Mo and S elements are observed (Fig. S2). Fig. 1(c) shows the SEM image of the Au monomer@MoS₂ sample. The sphere-like structures with a size of about 450 nm are obtained, from which Au NP core is faintly observed due to the loose structure of the MoS₂ shell. The apparent contrast between the inner core and the outer shell in the TEM images further confirms the existence of core-shell structure (Fig. 1(d) and Fig. S3). The Au NPs with 60 nm size is clearly observed, however, the shell thickness of MoS₂ is not fixed and varied in the range of 80–150 nm. In the high-resolution TEM (HRTEM) image, an interlayer spacing of 0.61 nm is obtained in the shell region, complying with the lattice spacing of the (002) planes of the MoS₂ [15,54]. EDXA further reflects that only Mo, S, and Au elements are existing in the hybrid nanostructures (Fig. S4).

Fig. 1(e)–(g) shows the morphology of the Au multimer@MoS₂ sample. The morphological appearance is similar to the pure MoS₂ spheres and Au monomer@MoS₂ spheres. The TEM images reveal that each core is composed of several Au NPs with the size of 55 ± 5 nm, and the numbers of Au NPs are varied in different Au multimer@MoS₂ units (Figure (f) and Fig. S5). EDXA further reflects that more Au components exist in the hybrid nanostructures (Fig. S6). To analyze the number distributions of Au NPs in the Au multimer cores, 100 Au multimer@MoS₂ core-shell units have been counted. As shown in Fig. S7, the numbers of Au NPs in one core are distributed from 1, 2, 3–6, and to above 6, and the corresponding distribution ratios are around 8%, 15%, 55%, and 20%, respectively. Thus, the number of Au NPs above 3 is dominant in the Au multimer cores. The HRTEM images further show a gap between Au nanoparticles with the distance of 5–10 nm (Fig. 1(h) and Fig. S8), which is very beneficial for producing giant electromagnetic enhancement because of the strong coupling between the closely packed Au NPs. In addition, an interlayer spacing of 0.61 nm is obtained, complying with the lattice spacing of the (002)

planes of the MoS₂ [15,54].

The absorption spectra of photocatalysts are very important in evaluating their optical properties. Fig. 2(a) shows the ultraviolet-visible (UV–vis) absorption spectra of the five samples, including Au monomers, Au multimers, MoS₂ spheres, Au monomer@MoS₂ hybrids, and Au multimer@MoS₂ hybrids. As shown in Fig. 2(a), the characteristic peaks of the MoS₂ spheres locate at about 607 nm and 670 nm, which agrees well with previous reports [55,56]. The absorption peak of the Au monomers locates at about 530 nm, which is consistent with localized surface plasmon resonance (LSPR) peak of the Au nano-spheres [57]. For the Au multimers, an additional broadband peak around 630 nm has been observed, which is due to the strongly in-phase coupling between Au NPs. The theoretical modeling further illuminates these points. The strength of the near-field becomes much stronger from Au monomer, dimer, to multimer under the same excitation light. Because the inter-particle distance is around 5–10 nm, the LSPR of Au NPs and their in-phase couplings produce the very strong near-field enhancement under the on-resonant excitation light, i.e. 532 nm for the Au monomer and the Au multimer, and 630 nm for the Au multimer. Thus, the large amount of light energy can be stored in the inter-particle gaps. In contrast, the weak near fields are produced regardless of the Au monomer or the Au multimer under the excitation of off-resonant wavelength, i.e. 325 nm.

After the Au monomer or multimer is introduced into the MoS₂ spheres, two strong absorption regions can be observed around 510 nm and 640 nm, which can be attributed to the LSPR peak of the Au NPs, and the characteristic peaks of the MoS₂ spheres, respectively. However, two obvious changes have also been noticed. On the one hand, the LSPR absorption of Au NPs blue shifts after the growth of MoS₂ shell. This is due to the electron transfer from the MoS₂ to Au NPs because of the different Fermi levels, as shown in Fig. 2(b). On the other side, the absorption intensity of the Au NPs @MoS₂ nanostructures is stronger than the absorption intensity of the pure MoS₂ spheres. For the Au monomer@MoS₂ hybrid nanostructures, an enhancement peak around 450–560 nm has been observed, which further proves that the plasmonic effect induced by the Au NPs plays an important role in enhancing the light absorption of the MoS₂. Interestingly, a stronger absorption enhancement has been observed after Au multimers are introduced as the cores into the MoS₂ spheres. More importantly, a broadband enhancement has been achieved, which not only covers the 450–560 wavelength region but also extends the absorption peak of the MoS₂ to around 560–670 nm.

3.2. The effective photocatalytic reaction of the Au multimer@MoS₂ core-shell nanostructures under illumination with visible light or selected wavelengths

Fig. 3(a) shows the results of visible light ($\lambda > 420$ nm) driven photocatalytic hydrogen gas production of the pure MoS₂, the Au monomer@MoS₂, and the Au multimer@MoS₂ samples. The average gas production amount of the pure MoS₂ spheres is 881.6 $\mu\text{mol/g}$. After the introduction of the Au NPs onto the MoS₂ spheres, the hydrogen gas production amount is significantly improved. For the sake of clarification, the photocatalytic activity of Au NPs is also measured under the same conditions; and no trace amount of H₂ gas is detected after 4 h of reaction. By referring to Fig. 3(b), the introduction of the Au monomer to the MoS₂ has increased the H₂ gas production amount by 139.8%. Interestingly, introducing the Au multimers greatly boosts the photocatalytic performance and exhibits a 41.9% increment in hydrogen gas production amount (2997.2 $\mu\text{mol/g}$) compared to that of the as-synthesized Au monomer@MoS₂ spheres (2112.3 $\mu\text{mol/g}$), and a 240.2% enhancement compared to that of the pure MoS₂ spheres. When the Au multimers and MoS₂ spheres are simply mixed together, the hydrogen gas production amount is about 1543.4 $\mu\text{mol/g}$, which is incomparable with that of the Au multimer @ MoS₂ sample (Fig. S10). The main reason is that the plasmonic light

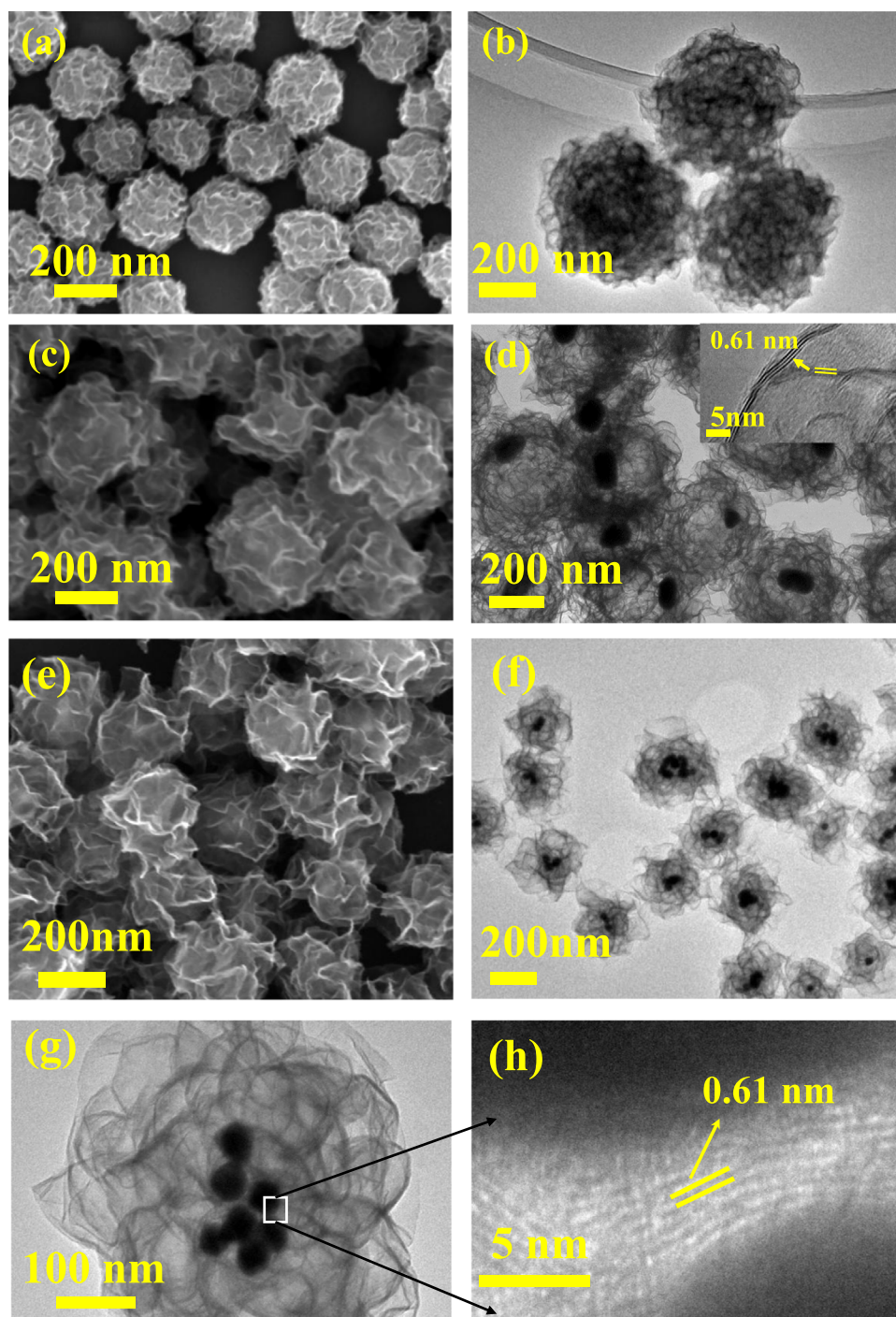


Fig. 1. SEM images of (a) the pure MoS₂, (c) Au monomer@MoS₂, and (e) Au multimer@MoS₂. TEM images of (b) the pure MoS₂, (d) Au monomer@MoS₂, and (f) and (g) Au multimer@MoS₂. The inset of Fig. 1(d) is the HRTEM image of the Au monomer@MoS₂. (h) HRTEM image of the Au multimer@MoS₂.

trapping is not fully utilized when the Au NPs are randomly and simply placed on the surface of the MoS₂ spheres. More importantly, the efficient dissociation of photo-induced hole-electron pairs in the Au-MoS₂ junctions is blocked under the physical contact of Au NPs and MoS₂ (discussed in Section 3.3 below). It is noted that the hydrogen gas production amount of the Au multimer@MoS₂ sphere is one of the highest values reported in the plasmon-enhanced photocatalysts [35,58–61]. Furthermore, the photocatalytic stability of the samples have been evaluated. The photocatalytic reaction is carried out for 4 cycles, and every cycle lasts for 4 h. As shown in Fig. S11 and Table S1, about 80.2% and 79.3% photocatalytic activity retains for the pure MoS₂ spheres and the physical mixture of Au multimer and MoS₂ spheres,

respectively. However, the Au monomer @MoS₂ and Au multimer @MoS₂ core-shell structures show better photocatalytic stability with about 87.6% and 86.4% photocatalytic activity retained, respectively, which show better photocatalytic stability. The main reason is that the MoS₂ shells are anchoring onto the Au core by Au-S bond, so reducing the peeling off from the spheres. In addition, the photocorrosion is partially restrained because of a charge transfer between the Au NPs and MoS₂.

Regarding the plasmon-enhanced photocatalytic reaction, it is indispensable to measure the photocatalytic activity under the illumination at the selected wavelengths around the plasmonic peak at 530 nm and 630 nm, respectively. In addition, the off-resonant wave-

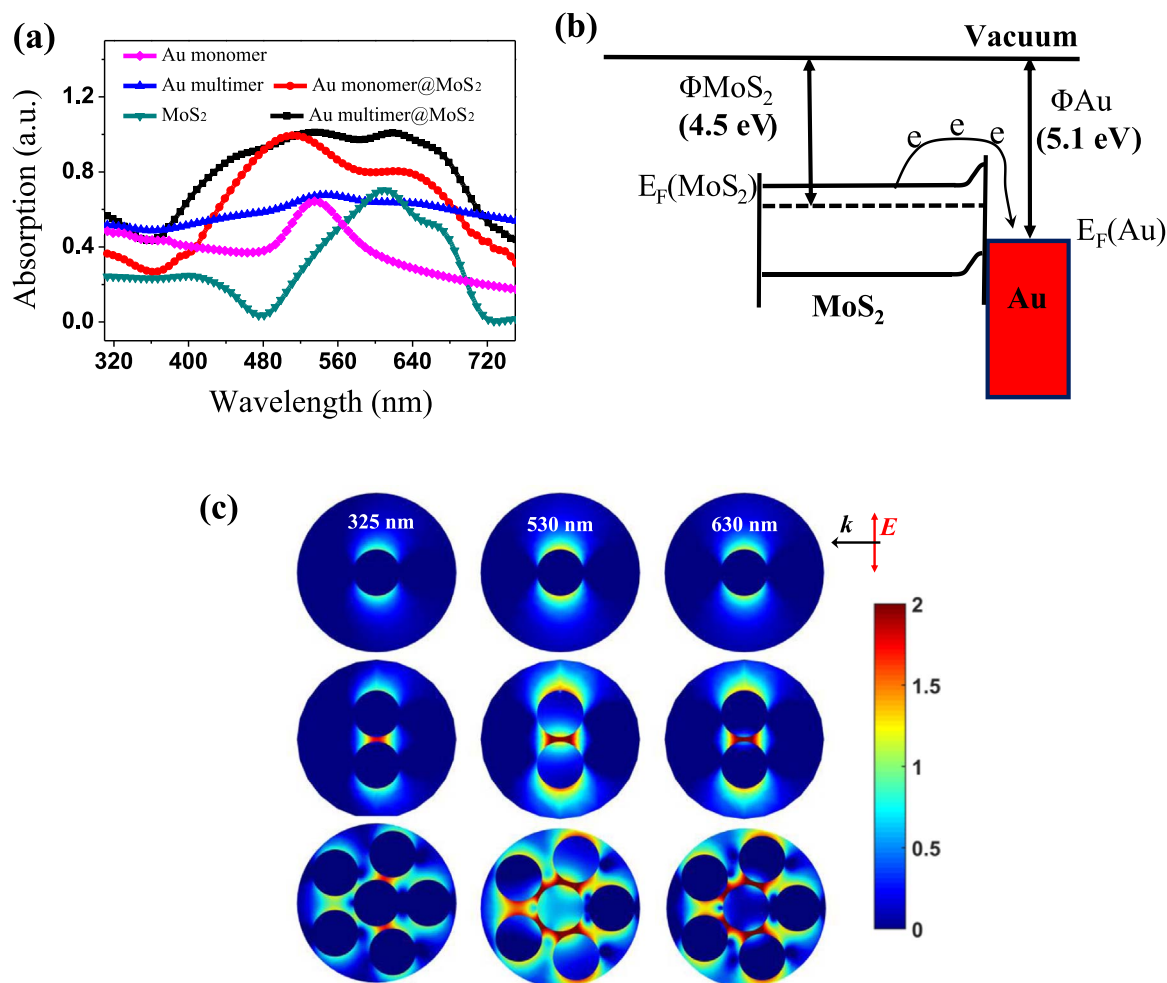


Fig. 2. (a) UV–visible absorption spectra of the Au monomers, Au multimers, MoS₂ spheres, Au monomer@MoS₂, and Au multimer@MoS₂. (b) Schematic diagram of the band gap between Au NPs and MoS₂ materials. (c) The top view of the electrical field distribution of the Au monomer@MoS₂, Au dimer@MoS₂, and Au multimer@MoS₂ under different excited wavelengths.

length region below 420 nm is also selected as an incident light for comparison. Fig. 4 and Fig. S9 show the time-dependent photocatalytic hydrogen gas production profiles, and the hydrogen gas production rate for different samples, respectively. Under the illumination of the light with a wavelength of 530 nm, there is an obvious improvement of the hydrogen amount from the Au monomer@MoS₂ (275.64 $\mu\text{mol/g}$)

and Au multimer@MoS₂ (408.32 $\mu\text{mol/g}$) compared to the pure MoS₂ spheres (76.50 $\mu\text{mol/g}$) (Fig. 4). The increments of the gas production for the Au monomer@MoS₂ and multimer@MoS₂ are enhanced by 261.8% and 433.8%, respectively (Fig. 4(d)). Furthermore, under the illumination of the light with a wavelength of 630 nm, the hydrogen gas yields of the Au monomer@MoS₂ (454.41 $\mu\text{mol/g}$) and Au multimers@

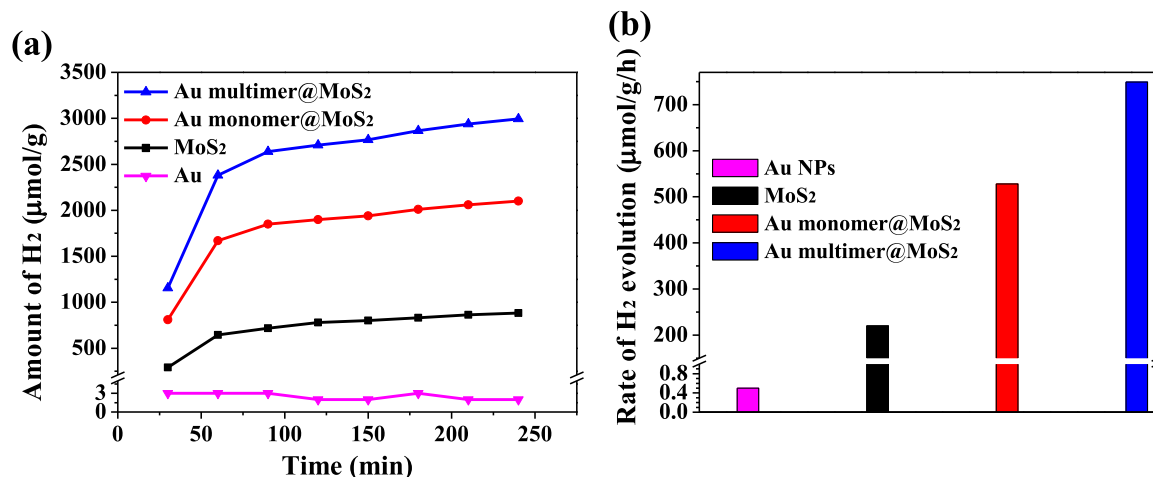


Fig. 3. (a) Time-dependent photocatalytic hydrogen gas production profiles, and (b) photocatalytic hydrogen production rate for the different samples, including: the Au monomers, MoS₂ spheres, Au monomer@MoS₂ samples, and Au multimer@MoS₂ samples.

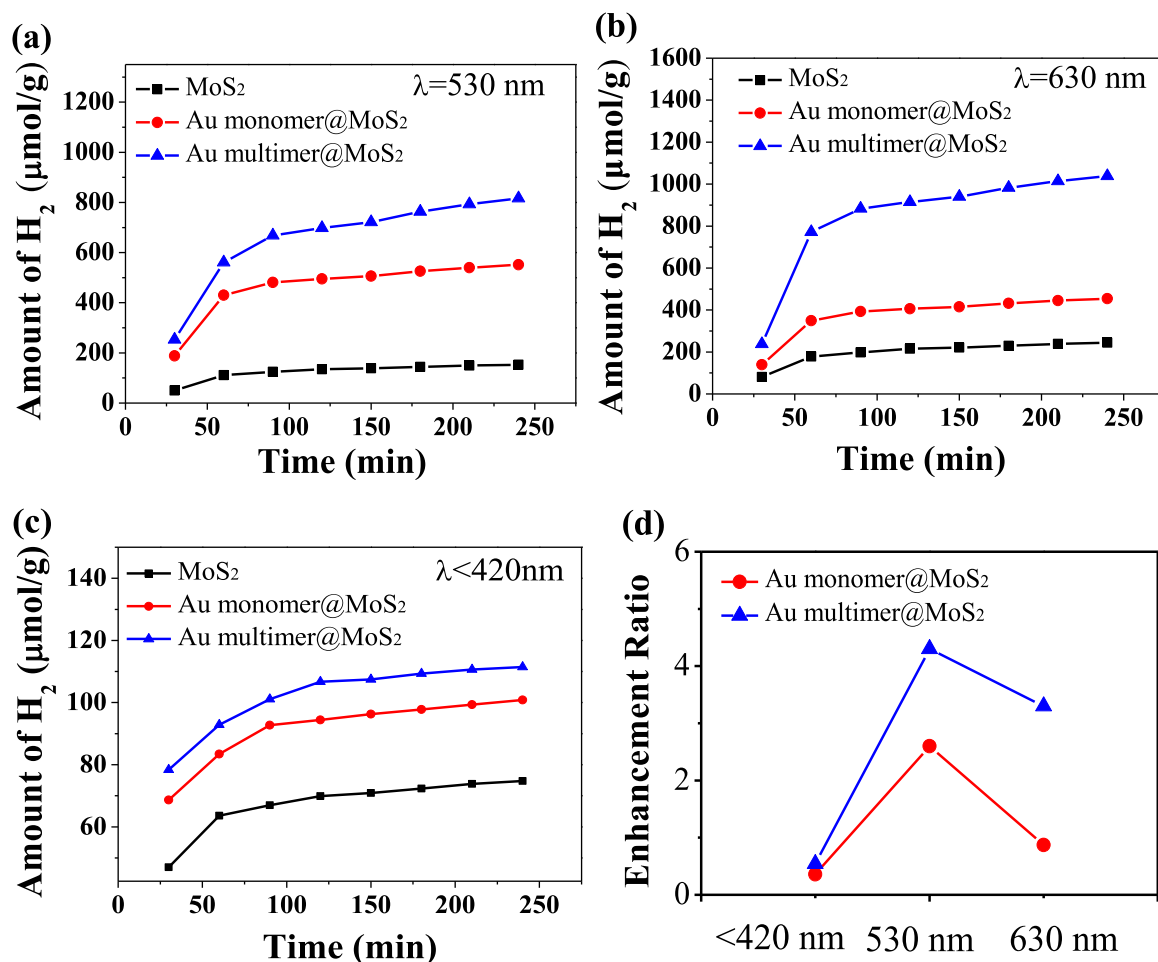


Fig. 4. (a), (b), and (c) Time-dependent photocatalytic hydrogen gas production profiles for the MoS₂ spheres, Au monomer@MoS₂, and Au multimer@MoS₂ at the selected wavelengths of 530 nm, 630 nm, and below 420 nm, respectively. (d) The enhancement ratio (i.e. (the amount of H₂ produced from the Au monomer@MoS₂ or Au multimer@MoS₂ – the amount of H₂ produced from the pure MoS₂ spheres)/the amount of H₂ produced from the pure MoS₂ spheres) under same illuminated light).

MoS₂ (1038.86 μmol/g) are obviously increased compared to the MoS₂ spheres (244.41 μmol/g), which is nearly 87.5% and 329.2% for the Au monomer@MoS₂ and Au multimer@MoS₂ spheres, respectively. Moreover, Fig. 4(c) shows the photocatalytic performance of three samples under the illumination of light with wavelength region below 420 nm. Interestingly, the enhancement of gas production is also observed. Compared to pure MoS₂ (70.06 μmol/g), the enhancement ratio is nearly 35.7% and 54.3% for the Au monomer@MoS₂ (95.25 μmol/g) and Au multimer@MoS₂ (108.78 μmol/g), respectively. Obviously, the enhancement ratio of photocatalytic hydrogen production is strongly affected by the wavelength of incident light for the Au monomer@MoS₂ and Au multimer@MoS₂, as shown in Fig. 4(d).

3.3. Photocatalytic mechanisms: a strong plasmonic coupling for positively optical effects and electrical effects

It is very important to understand the different photocatalytic performance for the three samples. The photocatalytic process involves two parts, including optical processes and electrical processes. During optical processes, the device should strongly absorb light for producing a large number of excitons. For the electrical processes, the exciton dissociation and recombination are involved. Plasmon-enhanced Raman spectra is a well-known tool for studying the optical effects of the plasmon-enhanced devices [2]. Through measurement of the Raman intensity of MoS₂, the near-field enhancement can be indirectly evaluated. Fig. 5(a) shows the Raman spectra of MoS₂ from the pure MoS₂ nanosphere, Au monomer @MoS₂, and Au multimer @MoS₂ core-shell

nanocomposites excited by a laser with different excited wavelength, including 325 nm, 532 nm, and 633 nm. For all of the samples, the characteristic peaks of MoS₂ with E_{2g}¹ (~378 cm⁻¹) and A_{1g} (~401 cm⁻¹) modes are observed [62]. After the Au monomers or multimers are introduced into the MoS₂ spheres as hybrid nanostructures, different change of the relative Raman intensity of the MoS₂ can be observed under the different excited laser light. Under the excited light with 532 nm, both the Raman intensity of MoS₂ from Au monomer@MoS₂ and Au multimer@MoS₂ are increased compared to that from pure MoS₂; and the enhancement ratio is 7.4 and 10.5 for Au monomer@MoS₂ and Au multimer@MoS₂, respectively (Fig. 5(a) and (d)). The main reason is the strongly excited near field, which is preferable for enhancing the Raman signals of the neighboring MoS₂ nanomaterials. Because of more quantity and stronger plasmonic effect of Au NPs in the Au multimer@MoS₂ compared to that of the Au NPs in the Au monomer@MoS₂, the enhancement ratio of Au multimer@MoS₂ is bigger. When the samples are excited with the 633 nm wavelength laser, the enhancement of Raman intensity of the MoS₂ from the Au monomer@MoS₂ and Au multimer@MoS₂ are also observed (Fig. 5(b)). The enhancement ratio is 4.6 and 12.8 for the Au monomer@MoS₂ and Au multimer @MoS₂, respectively (Fig. 5(d)). Compared to the Au monomer@MoS₂, the enhancement is more obvious, which is due to the excited wavelength with 633 nm overlaps with the resonant peak of Au multimer around 630 nm. However, the Raman enhancement of MoS₂ is not obvious for the Au monomer@MoS₂ and Au multimer @MoS₂ when the excited wavelength is changed to 325 nm. The main reason can be attributed to the off-resonant excited wavelength, in which the strong near-field is not induced.

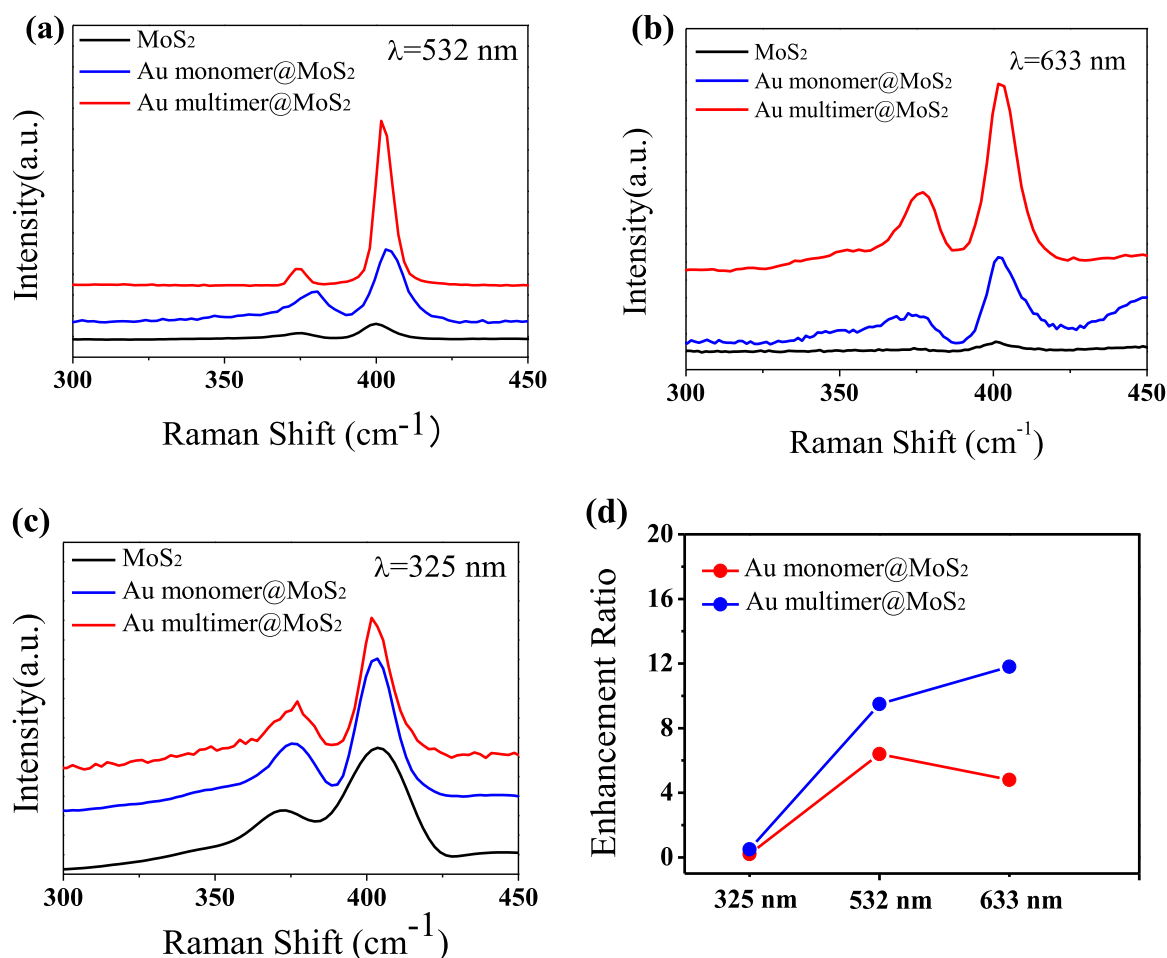


Fig. 5. Raman spectra of the MoS₂ sphere, Au monomer@MoS₂, and Au multimer@MoS₂ composites under different laser line: (a) 532 nm, (b) 633 nm, and (c) 325 nm, and (d) the corresponding enhancement ratio (i.e. the Raman intensity of MoS₂ from the Au monomer@MoS₂ or Au multimer@MoS₂ – the Raman intensity of MoS₂ from the pure MoS₂ spheres) / the Raman intensity of MoS₂ from the pure MoS₂ spheres under same excited light).

The results are consistent with the absorption results and photocatalytic measurement under illumination with the selected wavelengths. Thus, it is convinced to conclude that the near-field enhancement induced Au NPs plays a crucial role in promoting the light absorption of MoS₂ and then effectively enhancing the photocatalytic performance.

To study the plasmonic electrical effects (i.e. exciton dissociation), the photoelectrochemical characterizations and photoluminescence (PL) analysis are useful ways. Fig. 6(a) displays the photocurrent densities-time (I - t) curves of the pure MoS₂, Au monomer@MoS₂, and Au multimer@MoS₂ samples under the 325 nm light illumination. The Au multimer@MoS₂ sample shows the highest photocurrent, because of the better electron-hole separation performance. Fig. 6(b) exhibits the electrochemical impedance spectroscopy (EIS) Nyquist plots of the three samples under the 325 nm light irradiation. All the three samples show semicircles at the high frequencies. The smallest arc radius of the EIS Nyquist plot of the Au multimer@MoS₂ sample implies that it has the fastest interfacial electron transfer compared to that of the Au monomer @MoS₂ and pure MoS₂ samples. In addition, the most efficient transfer of charge carriers over the Au multimer@MoS₂ sample has been further verified by the PL analysis, which is often employed to study the surface processes involving the photoexcited energy and electron transfer and recombination. As shown in Fig. 6(c), the obvious emission peak is observed at 682 nm, this is agreed well with the literature data [63]. Interestingly, upon introducing Au NPs, the intensities of 682 nm are suppressed under excitation of 480 nm laser. The PL intensity of the MoS₂ from the Au monomer@MoS₂ and Au multimer@MoS₂ is decreased to 0.7 and 0.5, respectively.

According to Bhanu et al., who have studied the PL quenching in a gold-MoS₂ hybrid nanocomposite, photoexcited electrons in a higher Fermi level show a very high tendency to transfer to the adjacent gold NPs with a lower Fermi level during illumination [63]. Namely, the reduction is due to the electron sink effect, where the Au NPs can act as a “pool” to gather photoexcited electrons of the MoS₂ sphere and suppress the drawback of recombination. In the current work, the strong local electromagnetic field around Au multimer can more effectively interact with photogenerated excitons in the adjacent MoS₂. Hence, such a plasmon-exciton coupling can accelerate the separation efficiency of electron-hole pairs and result in a more efficient charge transfer (Fig. 6(d)). As a result, the reduction of water molecules is greatly eased at the surface of Au NPs that serve as an “electron pool” in gathering the photoexcited electron for further conversion of the hydrogen ions to H₂ molecules, while oxidation will take place on the active edges of the MoS₂ nanoflakes.

4. Conclusions

In summary, the Au multimer@MoS₂ photocatalyst nanocomposite has been successfully synthesized and characterized. The Au multimer composed of 3–6 NPs with 5–10 nm inter-particle distance realized via pre-decoration is integrated with MoS₂ to produce very strong near-field enhancement and then drastically promote the light absorption and exciton generation of the MoS₂. As a result, the yield of hydrogen gas production for the Au multimer@MoS₂ is about 2997.2 $\mu\text{mol/g}$, which is nearly 3.4 times and 1.4 times for the pure MoS₂ and Au monomer@

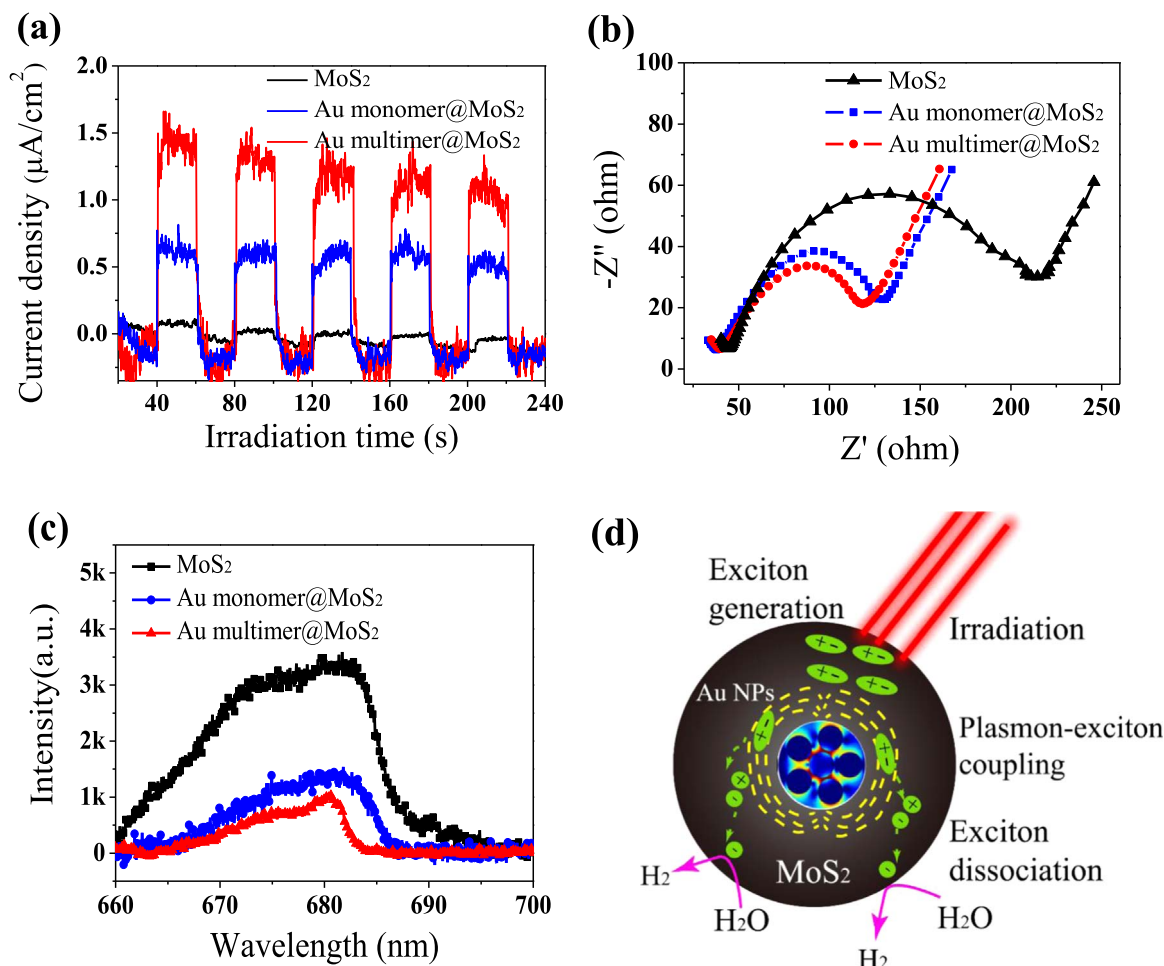


Fig. 6. (a) Photocurrent density-time curves of the MoS₂, Au monomer@MoS₂, and Au multimer@MoS₂ samples (bias: 0.2 V vs Ag/AgCl, 0.1 M Na₂SO₄, light irradiation: 325 nm). (b) Electrochemical impedance spectroscopy (EIS) Nyquist plots of the MoS₂, Au monomer@MoS₂, and Au multimer@MoS₂ samples under the 325 nm light illumination. (c) PL spectra of MoS₂ from the pure MoS₂ sphere, Au monomer @MoS₂ hybrids, and Au multimer @MoS₂ hybrids, excited under 480 nm laser line. (d) Schematic representations for hydrogen gas evolution over MoS₂ in the presence of the Au multimer core.

MoS₂, respectively. More importantly, the hydrogen gas production rate is one of highest values reported in the plasmon-enhanced photocatalysts to date. The possible mechanisms can be attributed to strongly plasmon-enhanced absorption and effective exciton dissociation because of the plasmon-exciton coupling between the Au and MoS₂.

Acknowledgments

This research is supported by the National Natural Science Foundation of China (51221001, 51472204, 51571166, 51521061, and 61505167) and the Program of Introducing Talents of Discipline to Universities (B08040). We also thank the support of the Natural Science Research Project of Shaanxi Province (2016JM5001), the Research Fund of the State Key Laboratory of Solidification Processing (NWPU) (Grant No. 147-QZ-2016), and the Key Scientific and Technological Team from Shaanxi Province (No. 2015KCT-12).

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.nanoen.2016.10.047](https://doi.org/10.1016/j.nanoen.2016.10.047).

References

- [1] W.J. Ong, L.L. Tan, Y.H. Ng, S.T. Yong, S.P. Chai, *Chem. Rev.* 116 (2016) 7159–7329.
- [2] X. Li, J. Zhu, B. Wei, *Chem. Soc. Rev.* (11) (2016) 3145–3187.
- [3] K. Chang, M. Li, T. Wang, S.X. Ouyang, P. Li, L.Q. Liu, J.H. Ye, *Adv. Energy Mater.* 5 (2015) 1402279.
- [4] X.Y. Chia, A.Y.S. Eng, A. Ambrosi, S.M. Tan, M. Pumera, *Chem. Rev.* 115 (2015) 11941–11966.
- [5] X. Ding, Y. Li, J. Zhao, Y. Zhu, Y. Li, W. Deng, C. Wang, *APL Mater.* 3 (2015) 104410.
- [6] S.J.A. Moniz, S.A. Shevlin, D.J. Martin, Z.X. Guo, J. Tang, *Energy Environ. Sci.* 8 (2015) 731–759.
- [7] K. Iwashina, A. Iwase, Y.H. Ng, R. Amal, A. Kudo, *J. Am. Chem. Soc.* 137 (2015) 604–607.
- [8] B.H. Wu, D.Y. Liu, S. Mubeen, T.T. Chuong, M. Moskovits, G.D. Stucky, *J. Am. Chem. Soc.* 138 (2016) 1114–1117.
- [9] J.S. DuChene, B.P. Williams, A.C. Johnston-Peck, J.J. Qiu, M. Gomes, M. Amilhan, D. Bejleri, J.N. Weng, D. Su, F.W. Huo, E.A. Stach, W.D. Wei, *Adv. Energy Mater.* 6 (2016) 1501250.
- [10] Z.H. Deng, L. Li, W. Ding, K. Xiong, Z.D. Wei, *Chem. Commun.* 51 (2015) 1893–1896.
- [11] N. Waiskopf, Y. Ben-Shahar, M. Galchenko, I. Carmel, G. Moshitzky, H. Soreq, U. Banin, *Nano Lett.* (2016). <http://dx.doi.org/10.1021/acs.nanolett.6b01298>.
- [12] H. He, J. Lin, W. Fu, X. Wang, H. Wang, Q. Zeng, Q. Gu, Y. Li, C. Yan, B.K. Tay, C. Xue, X. Hu, S.T. Pantelides, W. Zhou, Z. Liu, *Adv. Energy Mater.* (2016). <http://dx.doi.org/10.1002/aenm.201600464>.
- [13] M.Z. Liu, J.L. Lyons, D.H. Yan, M.S. Hybertsen, *Adv. Funct. Mater.* 26 (2016) 219–225.

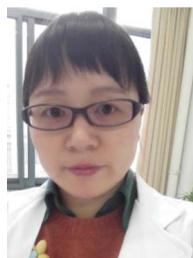
- [14] K. Chang, X. Hai, J. Ye, *Adv. Energy Mater.* 6 (2016) 1502555.
- [15] S. Xu, D. Li, P. Wu, *Adv. Funct. Mater.* 25 (2015) 1127–1136.
- [16] A. Vojvodic, B. Hinnemann, J.K. Nørskov, *Phys. Rev. B* 80 (2009) 125416.
- [17] J. Zhang, X. Jin, P.I. Morales-Guzman, X. Yu, H. Liu, H. Zhang, L. Razzari, J.P. Claverie, *ACS Nano* 10 (2016) 4496–4503.
- [18] X. Wei, C. Shao, X. Li, N. Lu, K. Wang, Z. Zhang, Y. Liu, *Nanoscale* 8 (2016) 11034–11043.
- [19] X. Li, X. Ren, F. Xie, Y. Zhang, T. Xu, B. Wei, W.C.H. Choy, *Adv. Opt. Mater.* 3 (2015) 1220–1231.
- [20] X. Zhang, Y.L. Chen, R.S. Liu, D.P. Tsai, *Rep. Prog. Phys.* 76 (2013) 046401.
- [21] T.T. Zhuang, Y. Liu, M. Sun, S.L. Jiang, M.W. Zhang, X.C. Wang, Q. Zhang, J. Jiang, S.H. Yu, *Angew. Chem. Int. Ed.* 54 (2015) 11495–11500.
- [22] Z.B. Zhan, F. Grote, Z.J. Wang, R. Xu, Y. Lei, *Adv. Energy Mater.* 5 (2015) 1501654.
- [23] Y.M. Kang, Y.J. Gong, Z.J. Hu, Z.W. Li, Z.W. Qiu, X. Zhu, P.M. Ajayan, Z.Y. Fang, *Nanoscale* 7 (2015) 4482–4488.
- [24] S.F. Hung, F.X. Xiao, Y.Y. Hsu, N.T. Suen, H.B. Yang, H.M. Chen, B. Liu, *Adv. Energy Mater.* 6 (2016) 1501339.
- [25] R. Jiang, B. Li, C. Fang, J. Wang, *Adv. Mater.* 26 (2014) 5274–5309.
- [26] G.Y. Yu, X. Wang, J.G. Cao, S.J. Wu, W.F. Yan, G. Liu, *Chem. Commun.* 52 (2016) 2394–2397.
- [27] X. Li, X. Ren, Y. Zhang, W.C. Choy, B. Wei, *Nanoscale* 7 (2015) 11291–11299.
- [28] H. Zhu, J.F. Zhang, R.P. Yanzhang, M.L. Du, Q.F. Wang, G.H. Gao, J.D. Wu, G.M. Wu, M. Zhang, B. Liu, J.M. Yao, X.W. Zhang, *Adv. Mater.* 27 (2015) 4752–4759.
- [29] X. Ma, K. Zhao, H.J. Tang, Y. Chen, C.G. Lu, W. Liu, Y. Gao, H.J. Zhao, Z.Y. Tang, *Small* 10 (2014) 4664–4670.
- [30] W. Gao, Y.H. Lee, R.B. Jiang, J.F. Wang, T.X. Liu, X.Y. Ling, *Adv. Mater.* 28 (2016) 701–706.
- [31] S.S. Chen, Y. Qi, T. Hisatomi, Q. Ding, T. Asai, Z. Li, S.S.K. Ma, F.X. Zhang, K. Domen, C. Li, *Angew. Chem. Int. Ed.* 54 (2015) 8498–8501.
- [32] S.C. Han, L.F. Hu, N. Gao, A.A. Al-Ghamdi, X.S. Fang, *Adv. Funct. Mater.* (24) (2014) 3725–3733.
- [33] C. Li, X. Zhu, H. Zhang, Z. Zhu, B. Liu, C. Cheng, *Adv. Mater. Int.* 2 (2015) 1500428.
- [34] S. Guo, X. Li, J. Zhu, T. Tong, B. Wei, *Small* (2016). <http://dx.doi.org/10.1002/sml.201602122>.
- [35] S. Zu, B. Li, Y. Gong, Z. Li, P.M. Ajayan, Z. Fang, *Adv. Opt. Mater.* (2016). <http://dx.doi.org/10.1002/adom.201600188>.
- [36] H.A. Atwater, A. Polman, *Nat. Mater.* 9 (2010) 205–213.
- [37] M. Wang, M. Ye, J. Iocozzia, C. Lin, Z. Lin, *Adv. Sci.* (2016). <http://dx.doi.org/10.1002/advs.201600024>.
- [38] Y. Shi, J. Wang, C. Wang, T.T. Zhai, W.J. Bao, J.J. Xu, X.H. Xia, H.Y. Chen, *J. Am. Chem. Soc.* 137 (2015) 7365–7370.
- [39] H. Huang, L. Zhang, Z.H. Lv, R. Long, C. Zhang, Y. Ling, K.C. Wei, C.M. Wang, L. Chen, Z.Y. Li, Q. Zhang, Y. Luo, Y.J. Xiong, *J. Am. Chem. Soc.* 138 (2016) 6822–6828.
- [40] L. Ma, S. Liang, X.L. Liu, D.J. Yang, L. Zhou, Q.Q. Wang, *Adv. Funct. Mater.* 25 (2015) 898–904.
- [41] A.J. Cheah, W.S. Chiu, P.S. Khiew, H. Nakajima, T. Saisopa, P. Songsiririthigul, S. Radiman, M.A.A. Hamid, *Catal. Sci. Technol.* 5 (2015) 4133–4143.
- [42] Z. Yin, B. Chen, M. Bosman, X. Cao, J. Chen, B. Zheng, H. Zhang, *Small* 10 (2014) 3537–3543.
- [43] Y. Hu, Y. Liu, Z. Li, Y. Sun, *Adv. Funct. Mater.* 24 (2014) 2828–2836.
- [44] X. Ji, W. Yang, *Chem. Sci.* 5 (2014) 311–323.
- [45] F. Pastorelli, S. Bidault, J. Martorell, N. Bonod, *Adv. Opt. Mater.* 2 (2014) 171–175.
- [46] C. An, S. Wang, Y. Sun, Q. Zhang, J. Zhang, C. Wang, J. Fang, *J. Mater. Chem. A* 4 (2016) 4336–4352.
- [47] Y. Sun, J.J. t. Foley, S. Peng, Z. Li, S.K. Gray, *Nano Lett.* 13 (2013) 3958–3964.
- [48] M. Chen, J. Gu, C. Sun, Y. Zhao, R. Zhang, X. You, Q. Liu, W. Zhang, Y. Su, H. Su, D. Zhang, *ACS Nano* (2016). <http://dx.doi.org/10.1021/acsnano.6b01999>.
- [49] D.O. Sgile, L.W. Zhang, S. Ithurria, B. Dubertret, J.J. Baumberg, *J. Phys. Chem. Lett.* 6 (2015) 1099–1103.
- [50] N.G. Bastus, J. Comenge, V. Puentes, *Langmuir* 27 (2011) 11098–11105.
- [51] S.Q. He, W.E.I. Sha, L.J. Jiang, W.C.H. Choy, W.C. Chew, Z.P. Nie, *IEEE Trans. Nanotechnol.* 11 (2012) 336–345.
- [52] P.B. Johnson, R.W. Christy, *Phys. Rev. B* 6 (1972) 4370–4379.
- [53] X. Ren, Z. Huang, X. Wu, S. Lu, H. Wang, L. Wu, S. Li, *Comput. Phys. Commun.* 183 (2012) 1192–1200.
- [54] J. Xiong, Y. Liu, D. Wang, S. Liang, W. Wu, L. Wu, *J. Mater. Chem. A* 3 (2015) 12631–12635.
- [55] C.Y. Chen, H. Qiao, S.H. Lin, C.M. Luk, Y. Liu, Z.Q. Xu, J.C. Song, Y.Z. Xue, D.L. Li, J. Yuan, W.Z. Yu, C.X. Pan, S.P. Lau, Q.L. Bao, *Sci. Rep.* 5 (2015) 11830.
- [56] J.P. Lu, J.H. Lu, H.W. Liu, B. Liu, L.L. Gong, E.S. Tok, K.P. Loh, C.H. Sow, *Small* 11 (2015) 1792–1800.
- [57] Z.H. Sun, Z. Yang, J.H. Zhou, M.H. Yeung, W.H. Ni, H.K. Wu, J.F. Wang, *Angew. Chem. Int. Ed.* 48 (2009) 2881–2885.
- [58] S. Samanta, S. Martha, K. Parida, *Chemcatchem* 6 (2014) 1453–1462.
- [59] A. Tanaka, S. Sakaguchi, K. Hashimoto, H. Kominami, *ACS Catal.* 3 (2013) 79–85.
- [60] J. Fang, S.W. Cao, Z. Wang, M.M. Shahjamali, S.C.J. Loo, J. Barber, C. Xue, *Int. J. Hydrog. Energy* 37 (2012) 17853–17861.
- [61] O. Rosseler, M.V. Shankar, M.K.L. Du, L. Schmidlin, N. Keller, V. Keller, J. Catal. 269 (2010) 179–190.
- [62] F. Carraro, L. Calvillo, M. Cattelan, M. Favaro, M. Righetto, S. Nappini, I. Pis, V. Celorrio, D.J. Fermin, A. Martucci, S. Agnoli, G. Granozzi, *ACS Appl. Mater. Interfaces* 7 (2015) 25685–25692.
- [63] U. Bhanu, M.R. Islam, L. Tetard, S.I. Khondaker, *Sci. Rep.* 4 (2014) 5575.



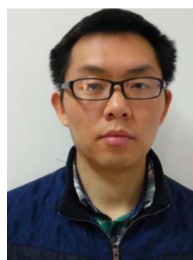
Dr. Xuanhua Li received his B.S. degree from Wuhan University of Technology in 2007, and M.S. degree from USTC in 2010. After that, he started his doctoral studies and received a Ph.D. degree at Department of Electrical and Electronic Engineering, University of Hong Kong in 2014. After a short research in the Institute of Intelligent Machines, CAS, he began his career at the Center of Nano Energy Materials, Northwestern Polytechnical University as a professor. His research is focused on synthesis of 2D nanomaterials and novel metal NPs. He is also interested in plasmon-enhanced solar cells, photocatalytic reaction, and optical sensors.



Shaohui Guo received his B.S. degree from NorthWestern Polytechnical University in 2014, and he is now an M.S. candidate at Northwestern Polytechnical University under the supervision of Professor Bingqing Wei and Professor Xuanhua Li. His current research includes the development of nanostructured materials for photocatalysis and surface enhanced Raman scattering (SERS).



Dr. Caixia Kan graduated with Ph.D. degree from Institute of Solid State Physics, Chinese Academy of Sciences in 2004. In 2002, she worked in the Max-Planck-Institute of Microstructure Physics (Germany) with the cooperation of TEM study. She received post-doctoral training in Nanjing University in 2006. Then she assumed current position in College of Science, Nanjing University of Aeronautics and Astronautics and became a professor in 2009. Her research was focused on noble metal nanostructures, which was supported by 2 National Natural Science Foundation grants.



Jinmeng Zhu received his bachelor degree in Mineral Processing and Engineering at Henan Polytechnic University in 2012. Then, he moved to Xi'an University of Science and Technology to do research on SiO₂ aerogel and received his master degree in 2015. During the post-graduate, he developed great interest in the synthesis and application of nanomaterials. Now, he is pursuing his doctoral degree at Northwestern Polytechnical University under the supervision of Professor Bingqing Wei and Professor Xuanhua Li. His research focus on the synthesis and related applications of two-dimensional nanosheets (e.g. graphene, BN, MoS₂) and their hybrids.



Tengfeng Tong received his B.S. degree from Anhui University Of Technology in 2014, and he is now an M.S. candidate at Northwestern Polytechnical University under the supervision of Professor Bingqing Wei and Professor Xuanhua Li. His research focuses on perovskite solar cells.



Shanlin Ke received his B.S. degree in Physics from Hubei Normal University in 2008, and obtained the M.S. degree in Condensed Matter Physics from the College of Science, Nanjing University of Aeronautics and Astronautics (NUAA) in 2013. After that, he worked as a Research Assistant at Aalto University, Finland. Currently, he is working on his Ph.D. program in the Department of Applied Physics, NUAA. His research areas include Plasmonics and Noble-metal nanomaterials.



Dr. Bingqing Wei is a Professor in the Department of Mechanical Engineering at the University of Delaware, USA. He was an Assistant Professor in the Department of Electrical & Computer Engineering and Center for Computation & Technology at Louisiana State University from 2003 to 2007. From 2000 to 2003, he was a Research Scientist at Rensselaer Polytechnic Institute, Department of Materials Science and Engineering and Rensselaer Nanotechnology Center. Dr. Wei was a visiting scientist at Max-Planck-Institut für Metallforschung, Stuttgart, Germany in 1998 and 1999. From 1992 to 2001, he was a faculty member at Tsinghua University in Beijing.



Wallace Choy received his Ph.D. Degree from University of Surrey, UK in 1999. After his work in NRC Canada and Fujitsu, he is now a professor of HKU. His research interests are organic/inorganic optoelectronic devices, plasmonic structures, and nano-material devices and physics. He was the Top 1% of most-cited scientists in Thomson Reuter's Essential Science Indicators in 2014 and 2015. He has published over 160 journal papers, seven book chapters, US and China patents and edited one book published in Springer. He serves as Editorial Board Member of Scientific Reports and J Physics D, senior editor of IEEE Photonics Journal, topical editor of OSA JOSA-B.