

The reduction mechanism of HAuCl_4 on the surface of edge-rich molybdenum disulfide

Yuan Yuan^{a,c}, Wei-quan Zhan^{a,b}, Feifei Jia^{a,*}, Shaoxian Song^a, Alejandro López-Valdivieso^c

^a Hubei Key Laboratory of Mineral Resources Processing and Environment, Wuhan University of Technology, Luoshi Road 122, Wuhan, Hubei 430070, China

^b Instituto de Física, Universidad Autónoma de San Luis Potosí, Av. Manuel Nava 6, Zona Universitaria, C.P., San Luis Potosí 78290, Mexico

^c Instituto de Metalurgia, Universidad Autónoma de San Luis Potosí, Av. Sierra Leona 550, Lomas de San Luis, C.P., San Luis Potosí 78210, Mexico

ARTICLE INFO

Keywords:

Edge-rich
Molybdenum disulfide
 HAuCl_4
Reduction

ABSTRACT

The reduction mechanism and behaviors of HAuCl_4 on the surface of edge-rich molybdenum disulfide (ER-MoS₂) was explored based on atomic force microscopy (AFM) in this work. ER-MoS₂ was prepared through a simple thermal modification process. It was found that edges on MoS₂ could enhance the reduction ability of HAuCl_4 . There were large and plenty of gold particles on the edges, which was due to the high electrons transfer rate and transferred efficiency of photo-generated electrons-holes pairs. The light could facilitate the transfer of photo-electrons and then enhance the surface potential, thus promoting the reduction of HAuCl_4 on it. The edges of ER-MoS₂ could promote the reduction as well as growth of Au⁰. Furthermore, the new appearance of Au particles on edges had a strong influence on the surface potential of ER-MoS₂. The work provided an insight view on the role of edge in the control and growth of noble metal nanoparticles on MoS₂ substrate.

1. Introduction

Gold, a kind of noble metals (including Au, Ag, Pt, etc.) [1], exhibited enormous potential in biomedicine [2], water purification [3] and even cancer therapy [4] due to its high electrical conductivity and corrosion resistance. Whereas, gold nanoparticles were easy to aggregate in the synthesis process because of the high surface energy [5–7]. Supporting gold nanoparticles on substrates was an effective way to solve the aggregation problem [8,9]. Moreover, the merger of substrate and gold nanoparticles would strengthen performances [10] (such as Raman effect, electrocatalytic activity, or bio-imaging) of individual gold nanoparticles or substrates.

Molybdenum disulfide (MoS₂) was a promising material among layered transition-metal dichalcogenide [11–13]. MoS₂ with a “sandwich” type structure (S-Mo-S) in which Mo atoms were located between two layers of S atoms possessed a bandgap between 1.29 and 1.90 eV dependent on its thickness [14], which endowed it with these advantages: capacity of absorbing visible light and a high on/off current range and low off-state current [15]. Thus, MoS₂ had an exciting prospect as substrate for the support of gold nanoparticles in the application of optoelectronic and nanoelectronic devices [16].

It had been widely researched of the decoration of MoS₂ with gold

nanoparticles for controlling over the optical and photoelectrical properties [17]. Various methods (including wet, annealing and microwave-assisted hydrothermal method) were employed to prepare gold nanoparticles and MoS₂ hybrids [18–20]. Besides, the size and distribution of gold nanoparticles on the MoS₂ could be well regulated under solution environment. In these researches, Au atoms tended to form clusters on surface of MoS₂, thus exhibiting a strong Raman signal enhancement and catalytic ability [21]. HAuCl_4 approached to the surface of MoS₂ and then were reduced into Au nanoparticles and grew on MoS₂ [22,23]. It was found in the applications of MoS₂ that vacancies would affect the electronic properties [24–26]. However, the mechanism about the interaction between Au nanoparticles and defects on MoS₂ was still under the veil.

In this article, the decoration of HAuCl_4 on ER-MoS₂ in different solution environments was observed through atomic force microscopy (AFM). AFM was applied for observing the morphologies as well as studying the reaction mechanism. The structure and optical properties of ER-MoS₂ before and after reduction of HAuCl_4 were analyzed. The attempt was aimed to make a clear understanding of the mechanism and behaviors of the reduction of HAuCl_4 on the surface of ER-MoS₂ as substrate.

* Corresponding author.

E-mail address: feifeijia@whut.edu.cn (F. Jia).

<https://doi.org/10.1016/j.surfin.2022.102199>

Received 20 January 2022; Received in revised form 27 June 2022; Accepted 9 July 2022

Available online 14 July 2022

2468-0230/© 2022 Published by Elsevier B.V.

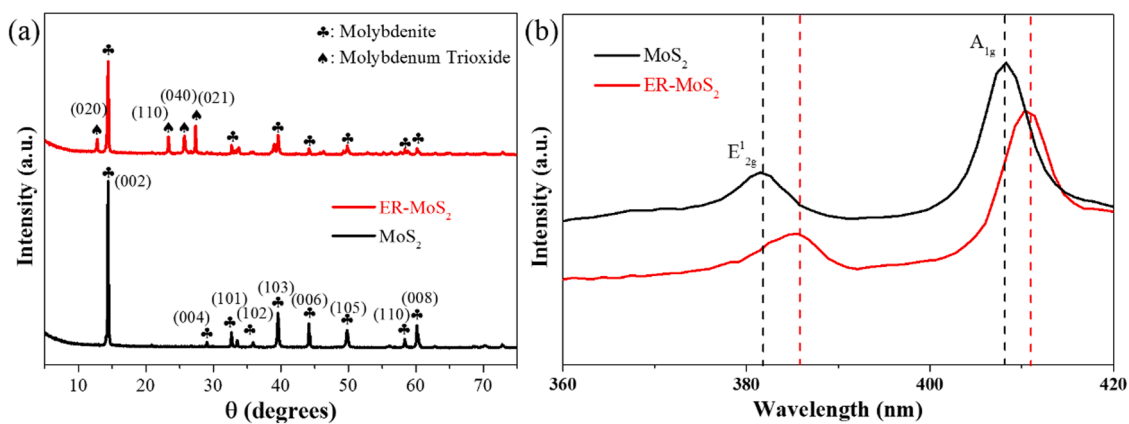


Fig. 1. XRD patterns (a) and Raman spectra (b) of MoS₂ and ER-MoS₂.

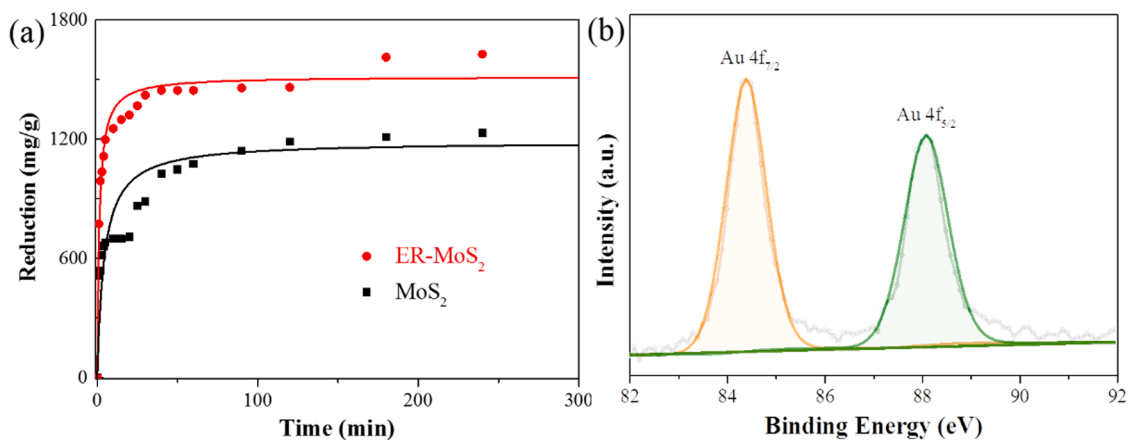


Fig. 2. Reduction performances of HAuCl₄ on MoS₂ and ER-MoS₂ (a); XPS spectra of ER-MoS₂ after the reduction of HAuCl₄ (b).

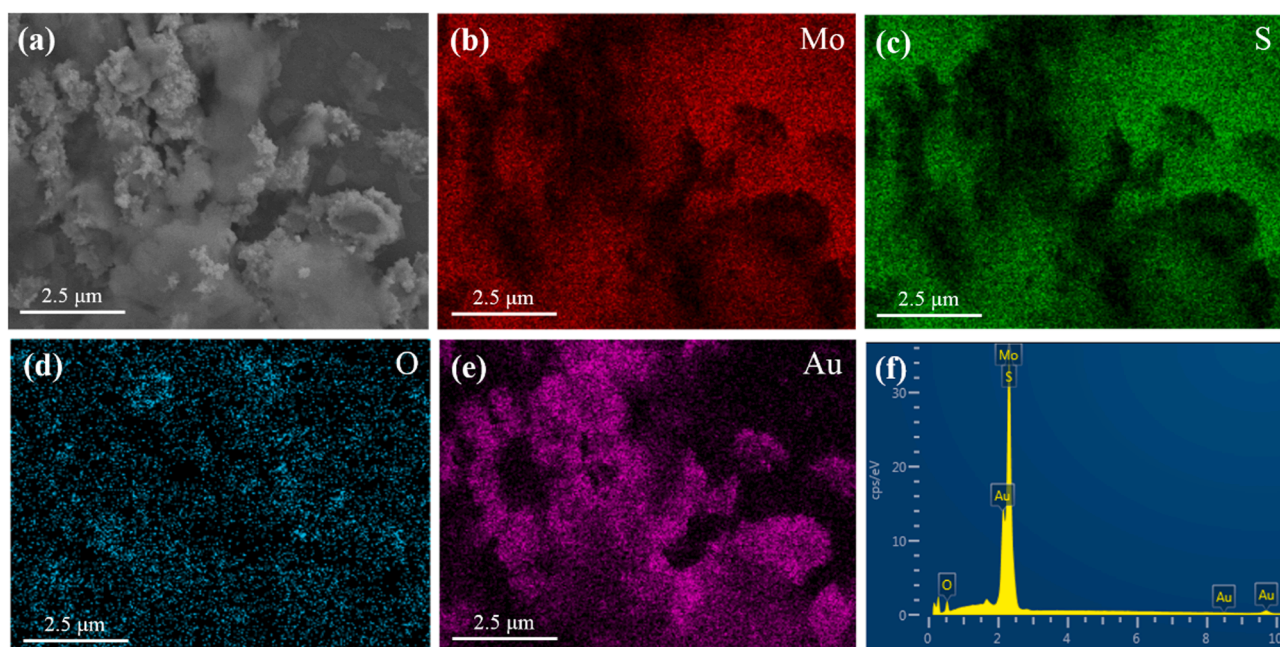


Fig. 3. SEM images of ER-MoS₂ after the reduction of HAuCl₄.

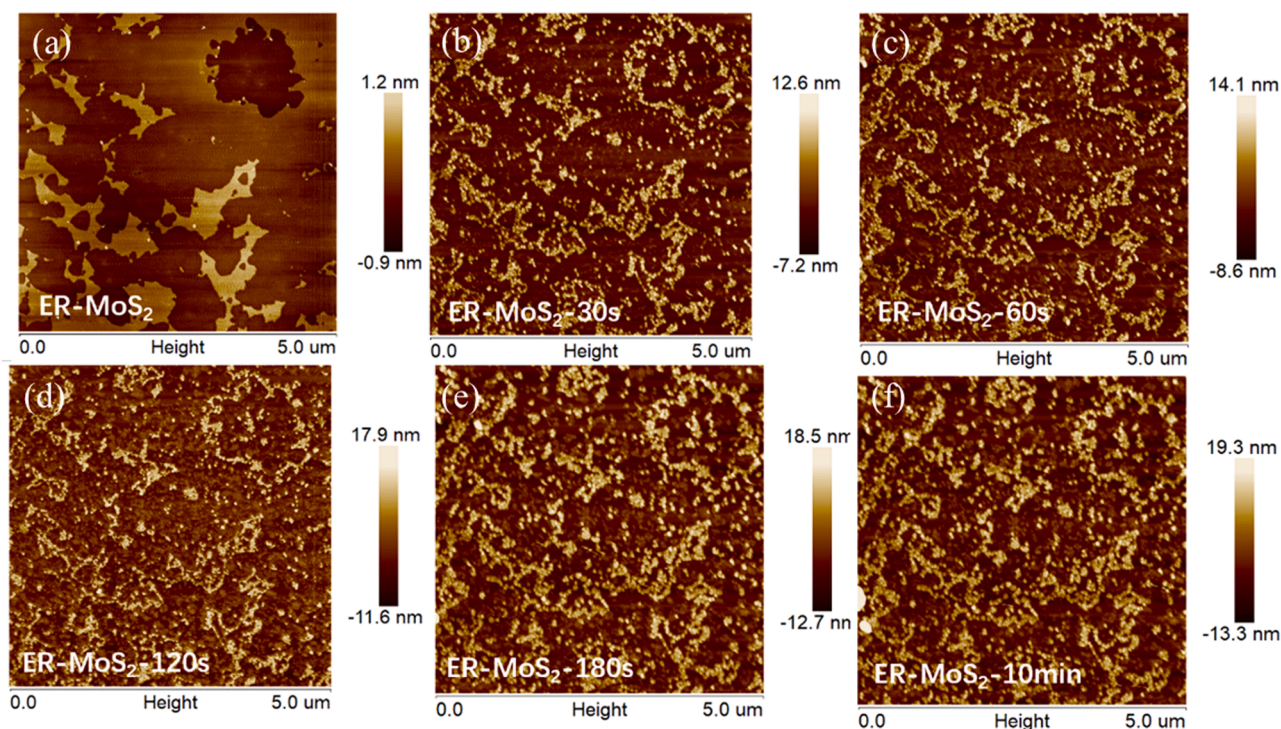


Fig. 4. *In-situ* reduction of HAuCl_4 on the surface of ER- MoS_2 using AFM after: 0s (a), 30s (b), 60s (c), 120s (d), 180s (e) and 600s (f).

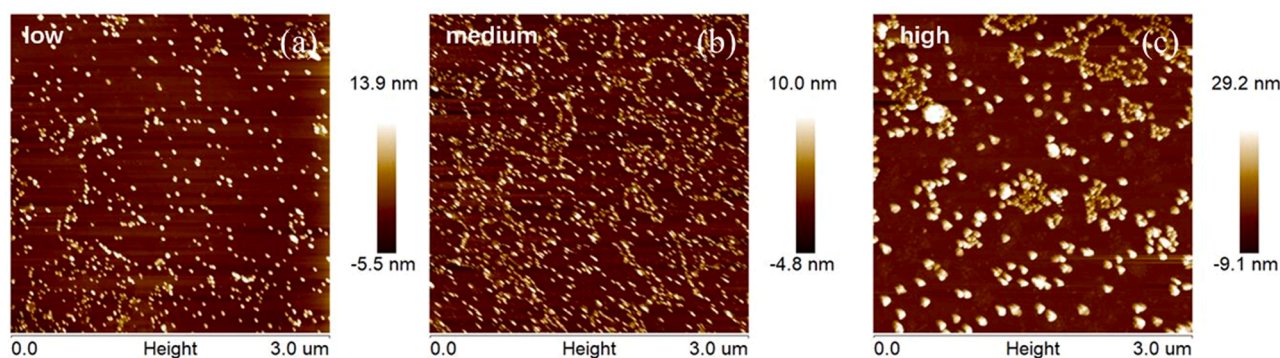


Fig. 5. AFM images of ER- MoS_2 after being exposed to HAuCl_4 under 420–780 nm irradiation with different light intensities: low light intensity (100 W) (a), medium light intensity (200 W) (b), and high light intensity (300 W) (c).

2. Experimental

2.1. Materials

Molybdenite used in the work was bought from Wuzhou Mine, Guangxi Province, China. Standard chloroauric acid (HAuCl_4 , 1000 mg/L) was purchased from Well Group Scientific Ltd., USA. Deionized water with a resistivity of 18.2 $\text{M}\Omega\text{ cm}$ was produced by Millipore SAS, France.

2.2. Preparation of ER- MoS_2

The ER- MoS_2 sample was prepared through a simple thermal treatment on molybdenite. Molybdenite was put in a ceramic crucible, and then was heated from room temperature to 500 $^\circ\text{C}$ with a heating rate of 10 $^\circ\text{C}/\text{min}$ in a muffle furnace (Vulcan 3–550), as described in previous literature [27]. When the reaction was over, the samples were washed with distilled water and then filtrated while the sample for AFM observation was with no further treatment.

2.3. AFM measurements

The reduction process of HAuCl_4 on the surface of samples were observed by the AFM and KPFM measurements which were conducted with a Bruker Multimode 8 system. For the normal morphology observation, the MoS_2 and ER- MoS_2 samples could directly be researched by AFM due to their super-flat surface which was the natural properties of this sandwich-like material. All the details of experiments were totally the same as our previous work [21]. For the KPFM test, however, the conductive silver pulp was needed to make sure the good conductivity of the tip-sample-sample table system since the conductivity of natural molybdenite was weak. The conductive silver pulp was a mixture of silver and vaseline which could transfer from liquid to solid form which exhibited excellent conductivity of electricity when heated. An appropriate amount of the liquid conductive silver should be injected to the brims of samples, to make sure that a good connection would be well conducted between the sample and substrate. Then the sample would be heated at 60 $^\circ\text{C}$ for 20 min to dry up. Then the surface potential function of AM-KPFM module under Electrical and Magnetic Lift Mode was

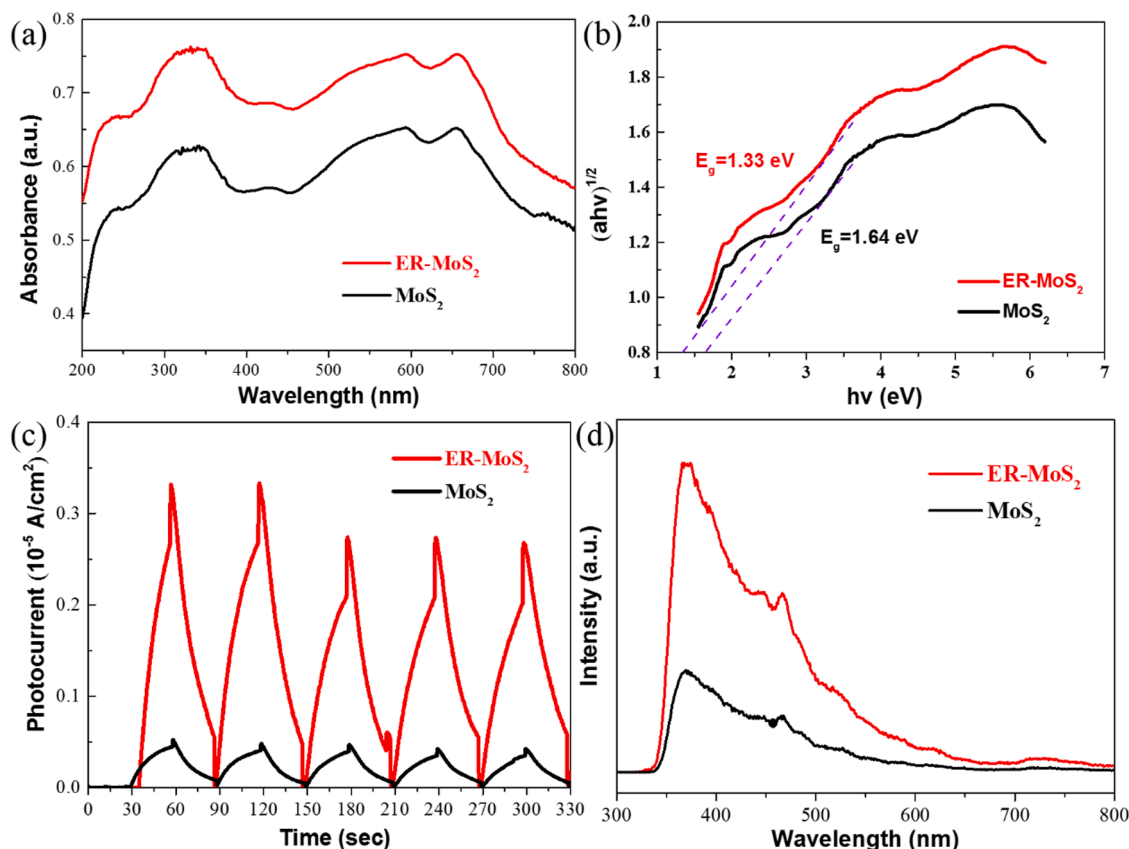


Fig. 6. UV-Vis spectra (a), Bandgap energies (b), photocurrent responses (c) and photoluminescence spectra (d) of MoS₂ and ER-MoS₂.

mainly used to realize the electrical tests, where the life height of the tip was set as 90 nm and the scanning rate was 0.977Hz to guarantee the best results. KPFM provided an image of the local work function of the surface in parallel to the acquisition of the topography image. It is used for measuring the work function [28].

2.4. HAuCl₄ reduction experimental

Batch experiments were performed for studying the reduction abilities of HAuCl₄ on MoS₂ and ER-MoS₂. Reduction kinetics studies of HAuCl₄ on samples were carried out at pH of 1 with the HAuCl₄ concentration of 100 mg/L. 10 mg of MoS₂ and ER-MoS₂ samples were added to the HAuCl₄ solution and the solution was shaken at 150 rpm. At certain time, 1~2 mL suspension was extracted and then filtered by filter membrane. The concentration of gold was detected using AAS analysis. The reduction capacity was calculated by the following equation:

$$q = \frac{C_0 V_0 - C_f V_f}{m}$$

where q was reduction capacity (mg/g); V_0 and V_f meant the volume (L) of reaction solution before and after reduction, respectively; C_0 and C_f represented the Au concentration (mg/L) before and after reaction, respectively; m was the amount of samples (mg).

2.5. Characterization

XRD patterns were detected by a D8 Advance X-ray diffractometer. A Zeiss Gemini 300 electron microscope was applied for obtaining SEM images and corresponding EDS of samples. An INVIA Raman microscope with a 514.5 nm Ar laser was carried out to record Raman patterns. A ESCALB 250 Xi photoelectron spectrometer was used to get the XPS spectrum. A UV-Vis spectrophotometer (Lambda 750S UV-Vis, USA) was

used to record ultraviolet visible absorption spectrum. Photoluminescence spectrum were obtained on excitation with a wavelength of about 325 nm using a Xe lamp as the excitation source on Edinburgh FLS1000. A CHI1030B electrochemical station was applied for test the electrochemical characterizations. The test was conducted in three electrode cell system. The working electrode, counter electrode and reference electrode were ITO glass deposited with reductants, Pt flake and saturated calomel electrode. 10 mg samples were dispersed in ethanol containing 0.5% nafion under ultrasound for 1 h. Photocurrent measurements were measured with xenon lamp with light intensity of 300 W. Electrochemical impedance spectroscopy was detected in a 1 M potassium ferricyanide solution.

3. Results and discussion

3.1. Structure characterization

The micro-structure of MoS₂ and ER-MoS₂ were detected by XRD and Raman. Fig. 1a exhibited XRD patterns of MoS₂ and ER-MoS₂. It was clear that the diffraction peaks at 2θ of 14.38°, 29.02°, 32.67°, 35.87°, 39.54°, 44.15°, 49.79°, 58.31° and 60.12° of molybdenite could all be ascribed to the diffraction planes of (002), (004), (101), (102), (103), (006), (105), (110) and (008) in MoS₂ [29], indicating the sample with high purity. After thermal modification, the diffraction peaks at 2θ = 12.77°, 23.36°, 25.71° and 27.34° allotted to the planes of (020), (110), (040) and (021) originated from molybdenum trioxide (MoO₃) [30], which demonstrated the oxidation of MoS₂. Raman spectra of MoS₂ and ER-MoS₂ were given in Fig. 1b. The characteristic peaks at 381.52 cm⁻¹ and 408.23 cm⁻¹ in-plane E_{2g}¹ mode and out-of-plane A_{1g} mode of MoS₂ were observed in the samples [31]. The characteristic peaks at 381.52 cm⁻¹ and 408.23 cm⁻¹ in-plane E_{2g}¹ mode and out-of-plane A_{1g} mode of MoS₂ were observed in the samples. The dependence of E_{1g}² mode

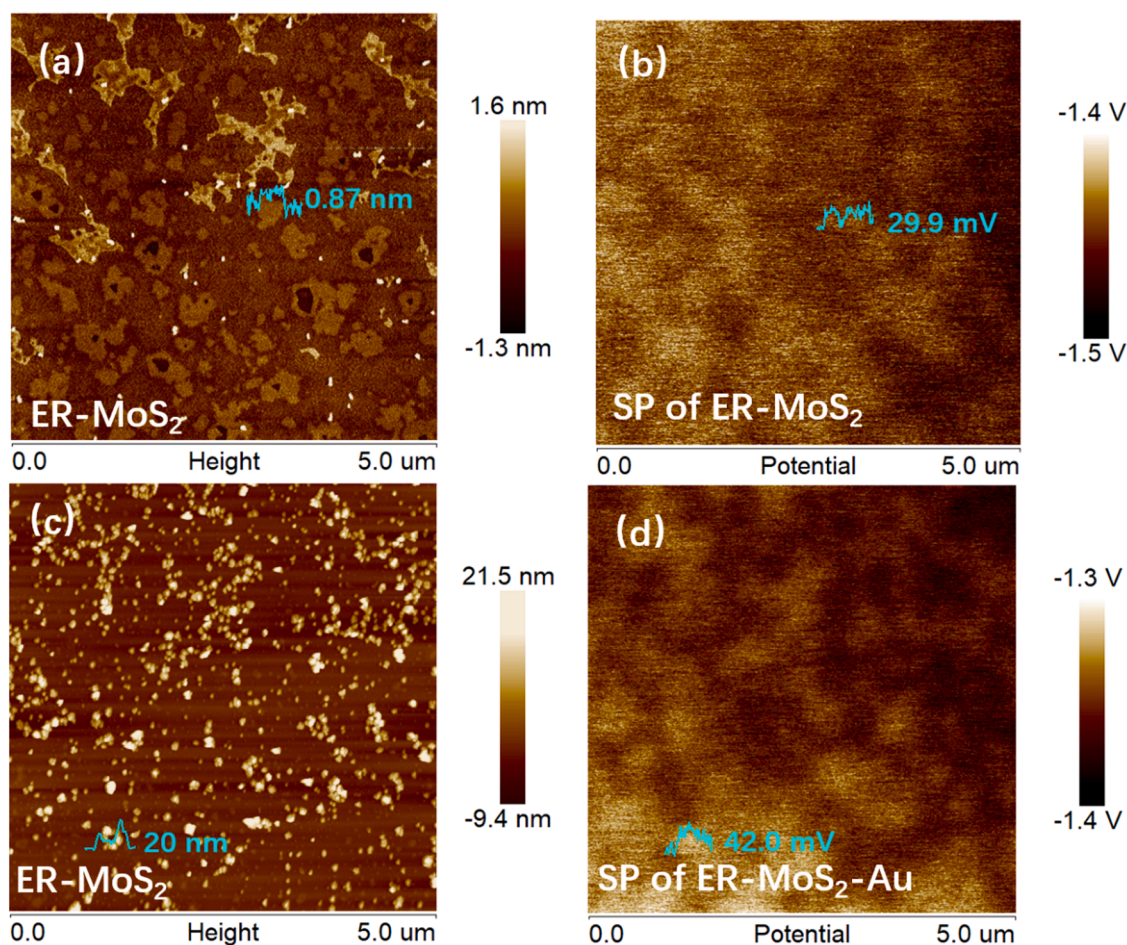


Fig. 7. Morphology and SP distribution of ER-MoS₂ before (a, b) and after (c, d) the reduction of HAuCl₄, respectively.

wavelength on the layer has been studied. The interaction between Mo atoms decreases with the increase of layer number because of the enhanced dielectric tensor. In addition, as the A_{1g} mode wavenumber increased, the restoring forces on S atoms improved [32]. When the thickness of MoS₂ became thinner, the van der Waals force between layers decreases and the coupling interaction between layers disappeared gradually, leading to the shift of E_{1g}^{2s} and A_{1g}. Compared with the peaks of MoS₂, the peaks of E_{1g}^{2s} and A_{1g} of ER-MoS₂ showed a slight red shift, indicating the decrease of thickness as well as the oxidation of MoS₂, which was agreed with previous work [33].

3.2. Reduction performance

After further treatment using deionized water and filtered until no MoO₃ was detected, DR-MoS₂ was used for reduction experiment. The reduction performances of HAuCl₄ on MoS₂ and ER-MoS₂ were investigated under natural light, and the corresponding results were shown in Fig. 2a. As seen, with the increase of time, the reduction capacity of HAuCl₄ on both MoS₂ and ER-MoS₂ occurred very fast in the first 30 min, then achieving an equilibrium within 60 min. In addition, both the reduction rate and equilibrium reduction capacity of ER-MoS₂ was higher than that of MoS₂, expressing that the vacancy on ER-MoS₂ would significantly improve the reduction ability. Fig. 2b displayed the Au 4f spectra of ER-MoS₂ after the reduction of HAuCl₄. Two peaks observed at 84.4 and 88.1 eV were assigned to Au⁰ 4f_{7/2} and 4f_{5/2} [34], respectively, which demonstrated that HAuCl₄ was reduced into Au⁰ on ER-MoS₂.

Fig. 3 showed the SEM images of ER-MoS₂ after reducing HAuCl₄. It was obvious that the same distribution of Mo and S on the surface.

Uniform distribution of O on the surface. Fig. 3e and f demonstrated that plenty of gold was present on ER-MoS₂, while no elemental Cl was detected, which demonstrated the reduction of HAuCl₄ on ER-MoS₂.

In order to further study on the reduction behaviors of HAuCl₄ on ER-MoS₂, the AFM was applied on observing ER-MoS₂ after being exposed to HAuCl₄ solution for 0s, 30s, 60s, 120s, 180s and 600s (Fig. 4). It was clear that compared to the facet of ER-MoS₂, there were always plenty of Au particles gathering on the edges. Besides, the number of larger particles on edges were getting saturation quickly within 30s, while the number of small ones on the facet firstly ascended and then declined to form large particles on edges. The lateral size of Au particles was getting large, which might result from the gather of Au particles.

The reduction behaviors of HAuCl₄ on ER-MoS₂ under different light intensities were exhibited in Fig. 5. When the light intensity increased, the lateral size and thickness of nanoparticles increased. The phenomenon could be ascribed to the fact that higher light intensity enabled ER-MoS₂ produce more electrons, which promoted the growth of Au particles.

3.3. Reduction mechanism

The optical properties of MoS₂ and ER-MoS₂ were explored by UV-Vis measurements, as expressed in Fig. 6a. The characteristic absorption peaks are located in the range of 300–400 and 500–700 nm, which are consistent to the general characteristics of MoS₂ with trigonal prismatic coordination. It was obvious that ER-MoS₂ had good adsorption in the visible light and ultraviolet region [35]. Moreover, the band energies of MoS₂ and ER-MoS₂ were calculated as the following equations:

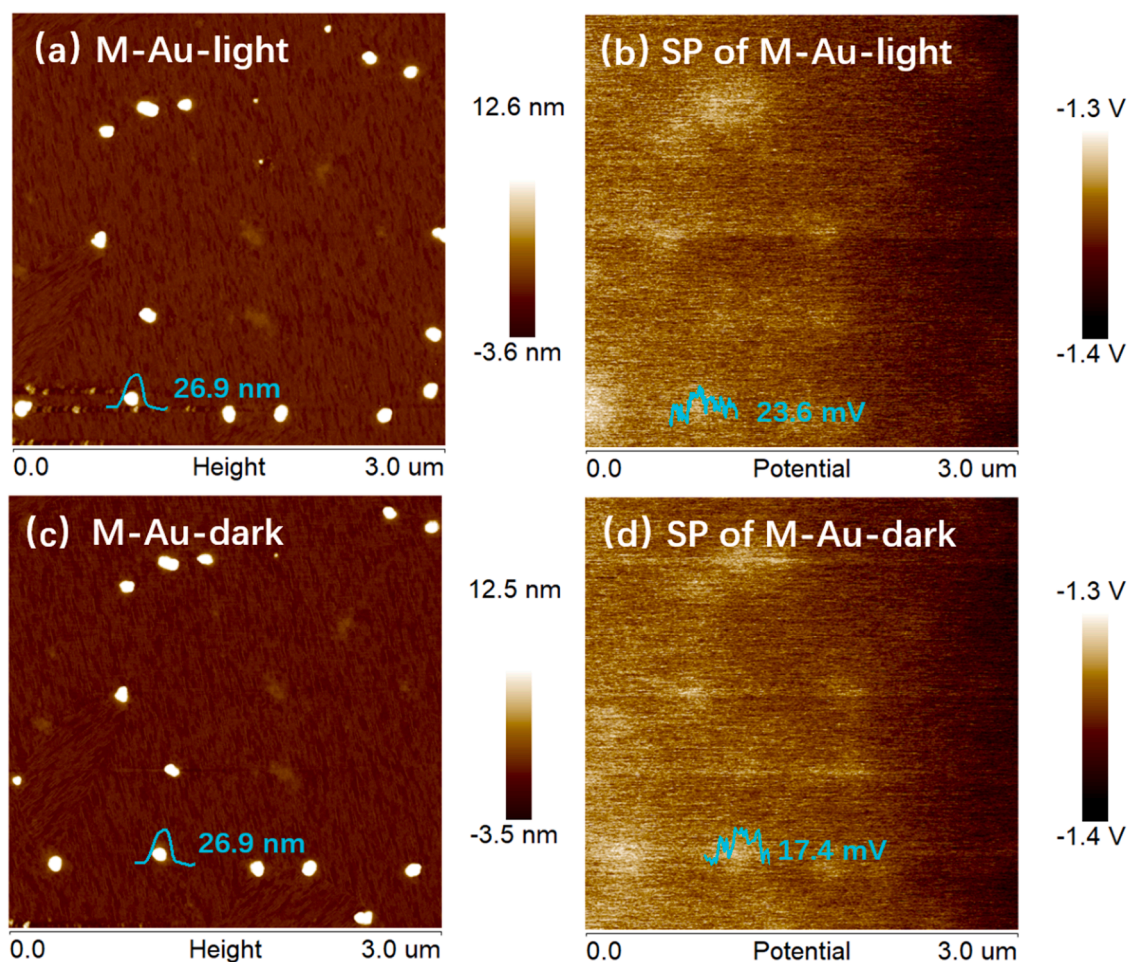


Fig. 8. Morphology and SP distribution of ER-MoS₂ after the reduction of HAuCl₄ under light (a, b) and dark (c, d) conditions.

$$(\alpha h\nu)^n = A(h - E_g)$$

where α represented the adsorption coefficient, h was the Planck's constant, ν and E_g meant the light frequency and the band constant, respectively, n was a constant which depended on the electronic transition of the semiconductor, and $n = 2$ for MoS₂ in the work. In Fig. 6b, compared with the band gap energy of MoS₂ (1.33 eV), the band gap of ER-MoS₂ decreased, which demonstrated that ER-MoS₂ possessed higher electron transfer rate.

The photocurrent responses (Fig. 6c) showed that the photocurrent of ER-MoS₂ was higher than MoS₂, indicating that ER-MoS₂ was quite responsive to light irradiation. Meanwhile, photoluminescence analysis was a key measurement to explore the efficiency of photogenerated electrons transfer and recombination. Fig. 6d revealed that ER-MoS₂ had stronger emission intensity than MoS₂, which could be ascribed to the thin layered morphology of ER-MoS₂. It is also reported that with the increase of defects at the surface would bring about higher photoluminescence emission intensity and hence the photo catalytic activity [26,36,37].

To further investigate the reduction mechanism of HAuCl₄ on the surface of ER-MoS₂, morphology and surface potential (SP) distribution of ER-MoS₂ before and after the reduction of HAuCl₄ were given in Fig. 7. It was found that the height and SP increased after the reaction of HAuCl₄ and ER-MoS₂, demonstrating the generation of Au⁰. In addition, the loaded Au⁰ would obviously affect the SP of ER-MoS₂. It was worth noting that in Fig. 7c, the Au⁰ tended to deem on the edge of ER-MoS₂, so the SP of edges after loading Au⁰ was higher than that of flat place (Fig. 7d).

Morphology and SP distribution of MoS₂ after reduction of HAuCl₄ (gold particles) under light and dark conditions were also studied to research the effect of light on SP, and showed in Fig. 8. It was obvious that Fig. 8a–d were the morphology and SP distribution of the same sample, only the light condition was changed here. Compared with Fig. 8b, the SP height of blue lined particles in Fig. 8d was lower. This phenomenon can be ascribed that for the contact position of MoS₂ and Au⁰ in dark condition, the SP height was due to the difference of their work function. While the sample was irradiated, the SP height was also influenced by the transition of photo-generated electrons. So, the SP height of Au⁰ on MoS₂ with irradiation was higher than that in dark environment. The SP of Au⁰ loaded ER-MoS₂ under light condition was higher than that under dark condition, which exhibited that the light could facilitate the transfer the photo-electrons and then enhance the SP, thus promoting the reduction of later HAuCl₄ ions.

As mentioned above, the edges of ER-MoS₂ could promote the reduction as well as growth of Au⁰, the influences of length and shape of edges on both natural MoS₂ and ER-MoS₂ were studied here. Fig. 9a displayed long and relatively sparse edges on natural MoS₂ while Fig. 9c showed short and dense edges of ER-MoS₂ where Au⁰ deemed on edges of both. And Fig. 9b and d showed the SP of Fig. 9a and c. By comparing Fig. 9a and b, it was clear that there was a quite thick Au⁰ particles with a high height in SP, which was because that the thicker the Au⁰, the higher the SP. Besides, the SP of long edge also showed a similar distribution with its morphology result, which meant that small Au⁰ particles deemed on edges of ER-MoS₂ could show the same effect with one thick Au⁰ particle. This phenomenon was also demonstrated in Fig. c and d. But unlike the long and sparse edge in Fig. 9a, the small circle-like

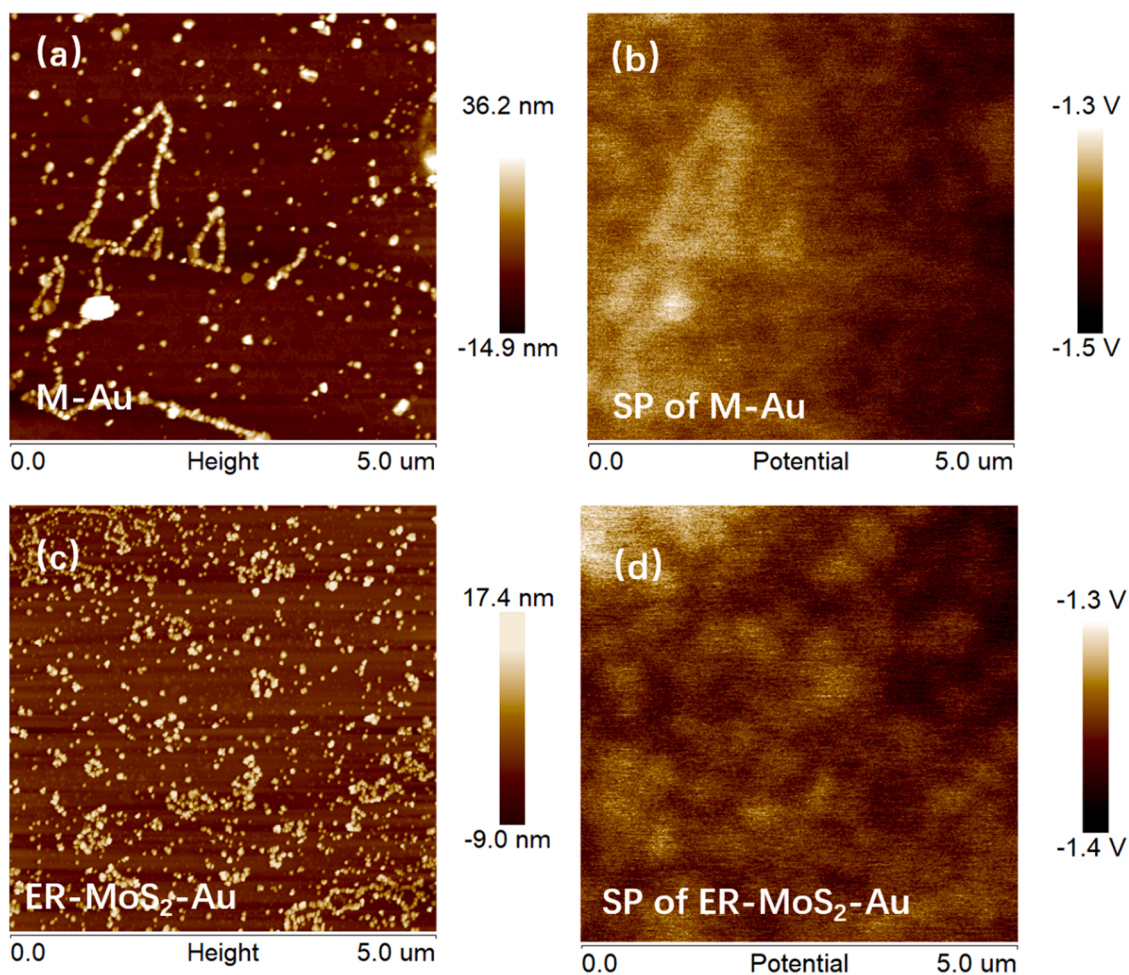


Fig. 9. Morphology and SP distribution of MoS₂ (a, b) and ER-MoS₂ (c, d) after reduction of HAuCl₄, respectively.

edges showed a whole light area of the circle instead of a similar shape with its own shape, and the brighter areas were more dispersed, which might be propitious to the transition of photoelectrons, thus promoting the reduction of Au ions on ER-MoS₂.

4. Conclusions

In the work, ER-MoS₂ was prepared through a simple thermal modification. AFM was applied for investigating the mechanism and behaviors of HAuCl₄ on ER-MoS₂. The experimental results showed that edges on MoS₂ could enhance the reduction ability. Large and plenty of Au particles gathered on the edges of MoS₂, which was due to the higher electron transfer rate and transferred efficiency of photo-generated electrons-holes pairs. Light would enhance the transfer of photoelectrons and the surface potential, promoting the reduction of HAuCl₄. The edges could promote the reduction as well as growth of Au⁰. Besides, the appearance of Au⁰ particles on edges had a strong influence on the surface potential of ER-MoS₂.

CRediT authorship contribution statement

Yuan Yuan: Writing – original draft, Software, Formal analysis. **Wei-quan Zhan:** Methodology, Investigation. **Feifei Jia:** Data curation, Supervision. **Shaoxian Song:** Visualization, Conceptualization. **Alejandro López-Valdivieso:** Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgment

The financial supports to this work from the National Key R&D Program of China (2021YFC2900900). Yuan gratefully acknowledges the Consejo Nacional de Ciencia y Tecnología (CONACYT) of Mexico for offering her the scholarship under the grant No. 812586 during her Ph. D. studies.

References

- [1] S. Linic, P. Christopher, D.B. Ingram, Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy, *Nat. Mater.* 10 (2011) 911–921, <https://doi.org/10.1038/nmat3151>.
- [2] J. Xi, H.S. Jung, Y. Xu, F. Xiao, J.W. Bae, S. Wang, Synthesis strategies, catalytic applications, and performance regulation of single-atom catalysts, *Adv. Funct. Mater.* 31 (2021) 1–39, <https://doi.org/10.1002/adfm.202008318>.
- [3] S.S. Yi, X.B. Zhang, B.R. Wulan, J.M. Yan, Q. Jiang, Non-noble metals applied to solar water splitting, *Energy Environ. Sci.* 11 (2018) 3128–3156, <https://doi.org/10.1039/c8ee02096e>.

