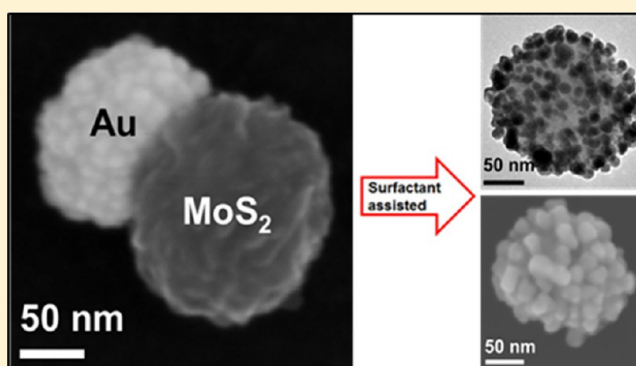


Decoration of Au Nanoparticles on MoS₂ Nanospheres: From Janus to Core/Shell Structure

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Supporting Information

ABSTRACT: A flexible route is presented for the controlled decoration of the Au nanoparticles (NPs) on the spherical MoS₂ particles, just by dropping the HAuCl₄ aqueous solution into the hydrothermal reaction-induced MoS₂ colloidal solution at room temperature. In the absence of surfactants in the colloidal solution, it has been found that the obtained products are mostly the MoS₂/Au Janus particles, in which the hemispherical Au particles are separately attached on the single MoS₂ spheres about 100 nm in size. The hemispherical Au particles are built of the ultrafine NPs (<10 nm) and comparable to the MoS₂ spheres in size. Further experiments have revealed that the existence of surfactants in the colloidal solution could significantly influence the distribution and decoration of Au NPs on the MoS₂ nanospheres. When the MoS₂ colloidal solution contains the nonionic or anionic surfactant, such as poly(vinylpyrrolidone) and sodium dodecyl benzene sulfonate, in appropriate content, the addition of HAuCl₄ induces the Au ultrafine NPs highly uniformly attached or decorated on the MoS₂ spheres. The distribution of the Au ultrafine NPs on the MoS₂ spheres evolves from a dispersed decoration to the intact core/shell structure with the rising HAuCl₄ addition amount. However, the cationic surfactant could prevent Au NPs from decoration on the MoS₂ spheres and induce the self-agglomeration of Au NPs. The formation of MoS₂/Au Janus particles is attributed to the aggregation growth of Au ultrafine NPs on the MoS₂ spheres, whereas the dispersed decoration of Au ultrafine NPs on the MoS₂ spheres is ascribed to the surfactant-induced uniform distribution of Au NPs. Interestingly, such decorated spherical MoS₂ NPs have exhibited a much higher surface-enhanced Raman scattering effect than the decorated MoS₂ nanoplates. This work presents a simple approach to the controllable decoration of Au NPs on the spherical MoS₂ particles.



1. INTRODUCTION

Molybdenum disulfide (MoS₂) belongs to the hexagonal crystal system with typical laminated structure and weak van der Waals forces between the adjacent atomic layers, and is of the intrinsic band gap about 1.8 eV in bulk.^{1,2} As an important member of two-dimensional materials, the MoS₂ nanosheets have aroused wide interest because of their excellent physical and chemical properties^{3–5} and potential applications in photoelectric catalysis,^{6–8} surface-enhanced Raman scattering (SERS) substrate, and so on.^{9,10} Importantly, the nanostructured MoS₂ decorated with other materials could exhibit some enhanced properties or improved performances due to the synergistic effect. The decoration materials include metal oxides,^{11,12} metal chalcogenides,¹³ carbon nanomaterials,^{14,15} noble metals,^{16–20} and so on. There are many reports on noble metals-decorated MoS₂ nanosheets. For instance, Wang et al.¹⁶ fabricated Au nanoparticles (NPs)-decorated MoS₂ nanosheets by microwave-assisted hydrothermal method and showed the enhanced SERS activity. Zhang et al.¹⁹ reported the decoration of Pd, Pt, and Ag NPs on MoS₂ nanosheets by wet-chemical

synthesis at ambient conditions and found the improved hydrogen-evolution reaction (HER) activity. Chen et al.²¹ prepared the Au nanorods-decorated MoS₂ nanosheets via mixing both the Au nanorods and the chemically exfoliated MoS₂ nanosheets in the colloidal solutions, which exhibited the significantly enhanced HER activity. However, all these decorations were on the MoS₂ nanosheets. To the best of our knowledge, the decoration of NPs on the spherical MoS₂ nano-objects has not been reported.

In this work, we present a flexible method for the controlled decoration of the Au NPs on the MoS₂ nanospheres based on the redox reactions and surface modification just by dropping the HAuCl₄ aqueous solution into the hydrothermal route-induced spherical MoS₂ colloidal solution at room temperature. It has been shown that in the absence of surfactants in the colloidal solution, the products are mostly the MoS₂/Au Janus

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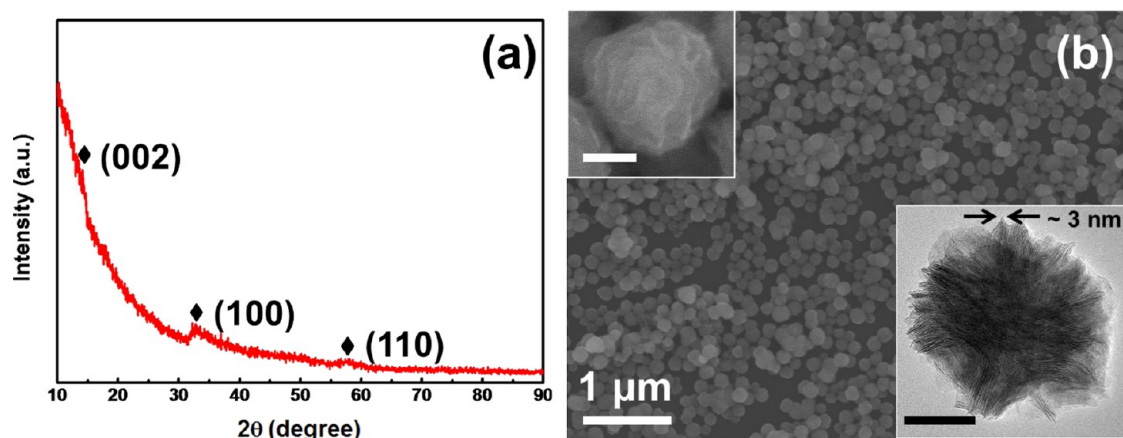


Figure 1. Phase structure and morphology of the hydrothermal reaction-induced products. (a) XRD pattern and (b) FESEM image. Up-left inset: the FESEM image of a single particle. Down-right inset: the TEM image of a single particle. The scale bars in the insets are 50 nm.

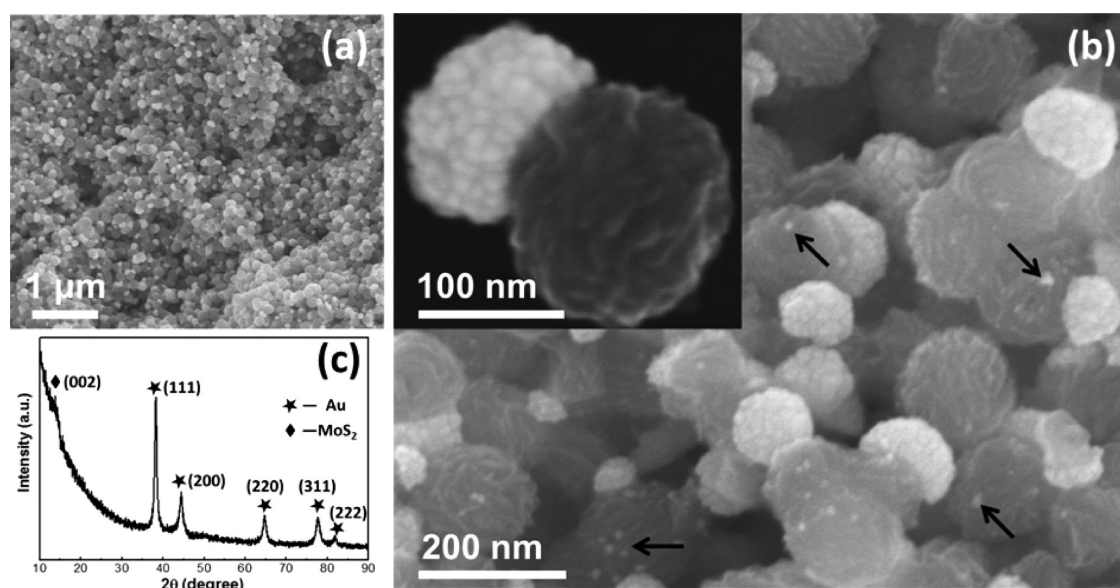


Figure 2. Morphology and structure of the as-prepared products after the addition of the HAuCl_4 solution without PVP into the MoS_2 colloidal solution. (a) The FESEM image of the products with low magnification. (b) The FESEM image with high magnification. The arrows point to the ultrafine NPs. The inset: the magnified image of a Janus particle. (c) The XRD pattern of the products. The indices correspond to the Au and MoS_2 crystal planes.

particles, which are the MoS_2 spheres (about 100 nm in size) separately attached to single hemispherical Au NPs. The hemispherical Au NPs are built of ultrafine NPs and comparable to the MoS_2 spheres in size. Further experiments have revealed that when the MoS_2 colloidal solution contains the appropriate contents of the nonionic or anion surfactant, the addition of HAuCl_4 results in the Au ultrafine NPs homogeneously dispersed on the MoS_2 spheres, showing a morphological evolution from the dispersed Au NPs' decoration to the intact core/shell structure with the rising HAuCl_4 addition amount. However, the cationic surfactant could prevent Au NPs from decoration on the MoS_2 spheres, leading to the self-agglomeration of Au NPs. This study presents a simple approach to the controllable decoration of Au NPs on the spherical MoS_2 particles. The details are reported in this article.

2. EXPERIMENTAL SECTION

2.1. Materials and Chemicals. Ammonium molybdate tetrahydrate ($\text{H}_24\text{Mo}_7\text{N}_6\text{O}_{24}\cdot 4\text{H}_2\text{O}$), thiourea (H_2NCSNH_2), poly(vinylpyrrolidone) (PVP), sodium dodecyl benzene sulfonate (SDBS), hexadecyltrimethylammonium chloride (CTAC), and chloroauric acid (HAuCl_4) were purchased from Aladdin Chemical Reagent Co., Ltd. Ethanol was bought from Sinopharm Chemical Reagent Co., Ltd. All of the reagents were used without any further purification. All the aqueous solutions were prepared with Millipore water (resistivity of 18.2 $\text{M}\Omega\text{ cm}$).

2.2. Preparation of Spherical MoS_2 Nanospheres. Spherical MoS_2 NPs were prepared by the hydrothermal method, as previously reported.^{13,22} Briefly, 0.35 g $\text{H}_24\text{Mo}_7\text{N}_6\text{O}_{24}\cdot 4\text{H}_2\text{O}$, 0.76 g H_2NCSNH_2 , and 0.25 g PVP were dissolved in 40 mL of deionized water in a clean beaker. The clear solution was obtained after stirring for 1 h at room temperature and transferred to a 100 mL Teflon-lined stainless steel autoclave, which was then sealed tightly, heated at 473 K

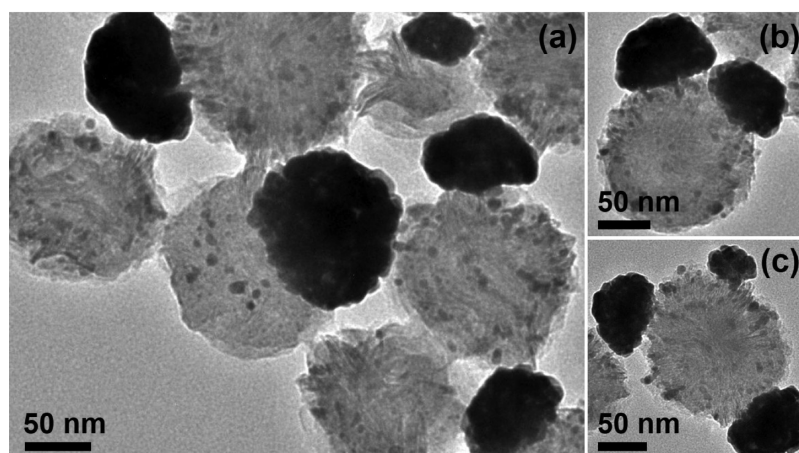


Figure 3. TEM observations of the final products. (a) The image of MoS₂/Au Janus NPs. (b, c) The typical images of two and three Au hemispherical NPs attached on the single MoS₂ nanospheres, respectively.

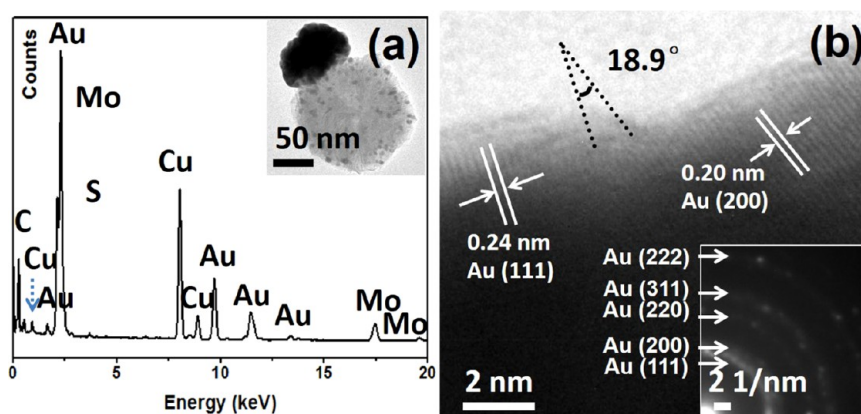


Figure 4. (a) EDS spectrum of the single Janus NP shown in the inset. (b) HRTEM image of the local area for a Au hemispherical particle. Inset: the SAED pattern of the Au hemispherical particle.

for 24 h, and cooled naturally to room temperature. The products or MoS₂ powders were collected and washed with ethanol and water for three times before dispersion in 50 mL water to form a MoS₂ colloidal solution. The molybdenum content in the colloidal solution was determined to be about 0.34 mM by inductively coupled plasma atomic emission spectroscopy (ICP-6300 Thermo Fisher Scientific).

2.3. Au NPs' Decoration on MoS₂ Nanospheres. The decoration of the Au NPs on the MoS₂ nanospheres was conducted by dropping the HAuCl₄ aqueous solution into the as-prepared MoS₂ colloidal solution at room temperature. Typically, 5 mL of the as-prepared MoS₂ colloidal solution was first loaded in a centrifugation tube and stirred for 30 min at room temperature. Then, 50 μ L HAuCl₄ aqueous solution (25 mM) without any reducing agent was added into the centrifuge tube with continuous stirring. After reaction for 10 min, the final products were collected from the mixed solution in the centrifuge tube by centrifugation at 8000 rpm and ultrasonic cleaning for three times.

2.4. Characterizations. X-ray diffraction (XRD) of the products was recorded on an X'Pert Philips Materials Research Diffractometer using a Cu K α radiation (0.15406 nm). A field emission scanning electron microscope (FESEM, FEI Sirion 200) equipped with an Oxford IE250X-Max50 energy dispersion spectrometer (EDS) and a transmission electron

microscope (TEM, JEM-200CX) were employed to examine the morphology and structure of the products.

3. RESULTS AND DISCUSSION

After the hydrothermal reaction, the products were obtained. Figure 1a shows the corresponding XRD pattern. The diffraction peaks at 14.3, 32.6, and 58.3° can be assigned to (002), (100), and (110) planes of MoS₂ (JCPDS No. 37-1492), respectively, indicating the formation of the hexagonal MoS₂. The corresponding morphological observations show that the products MoS₂ are spherical particles about 100 nm in diameter, as illustrated in Figure 1b and the up-left inset. The TEM examination has revealed that such MoS₂ nanospheres are built of the nanosheets about 3 nm in thickness, as typically demonstrated in the down-right inset of Figure 1b. These results are in agreement with the previous reports.^{13,22} The formation of such nanosheets-built spheres was attributed to the reaction of Mo source with S²⁻ released by NH₂CSNH₂ in the presence of PVP as structure direct reagent.²²

3.1. Janus Nanoparticles. The final products were obtained after the addition of the HAuCl₄ solution into the MoS₂ colloidal aqueous solution without any other reducing agents. Figure 2a gives the FESEM image of the corresponding products, which consist of two kinds of particles with bright and gray colors in contrast. The local magnification has revealed that the gray particles have similar morphology to those shown

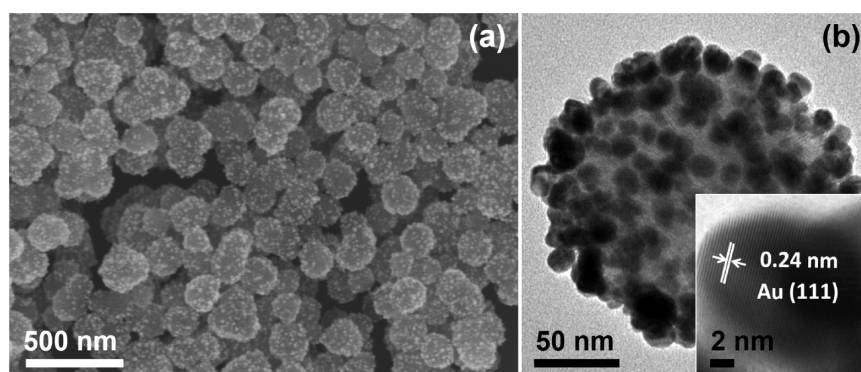


Figure 5. Morphology and structure of the products obtained by the addition of 50 μL HAuCl_4 solution into the MoS_2 colloidal solution with 0.03 mM PVP. (a) FESEM image of the products. (b) TEM image of a single MoS_2 nanosphere decorated with Au NPs. Inset: the HRTEM image of a single Au NP situated on the MoS_2 nanosphere.

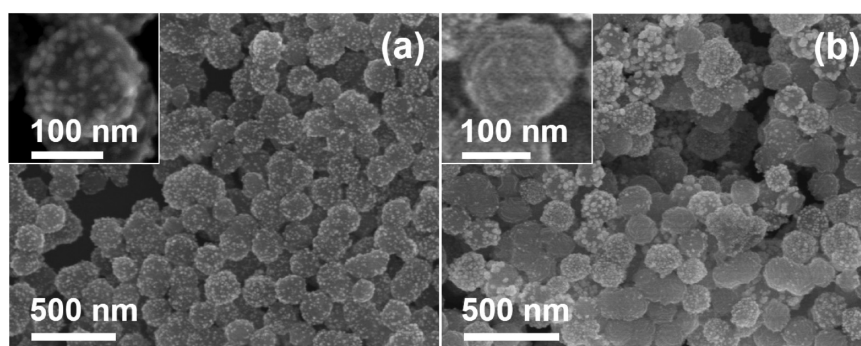


Figure 6. FESEM images of the products obtained after the addition of HAuCl_4 solution into the MoS_2 colloidal solution with different PVP contents. (a) 0.3 mM and (b) 0.003 mM.

in Figure 1b and should be the MoS_2 nanospheres. The bright particles are about 50–100 nm in size, nearly hemispherical in shape, and attached on the gray nanospheres, showing a Janus-like structure, as clearly illustrated in the inset of Figure 2b. A closer look shows that such bright hemispherical particles are actually built of ultrafine NPs with several nanometers (<10 nm) in size. Also, we can observe the sporadic ultrafine NPs decorated on the edges of the nanosheets in the gray particles (or the MoS_2 nanospheres), as indicated by arrows in Figure 2b. Further, the corresponding XRD measurements were implemented for the products. There exist significant diffraction peaks at 38.3, 44.5, 64.7, 77.8, and 81.9°, which are well matched with the standard pattern of Au (JCPDS No. 96-110-0139), in addition to the peak at 14.3° belonging to the diffraction of (002) plane of MoS_2 phase, as shown in Figure 2c. This indicates that the Janus NPs were composed of MoS_2 nanospheres and the nearly hemispherical Au NPs. The disappearance of the other diffraction peaks for the MoS_2 is attributed to the strong Au diffractions, which obscure those of MoS_2 .

Further, the microstructural examination was conducted for such products. It has been found that the Au hemispherical NPs are mostly separately attached on the single MoS_2 nanospheres, as shown in Figure 3a, although there exist some MoS_2 nanospheres without attachment to the Au hemispherical NP. There are also a few cases, in which two, even three, Au hemispherical NPs are attached on the single MoS_2 nanosphere, as typically illustrated in Figure 3b,c. Besides, we can clearly see that some ultrafine Au NPs few nanometers (<10 nm) in size are sporadically dispersed on the MoS_2 nanospheres, as shown in Figure 3.

Further, the EDS measurements have revealed that the Janus NPs are composed of the elements Mo, S, and Au, as illustrated in Figure 4a, corresponding to a single Janus particle. As for the Cu and C signals, they should be from the carbon-coated copper grid. As mentioned above, the Au hemispherical particle seems to be built up of the ultrafine NPs. The high-resolution TEM (HRTEM) examination was thus carried out. Figure 4b shows the image of the local area for a Au hemispherical particle, where two ultrafine NPs and their lattice fringes are seen. The spacings of about 0.24 and 0.20 nm belong to the {111} and {200} planes of Au crystal, respectively. The angle between the two planes was measured to be 18.9°, which is not in agreement with the crystallographic relation between them, indicating that the Au hemispherical particle is polycrystalline. The selected area electron diffraction (SAED) for a single Au hemispherical particle has also confirmed the polycrystalline structure, as shown in the inset of Figure 4b.

Finally, it should be mentioned that such Janus NPs are very stable and strong enough because the gold hemispherical particles could not be detached from the MoS_2 nanospheres even under ultrasonic vibration with a power of 200 W for 30 min. No isolated gold hemispherical particles were observed in the TEM fields. There is the potential importance that such asymmetric Janus nanoparticles could be a new type of colloidal motors due to their asymmetric structure and heterogeneous components,²³ which will not be involved here. In addition, the higher addition amount of HAuCl_4 solution could lead to the more Au ultrafine NPs dispersed on the MoS_2 spheres, but did not significantly affect the Janus particles in morphology, as illustrated in Figure S1.

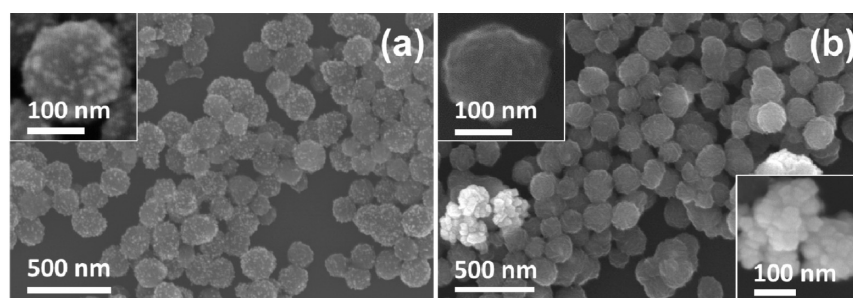


Figure 7. FESEM images of the products obtained after the addition of 50 μL HAuCl_4 solution into the MoS_2 colloidal solutions with (a) SDBS and (b) CTAC. The up-left insets in (a, b) are the magnified images of the single nanospheres and the down-right inset in (b) is the magnified image of Au NPs' agglomeration.

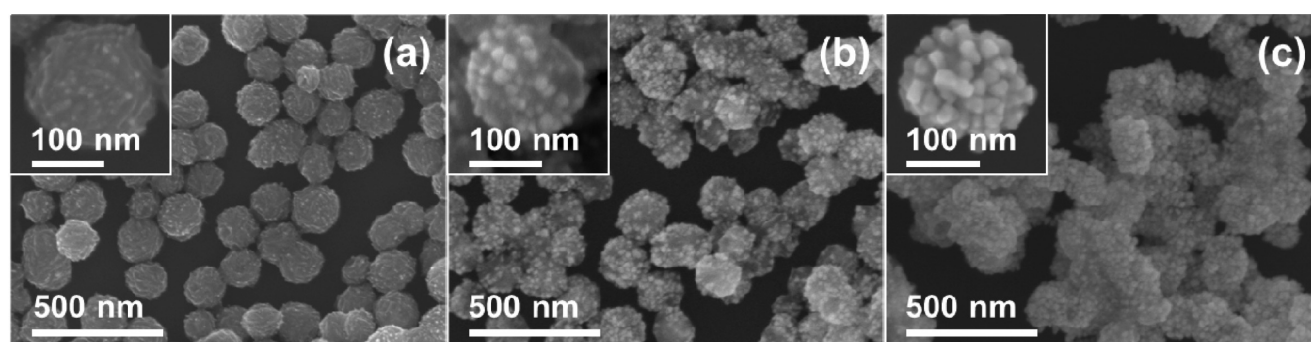


Figure 8. FESEM images of the products obtained after adding different amounts of HAuCl_4 solutions into the MoS_2 colloidal solution with 0.03 mM PVP. (a) 5 μL , (b) 100 μL , and (c) 200 μL .

3.2. Surfactant-Modulated Decoration. Further experiments have revealed that the existence of surfactants in the MoS_2 colloidal solution could significantly influence the distribution and decoration of Au NPs on the MoS_2 nanospheres. Different surfactants lead to different results.

3.2.1. PVP. PVP is an important nonionic surfactant. It has been found that PVP could make the Au ultrafine NPs to be homogeneously dispersed on the MoS_2 nanospheres. If the MoS_2 colloidal solution (5 mL) was added with a moderate amount PVP (say, 0.005 g, or about 0.03 mM in the solution) and stirred for 1 h at room temperature before the addition of 50 μL HAuCl_4 solution (25 mM), we could obtain the products with completely different morphology from that mentioned above, as demonstrated in Figure 5a. The Au hemispherical particles or the Janus particles shown in Figure 3 disappear. All the Au NPs fall into the range from several up to about 20 nm in size, and uniformly decorated or attached on the MoS_2 nanospheres. The corresponding XRD pattern (Figure S2) is similar to that shown in Figure 2c. The TEM examination has revealed that dispersed and isolated Au NPs are single crystal, as clearly shown in Figure 5b and its inset.

Further, the more PVP content (say, 0.3 mM) in the MoS_2 colloidal solution would lead to the similar Au NPs-decorated MoS_2 nanospheres to those shown in Figure 5, as typically illustrated in Figure 6a. However, if we add the HAuCl_4 solution into the MoS_2 colloidal solution with a very small PVP content (say, 0.003 mM), the MoS_2 nanospheres were nonuniformly decorated with the Au NPs, as shown in Figure 6b. Some of the MoS_2 nanospheres were only attached with very few Au NPs, as typically demonstrated in the inset of Figure 6b, whereas some other MoS_2 nanospheres are decorated with much more Au NPs. If no PVP was used, we can only obtain the extremely nonuniform results, or the Au/

MoS_2 Janus particles with sporadic or few NPs on the MoS_2 spheres, as demonstrated in Figure 2 or 3.

3.2.2. SDBS and CTAC. The influence of some other surfactants, such as SDBS (anionic surfactant) and CTAC (cationic surfactant), on Au decoration on the MoS_2 nanospheres was also examined. Typically, about 0.005 g SDBS or CTAC was added into 5 mL of the as-prepared MoS_2 colloidal solution (corresponding to 5.8 or 5.2 mM in the solution) before adding HAuCl_4 solution. For SDBS, the results similar to PVP were obtained and the Au NPs were uniformly decorated on the MoS_2 nanospheres, as shown in Figure 7a. However, the influence of the surfactant CTAC was completely different, as demonstrated in Figure 7b. The existence of CTAC in the MoS_2 colloidal solution induced the agglomeration of Au NPs, and no Au NP was attached on the MoS_2 nanospheres (see the insets of Figure 7b).

3.3. HAuCl_4 Amount-Modulated Decoration. Finally, the influence of the addition amount of HAuCl_4 on the decoration was also studied. Typically, under the existence of PVP with enough content in the solution, it has been found that increasing the addition amount of HAuCl_4 would increase the size and coverage of Au NPs on the MoS_2 nanospheres, as demonstrated in Figure 8. When the addition amount was small (say, 5 μL), only few ultrafine Au NPs about 5 nm in size were decorated on the MoS_2 nanospheres and the coverage was thus very low (Figure 8a). A moderate HAuCl_4 amount (50–100 μL) induced more and bigger (10–20 nm in size) Au NPs highly dispersed on the MoS_2 nanospheres (Figures 4 and 8b). If sufficiently large amount (say, 200 μL or higher) of HAuCl_4 solution was added, the formed Au NPs were mostly about 25–30 nm in size and the decoration-coverage was further increased, showing the intact core/shell structured MoS_2 @Au nanospheres, as illustrated in Figure 8c.

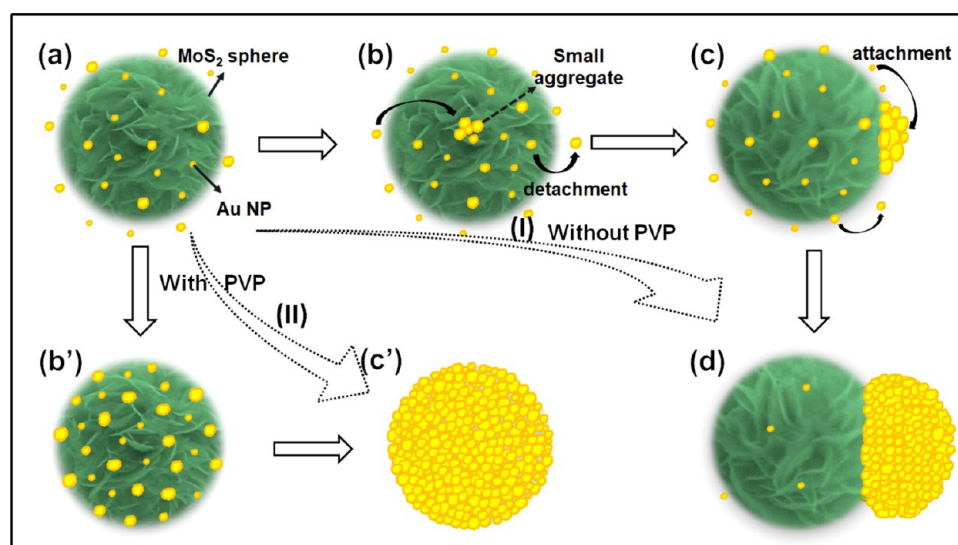


Figure 9. Schematic illustrations for the aggregation growth mechanism of the Au/MoS₂ Janus particles (I) and surfactant-induced dispersed decoration (II). (I) In the absence of PVP, (a) the formation and growth of Au nuclei on the edges of the nanosheets within the MoS₂ sphere. (b) A “small aggregate”, consisting of several ultrafine Au NPs, is attached on the MoS₂ sphere. (c) Ever-growing of the small aggregate by continuous attachment of the detached Au NPs. (d) The formation of the Au hemispherical particle and hence the Janus particle. (II) In the presence of PVP in the colloidal solution, the coverage of the dispersed Au NPs on MoS₂ spheres increase with the addition amount of HAuCl₄, evolving from the dispersed decoration (a, b') to the core/shell structure (c').

3.4. Formation of Janus and Dispersed Decoration. It was reported that the work function of MoS₂ is 5.2 eV,²⁴ situating the Fermi level of MoS₂ well above the reduction potential of AuCl₄⁻ (+1.002 V versus the standard hydrogen electrode).²⁵ It means that MoS₂/AuCl₄⁻ should form a redox pair. In our case, when a small amount of HAuCl₄ was added into the MoS₂ colloidal aqueous solution without any surfactant, the nanosheets-built MoS₂ nanospheres can adsorb AuCl₄⁻ ions to form MoS₂/AuCl₄⁻ redox pairs, which would induce the spontaneous electron transfer from MoS₂ to gold ions, or the reduction of Au³⁺ to Au⁰.²⁶ When the local concentration of the reduced Au⁰ atoms in the solution was saturated, the Au nuclei would preferentially nucleate at the highly energetic sites, such as the edges (or the ridges) of the nanosheets within the MoS₂ spheres, and grow into ultrafine Au NPs, as previously reported²⁷ or schematically demonstrated in Figure 9a. On the other hand, whereas the Au³⁺ ions were reduced to Au⁰ atoms by the MoS₂, a small portion of Mo ions in lattice would be dissolved or oxidized to the water-soluble and higher-valence forms (Mo⁵⁺ and Mo⁶⁺) and leached into the solution.²⁷

3.4.1. Aggregation Growth. Obviously, the formed Au ultrafine NPs would not be attached strongly enough on the edges of the MoS₂ nanosheets due to the small contact area between them and would be easily detached from the edges into the solution, especially when their sizes were bigger than the thickness of the nanosheets (Figure 9b). However, in the case that the several (three or more) Au ultrafine NPs were aggregated together and attached on the edges of the cross-linked MoS₂ nanosheets, forming, what we call, small aggregate, as schematically shown in Figure 9b, such a small aggregate would be much more stable than the single isolated ultrafine NP on the edge. In the absence of surfactant in the solution, the detached Au NPs would tend to be agglomerated together due to energy minimization. So, upon the attachment of such small aggregate on the MoS₂ sphere, more and more Au ultrafine NPs detached from the other sites would constantly attach on

it, leading to the ever-growing aggregate with the increasing adhesion to the MoS₂ nanospheres and the formation of nearly hemispherical Au particles with a much larger size, as shown in Figures 2 and 9b–d. If there was only one such small aggregate formed on the individual MoS₂ nanosphere in the initial stage, it would be Janus NP, as shown in Figure 3a or 9d. Similarly, when two or three small aggregates were formed on one single MoS₂ nanosphere, we would observe the composite particles consisting of two or three hemispherical Au particles and one MoS₂ sphere, as shown in Figure 3b,c. Obviously, the probability of the latter should be much lower than that of the former. So, the composite particles, built of Au hemisphere and MoS₂ nanosphere, were mostly the Janus NPs with the sporadic ultrafine Au NPs attached on the MoS₂ nanospheres, as shown in Figures 2 and 3. In contrast, if no such small aggregate were formed on some MoS₂ nanospheres, we can observe the MoS₂ nanospheres decorated only with the sporadic ultrafine Au NPs, but without Au hemispherical particles.

3.4.2. Surfactant-Induced Dispersed Decoration. Adding the HAuCl₄ into the MoS₂ colloidal solutions with surfactant also leads to the formation of the Au ultrafine NPs in the way similar to that mentioned above. However, the surfactant molecules would influence the surface state of the formed Au NPs in the solution due to the interaction between them. Here, the PVP is the typical nonionic surfactant.²⁸ The PVP molecules can not only be adsorbed on the Au NPs preferentially,²⁹ preventing them from aggregation, but also modify the MoS₂ spheres.^{13,22,30} Such Au NPs adsorbed on PVP molecules would thus be decorated on the PVP-modified MoS₂ spheres, showing a high dispersivity, as shown in Figure 5 or 9a,b'. Obviously, the PVP should be added with enough amount for the homogeneous decoration. Otherwise, if the added PVP was too small and not enough to modify all MoS₂ spheres after the preferential adsorption on Au NPs, the Au NPs would mainly be decorated on the PVP-modified MoS₂ spheres but not on the spheres without modification, showing

the inhomogeneous decoration, as shown in Figures 6b and 2a,b. Similarly, if the HAuCl_4 addition amount is increased, which would certainly generate more Au NPs with a larger size, the Au NPs would still homogeneously decorate the MoS_2 spheres, showing the increasing Au NPs coverage on the MoS_2 spheres and even forming the core/shell structure, as long as the PVP content in the solution is sufficient, as demonstrated in Figure 8 or 9c'.

For the addition of SDBS, it could also modify the Au NPs due to the anion surfactant.³¹ Such SDBS-modified Au NPs would decorate the defect sites (such as the higher valent localized Mo^{5+} or Mo^{6+} induced by reducing Au^{3+} ions) on the edges of the nanosheets within the MoS_2 spheres, exhibiting the dispersivity similar to that with the addition of PVP, as shown in Figure 7a.

As for the CTAC, which is a cation surfactant, it would thus tend to be adsorbed on the Mo vacancies on the edges of MoS_2 nanosheets, left by the Mo dissolution induced by reducing Au^{3+} ions because of their different charge properties. The surface of Au NPs would not be modified by CTAC. So, the formed Au NPs were not attached on the MoS_2 spheres but tended to be self-agglomerated based on the energy minimization, as shown in Figure 7b.

3.5. Spherical Structure-Enhanced SERS Effect. As mentioned in Section 1, the nanostructured MoS_2 decorated with other materials could improve some properties or performances because of the synergistic effect. The Au-decorated spherical MoS_2 NPs in this study have also exhibited some unique performances.

As an example, such decorated spherical MoS_2 NPs show a much higher SERS effect than those without decoration, and also higher than the Au-decorated MoS_2 nanoplates induced by the conventional methods (such as ultrasonic exfoliation) and the pure Au NPs (20 nm in size) prepared via one-pot seeded growth.³² Briefly, the SERS substrates (films) were prepared by alternatively dropping the MoS_2 colloidal solutions (with or without decoration) or the pure Au colloidal solution on silicon wafers and drying, as described in details in the Supporting Information. The film thickness was about several microns. The Rhodamine 6G (R6G) was chosen as the probe molecules. The as-prepared substrate films were soaked in the R6G solution with 10^{-6} M for 10 h before drying and Raman spectral measurements (see the details in the Supporting Information).

Figure 10 shows the Raman spectra of R6G molecules on different substrates. The Raman signals were very weak for the R6G molecules on the films built of the pure spherical MoS_2 NPs or MoS_2 nanoplates (curves IV, V in Figure 10), which was attributed to the chemical enhancement mechanism by photoinduced charge transfer between R6G and MoS_2 .^{33,34} For the R6G molecules on the films built of MoS_2 /Au Janus particles and Au-decorated spherical MoS_2 NPs, however, the Raman signals were very strong and much higher than those of the films without decoration, also one time higher than those of the film built with Au-decorated MoS_2 nanoplates and even obviously higher than those of the pure Au NPs-built film (curves I–VI in Figure 10), exhibiting a significantly enhanced SERS effect.

Such a Raman enhancement could be attributed to the configuration of the decorated spherical MoS_2 NPs. On the one hand, the MoS_2 particles with a spherical profile were actually built of the nanosheets (Figure 1b) and showed a much higher exposed surface than the pure nanoplates-built film, in which the pure nanoplates were easily overlapping. On the other

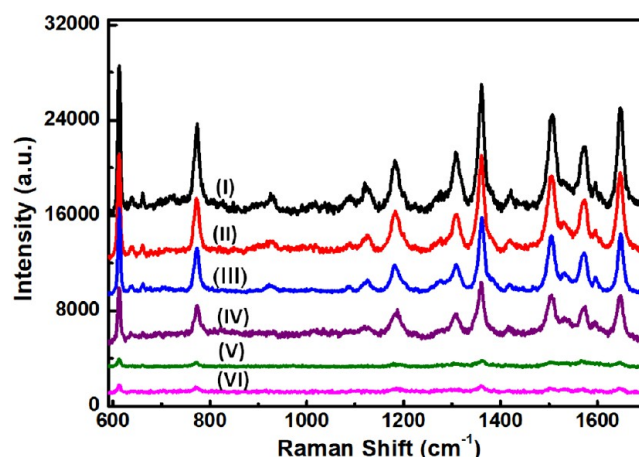


Figure 10. Raman spectra of R6G molecules on the different substrates. Curve (I) on the MoS_2 /Au Janus NPs-built film. Curve (II) on the film built of the spherical MoS_2 with dispersed Au NPs' decoration. Curve (III) on the film built of the pure Au NPs with 20 nm in size. Curve (IV) on the film built of the MoS_2 nanoplates with dispersed Au NPs' decoration. Curves (V) on the pure spherical MoS_2 NPs-built film. Curve (VI) on the pure MoS_2 nanoplates-built film (excited at 532 nm).

hand, the films built of MoS_2 /Au Janus particles and Au-decorated spherical MoS_2 NPs induced the highly uniform dispersion of the Au NPs. In such hybrid-built films, the Au NPs could show the SERS effect and the MoS_2 particles could enhance the adsorption of the target molecules, leading to the enhanced SERS performances.

4. CONCLUSIONS

In summary, we have provided a flexible route for the controllable decoration of the Au NPs on the spherical MoS_2 particles, based on the redox processes and surface modification, just by dropping the HAuCl_4 aqueous solution into the hydrothermal reaction-induced MoS_2 colloidal solution at room temperature. Using such an approach, we have realized the controlled decoration of the Au ultrafine NPs on the spherical MoS_2 spheres from the Janus particles to core/shell structure with the assistance of surfactants. Without the absence of the surfactants in the colloidal solution, the MoS_2 /Au Janus particles or the hemispherical Au particle/ MoS_2 sphere pairs were obtained, and the hemispherical Au particles were formed by the aggregation growth of Au ultrafine NPs on the MoS_2 spheres. Further, due to their role of surface modification, the existence of surfactants in the solution could significantly influence the distribution of Au NPs on the MoS_2 spheres. Typically, when the MoS_2 colloidal solution contains the appropriate amount of nonionic or anionic surfactant, such as PVP and SDBS, the addition of HAuCl_4 induces the Au ultrafine NPs uniformly decorated on the MoS_2 spheres, exhibiting the morphological evolution from the dispersed Au NPs' decoration to the complete core/shell structure with the rising HAuCl_4 addition amount. In contrast, because of their similar charge property, the cationic surfactant could prevent the Au NPs from decoration on the MoS_2 spheres, giving rise to the self-agglomeration of the Au NPs. Interestingly, such Au-decorated spherical MoS_2 NPs show a much stronger Raman signal to R6G molecules than the Au-decorated MoS_2 nanoplates and the pure Au NPs, exhibiting significantly spherical structure-enhanced SERS effect. This work has not

only presented a simple method for the controllable decoration of Au NPs on the spherical MoS₂ particles but also deepened the understanding of the interaction behaviors between them.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b01216.

Preparation of SERS substrates and Raman spectral measurements; FESEM image of the products (Figure S1); XRD pattern of the products (Figure S2) (PDF)

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Notes

The authors declare no competing financial interest.

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