



2D gold supercrystal-MoS₂ hybrids: Photoluminescence quenching

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ABSTRACT

We demonstrate heterogeneous integration of 2D self-assembled films of Au nanoparticles (NPs) and 2D MoS₂ monolayer. The Au NPs film has a compact, long-range-ordered structure, with its particles exhibiting a narrow size distribution. In addition, large-area coverage was achieved between the two components. Photoluminescence (PL) quenching was observed after the attachment of Au NPs film onto MoS₂ monolayer, which was attributed to electron transfer and shielding of light by Au NPs film. This work broadens our understanding of PL properties in such 2D hybrids.

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1. Introduction

As a hot research spot in 2D materials, monolayer MoS₂ has a tunable bandgap from 1.2 eV (bulk) to 1.88 eV (monolayer) [1]. This provides great possibility in optical/electrical related behaviors such as good potential for PL emission, which leads to promising future in opto-electronic devices, biosensing, etc. [2–5] To gain immediate benefit for tunability of MoS₂'s PL behavior, combining 2D MoS₂ with 0D plasmonic materials is widely accepted for its high efficiency and less functionalities impact towards 2D MoS₂. However, in previous studies, small amount of plasmonic materials (usually noble metal nanomaterials) were deposited on the MoS₂ with low density and less regularity [6,7]. That restricts further understanding of light-matter interaction in such hybrids.

Here, we fabricate a kind of 2D nanocomposite consisting of self-assembled Au NPs film and MoS₂ monolayer. The NPs are highly monodispersed, self-assembled in a compact structure with long-range order. The direct coverage of Au NPs film onto MoS₂ monolayer leads to preservation of these features. Importantly, the heterostructure shows PL quenching compared with bare MoS₂ monolayer. The study towards this phenomenon broadens our horizons in PL tunability of such hybrids.

2. Methods

MoS₂ monolayer was prepared by chemical vapor deposition (CVD) on SiO₂ (300 nm)/Si (SiO₂) substrate. S and MoO₃ powders (Aladdin Industrial Co. Ltd) were separately put in two quartz boats that were placed in different heating zone of a tube furnace (BTF-400C, BEQ Co. Ltd), with S powder on the upstream of MoO₃ powder. SiO₂ substrates were put face down above MoO₃. S and MoO₃ powder were then simultaneously heated to 200 and 650 °C, respectively, in 45 min, and then kept steadily for 5 min before naturally cooling to room temperature. N₂ flow was kept at 40 sccm during experiment.

We synthesized Au NPs film by using two solutions [8]. Solution A consisted of 0.25 mmol of chlorotriphenylphosphine gold (I) dissolved in 25 mL of toluene to which 2 mmol of a thiol derivative was added. Solution B was obtained by dissolving 5 mmol of *tert*-butylamine borane complex in 2 mL of toluene. Both solutions were heated to 100 °C and stirred until complete dissolution. After mixing, the solution rapidly changed from colorless to brown and finally dark red. The colloidal solution was then washed twice to remove impurities. At the end of synthesis, Au NPs were dispersed in hexane. One drop of this solution was dripped on the surface of ethylene glycol (EG) at room temperature. A hexane solution (~15 μL) containing Au NPs was spread onto the surface of EG in a Teflon well, and the well was then covered with a glass slide to slow down the evaporation of hexane. After 15 min, the Au NP film

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was directly taken out and transferred onto a MoS₂ monolayer, followed by drying in an oven to remove excess EG.

Scanning electron microscopy (SEM) was performed using a Zeiss SUPRA 55VP microscope. Transmission electron microscope (TEM) was carried out on a JEOL JEM-2100 microscope. Atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) were performed using a Park NX10. PL and Raman spectra were recorded on a Reinshaw inVia-Reflex confocal Raman system under an excitation wavelength of 532 nm. Reflection spectra were obtained using a CRAIC 508 PV Manual UV-Visible-NIR microscope spectrophotometer.

The absorption spectra of Au, Au/MoS₂ hybrid nanostructures, pristine MoS₂ were calculated by Boundary Element Method (BEM) using an open source program "MNPBEM" (MNP stands for Metallic Nanoparticles). Related parameter were set according to experimental results.

3. Results and discussion

As can be seen in Fig. 1a, triangular-shaped MoS₂ monolayer have a side length of 10–60 μm. Fig. 1b is a TEM image of the self-

assembled Au NP monofilm. The NPs are arranged together in a compact, long-range-ordered hexagonal close-packed (hcp) monolayer structure without further coalescence. The Au NPs show a narrow size distribution of 7 nm ± 0.4 nm, as shown in the inset of Fig. 1b. Fig. 1c is SEM image of the as-prepared hybrid nanostructure. A dense Au NP film covering a large area of the MoS₂ film can be observed. The high-resolution SEM image in Fig. 1d reveals small holes (50–600 nm) on the transferred Au NP film, and a flat, homogeneous MoS₂ domain can be observed under these holes. The dense, long-range-ordered hcp structure of the Au NP film is retained after transferring to the MoS₂ monolayer.

Next, AFM measurement was carried out. Fig. 1e and f show the AFM image and height profile of MoS₂ monolayer. The height of MoS₂ on SiO₂ substrate is about 1.6 nm, which reveals a monolayer structure [9]. Fig. 1g and h show the AFM image and height profile of the Au NP film on the MoS₂ monolayer. The thickness of the Au NP film is about 7.1 nm, which is consistent with the size distribution of Au NPs in Fig. 1b. This demonstrates the monolayer structure of Au NP film.

Then, as shown in Raman spectra on Fig. 2a, both samples have Raman shift difference of 20.8 cm⁻¹ between E_{2g} and A_{1g} peaks.

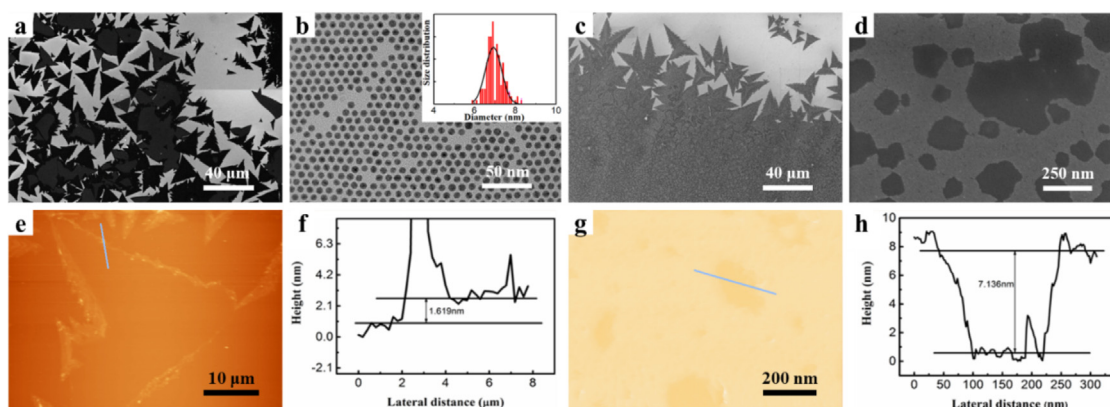


Fig. 1. (a) SEM image of chemical vapor-deposited MoS₂ monolayer. (b) TEM image of self-assembled Au NP film. (c) SEM image of hybrid nanostructure. (d) High-resolution SEM image of hybrid nanostructure. (e) AFM image of MoS₂ monolayer. (f) Height profile of MoS₂ monolayer shown in (e). (g) AFM image of hybrid nanostructure. (h) Height profile of hybrid nanostructure shown in (h).

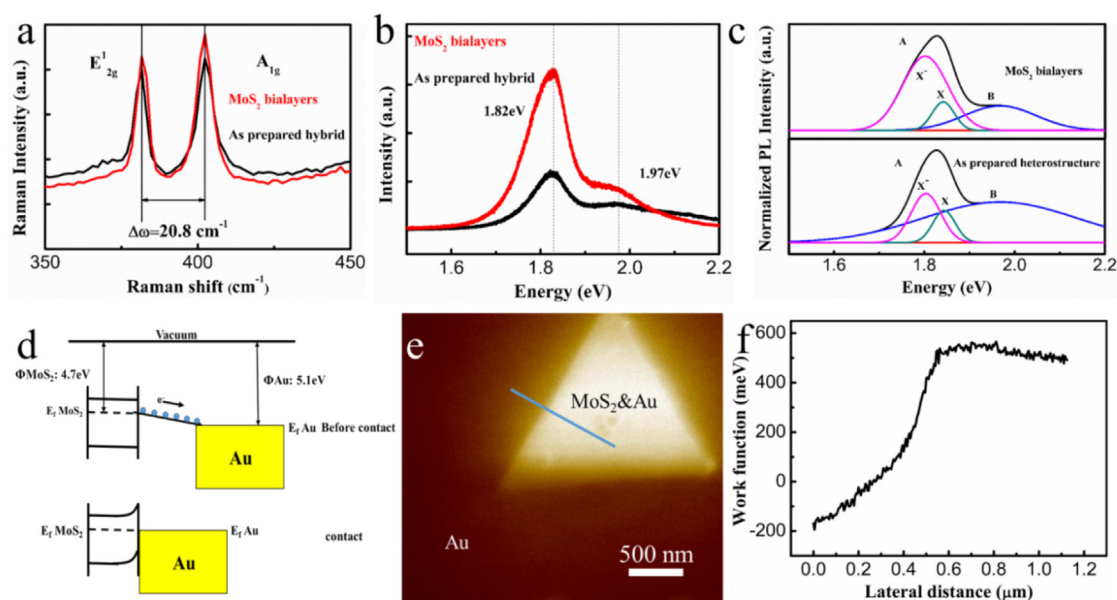


Fig. 2. (a) Raman spectra of MoS₂ (red) and hybrid nanostructure (black). (b) PL spectra of MoS₂ (red) and hybrid nanostructure (black). (c) Lorentzian peak fitting of PL spectra of MoS₂ (above) and nanocomposite (bottom) corresponding to excitons (X) and trions (X⁻). (d) Energy band diagram of Au and MoS₂ before (top) and after (bottom) integration. (e) KPFM image of hybrid nanostructure and (f) work function distribution along the line in (e). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

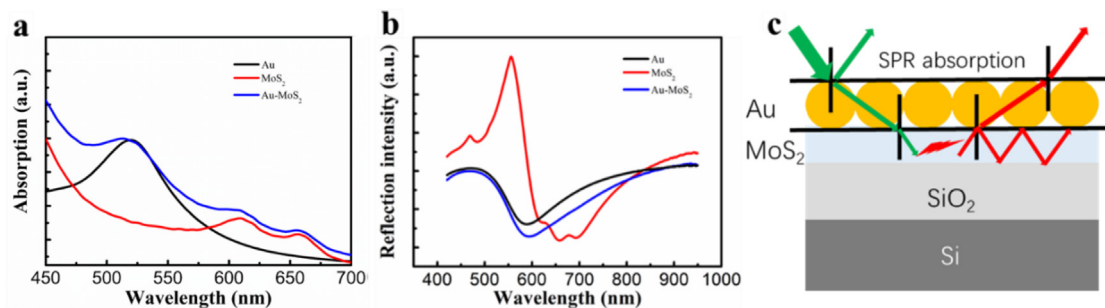


Fig. 3. (a) Calculated absorption spectra of Au NP film, MoS₂ monolayer and hybrid nanostructure. (b) Reflection spectra of Au NPs film, MoS₂ monolayer and hybrid nanostructure. (c) Lateral view of emitted and absorbed light routes in the hybrid.

That further confirms monolayer structure of MoS₂ in both samples [10]. PL peaks corresponding to different types of exciton (the so called A and B exciton) modes can be observed at 1.82 and 1.97 eV for both the samples in Fig. 3b, and the hybrid turns out to get PL quenching. No obvious spectral shift can be observed for MoS₂ and the hybrid, which confirms same monolayered MoS₂ structure in both samples. For A exciton emission, both trion (a bond state of two electrons and one hole) [11] recombination and exciton recombination contribute to PL peak A (Fig. 2c). Thus, we decompose A emission peak into negative trion peak X⁻ and neutral exciton peak X in Fig. 2c. The X⁻/X peak intensity ratio decreased from 2.62 to 1.54, indicating that the recombination of negative trions takes less spectral weight after connection between Au and MoS₂ is established. That suggests the decrease of electrons in MoS₂. The possible physical process are illustrated in Fig. 2d. The energy level offset between Au and the MoS₂ monolayer before their integration is 0.4 eV [12]. After establishing a contact, band bending occurred, and the excited electrons transferred to Au did not decay back to recombine with the holes in MoS₂. Thus, the energy needed to excite luminescence decreased. The electrons transfer from MoS₂ to Au NPs can be further confirmed by KPFM analysis in Fig. 2e and 2f, where the difference of work function between hybrid and surrounding Au NPs is about 700 meV. Besides, as shown in Fig. 2c, an obvious spectral broadening of B emission peak can be observed. It can also be an evidence for more nonradiative recombination paths that will affect the hybrid's PL behavior.

Additionally, with a dense Au NP film coverage, processes such as reflection and absorption of Au NPs may gradually become dominant, thereby affecting light path. Fig. 3a illustrates the calculated absorption spectra of the Au NP film, MoS₂ monolayer and as-prepared hybrid nanostructure. For Au NP film, a strong absorption peak at around 520 nm, which is located close to the excitation wavelength of 532 nm. This implies that the dense Au NP film can absorb much of the incident light before exciting luminescence. Fig. 3b shows reflection spectra of all the samples. The hybrid nanostructure maintains a relatively high degree of similarity with bare Au on SiO₂, which is resulted from the reflection of incident light and screening of the underneath signals caused by the compact Au NP film [13]. This can also lead to influence towards PL process, as shown in Fig. 3c.

4. Conclusion

In conclusion, we fabricate a hybrid nanostructure comprising MoS₂ monolayer covered with a compact, long-range-ordered, self-assembled Au nanoparticle film. PL quenching is observed

after the attachment of Au NP film onto MoS₂ monolayer. This can be derived mainly from following reasons: electron transfer from MoS₂ to Au NPs, influence of Au NP film on the light path. The study will broaden our horizons of light-matter interaction in such 2D nanostructures.

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.

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