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## Photoluminescence enhancement in few-layer WS<sub>2</sub> films via Au nanoparticles

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Nano-composites of two-dimensional atomic layered WS<sub>2</sub> and Au nanoparticles (AuNPs) have been fabricated by sulfurization of sputtered W films followed by immersing into HAuCl<sub>4</sub> aqueous solution. The morphology, structure and AuNPs distribution have been characterized by electron microscopy. The decorated AuNPs can be more densely formed on the edge and defective sites of triangle WS<sub>2</sub>. We have compared the optical absorption and photoluminescence of bare WS<sub>2</sub> and Au-decorated WS<sub>2</sub> layers. Enhancement in the photoluminescence is observed in the Au-WS<sub>2</sub> nano-composites, attributed to localized surface plasmonic effect. This work provides the possibility to develop photonic application in two-dimensional materials. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4923183>]

### I. INTRODUCTION

The unique properties of graphene with gapless at K and K' points in Brillouin zone have been exploited in the last decades. However, the applications of graphene are hindered in optoelectronic devices and field-effect transistors due to the absence of bandgap. Two-dimensional (2D) transition metal dichalcogenides (TMDCs) such as MoS<sub>2</sub> and WS<sub>2</sub> with different Coulombic potentials of metal and sulfur atoms lead to the non-zero Semenoff mass so as to non-zero bandgap energies.<sup>1</sup> In monolayer WS<sub>2</sub>, the W atom is hexagonally sandwiched by two trigonal coordinated sulfur atoms in covalent bonds. The bandgap of WS<sub>2</sub> materials shift from indirect to direct while thinning-out the number of layer of WS<sub>2</sub>. For instance, the band-gap energy of WS<sub>2</sub> transits from 1.4 eV in bulk structure to 2.1 eV in monolayer crystal.<sup>2-4</sup> The tunable bandgap favors the applications in optoelectronics, such as photodetectors<sup>3,4</sup> and solar cells.<sup>5-7</sup> Enhanced light-emission is vital for both fundamental material study and development of optoelectronic device. Localized surface plasmon resonance (LSPR) excited by the interaction between photon and metal surface is a known effective approach to enhance light-emission, which has been evident in many systems.<sup>8,9</sup> However, a few reports have been found about the photoluminescence (PL) enhancement from TMDCs materials via plasmonic effect.<sup>10,11</sup> Earlier study suggested that exciton-plasmon interaction could be established between plasmonic resonator and few-layers WS<sub>2</sub> to enhance PL emission from atomic layered TMDCs.<sup>12</sup> In this study, we decorated Au nanoparticles (AuNPs) on the WS<sub>2</sub> via a simple chemical method. The spatial distribution of nano-sized Au has been observed through electron microscopy characterization after the chemical treatment. The PL measurement has been performed for the WS<sub>2</sub> sample with and without AuNPs coating. The increase of PL emission is mainly attributed to the intensity enhancement by the LSPR of the AuNPs. Particularly, those enhanced excitonic emission after the decoration of AuNPs is the signature of the enhanced emission, which is amplified by the field enhancement arising from LSPR excitation.

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## II. EXPERIMENTAL

Highly-crystalline micro-flakes  $\text{WS}_2$  were grown by the sulfurization of thin sputtered tungsten film (W) on Si substrate with  $1\ \mu\text{m}$  thick  $\text{SiO}_2$ . As-prepared W film and 0.25 g sulfur powders were placed into two  $\text{Al}_2\text{O}_3$  made crucibles respectively. The boat with sulfur powders was placed on the upstream of quartz tube and the other carrying W film was put on the center of quartz tube. Argon was used as the carrier gas with a flow rate of 150 sccm. The pressure needed to control is 240 Pa during the reaction. The growth temperature was set to  $750\ ^\circ\text{C}$  for 15 min and at the same time the S powder was evaporated at above  $113\ ^\circ\text{C}$ . At the end of reaction, the furnace temperature was cooled down naturally and finally the as-grown  $\text{WS}_2$  samples were taken out from the system. Field-emission scanning electron microscopy (FE-SEM) (JEOL JSM -6335F) was used to capture the images.

## III. RESULTS AND DISCUSSION

As shown in Figure 1(a) of FE-SEM image, it is clear that few layer triangle  $\text{WS}_2$  has been fabricated with a size distribution approximately ranging from 10 to  $30\ \mu\text{m}$ . The sample can be transferred to another substrate using PMMA (MicroChem) with molecular weight of 950 K as the transfer medium. This process can be done by spin coating the PMMA on the sample initially at 500 rpm for 10 s, and subsequently at 300 rpm for 30 s. After that, the sample was baked at  $100\ ^\circ\text{C}$  for 10 min and then put into 1 M NaOH for 15 min. Finally the PMMA-capped  $\text{WS}_2$  was washed by DI water to remove all chemicals residues.

Figure 1(b) shows the high-resolution transmission electron microscopy (HR-TEM) images of  $\text{WS}_2$  labelled with (110) and (100) miller index notation (inset of Fig. 1(b)), which match with the previously reported result.<sup>13</sup> After the confirmation of successfully fabricated  $\text{WS}_2$  micro-sized

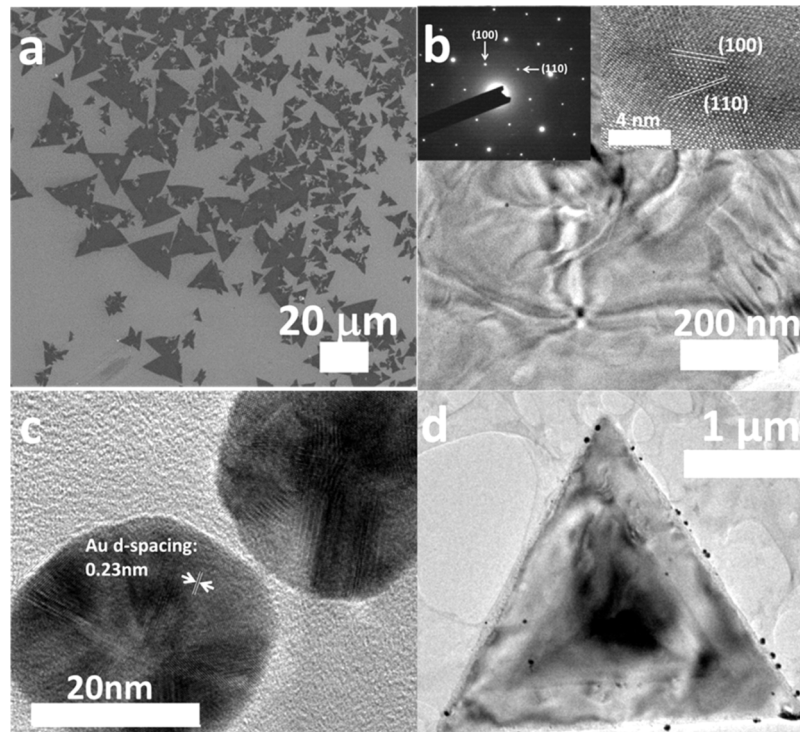


FIG. 1. Structural characterization of the synthesized nano-composites of 2D  $\text{WS}_2$  crystals and AuNPs. (a) FE-SEM image. (b) Low magnification TEM. The inset shows selected area electron diffraction (SAED) pattern (left panel) and HR-TEM image (right panel). (c) Enlarged TEM image showing the spherical AuNPs adhered onto the edge of  $\text{WS}_2$ . (d) Low magnification TEM image with the triangular Au- $\text{WS}_2$  flake.

flakes, the as-prepared WS<sub>2</sub> samples were immersed into 5 mM HAuCl<sub>4</sub> aqueous solution in time intervals of 40 s at room temperature. After that WS<sub>2</sub> was put into a dry box for 4 hr for drying.<sup>14</sup> The HR-TEM image in Figure 1(c) confirms the identity of AuNPs with interspacing of 0.23 nm and the HR-TEM image in Figure 1(d) reveals the distribution of AuNPs on WS<sub>2</sub> crystal. From the HR-TEM image, it is noted that the majority of the AuNPs exist along the edge of the single triangular WS<sub>2</sub>.

Measurements of PL spectra and mapping were carried out in a micro-Raman system (Horiba Jobin Yvon HR800) with PL mode by using an excitation laser with the wavelength of 488 nm. A 100x objective lens with numerical aperture NA of 0.9 was used for the measurement at room temperature. The spot size of laser is about 1 μm. The laser power needs to be set at below ~50 mW to avoid the appreciable heating effect. Figure 2(a) and 2(b) show the spatial mappings of PL intensity distribution on the surface of the bilayer WS<sub>2</sub> without and with AuNPs coating. The evidences claimed that the thickness of as-prepared WS<sub>2</sub> has been proven by Raman spectrum and height profile of AFM image in bilayer (not shown here). The light emission of the WS<sub>2</sub> can be observed in a range of 1-3 folded enhancement concentrated on the edge sites of WS<sub>2</sub> which is mainly due to the nucleation of Au NPs over there. The average PL enhancement of Au/WS<sub>2</sub> is about 2-folded. Such a phenomenon can be explained as follows. When WS<sub>2</sub> crystal was immersed into the aqueous HAuCl<sub>4</sub> solution, the precursor AuCl<sub>4</sub><sup>-</sup> ions have more chances to reduce the AuNPs at the edge sites of WS<sub>2</sub> due to the unsaturated sulfur atoms which makes it easy to form Au-S bonding.<sup>15</sup> When Au and WS<sub>2</sub> hybrid nanostructures are in a close vicinity, the exciton-plasmon interaction occurs.<sup>16</sup>

In order to gain an in-depth understanding of the PL enhancement, we have performed the optical absorption measurement on the obtained samples. Figure 2(c) and 2(d) show the absolute absorption spectra from the WS<sub>2</sub> sample without and with AuNPs decoration. Accordingly, the inset of Figure 2(d) shows the absorbance enhancement in existence of AuNPs. When AuNPs become an amplifier, the light field is enhanced due to the metal nanostructure in the proximity of the 2D semi-conducting crystal. A majority of incident photons are absorbed by the Au-WS<sub>2</sub> nano-composites such that the interaction between excitons and plasmons gives rise to a large optical absorption enhancement of the semiconductor WS<sub>2</sub> as shown in Figure 2(d). Enhanced localized electromagnetic field by the metal nanoparticles (MNP) from the certain configuration of AuNPs induces the effective band-to-band transition of WS<sub>2</sub> by probably reducing the distance between AuNPs and WS<sub>2</sub>.

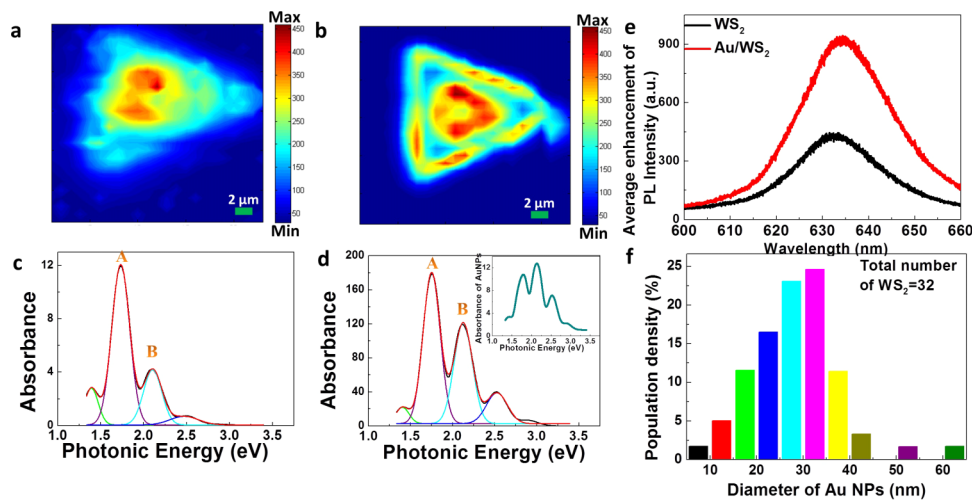


FIG. 2. Spatial distribution of the PL mapping of a bilayer WS<sub>2</sub> (a) without and (b) with Au NPs decoration. (c) and (d) are the absolute optical absorption spectra of the WS<sub>2</sub> flake with labelled exciton A and B representing direct and indirect emission energies from WS<sub>2</sub> crystal with and without AuNPs coating. The inset of (d) shows the absorbance enhancement in existence of AuNPs. (e) The average PL intensity enhancement extracted from (a) and (b). (f) The diameter of Au NPs size distribution estimated by TEM image.

From Figure 2(c) and 2(d), it also shows a manifest enhancement in the light absorption in contrast to the previous absorption spectrum featured a slightly blue shift in the absorption wavelength accompanying by the high energy emission and narrower line-width as well. The narrow line-width in the Au-decorating absorption spectrum also greatly improves the efficiency of light emission of  $\text{WS}_2$  due to the arisen LSPR.<sup>17</sup> It can be clearly seen that three prominent resonant frequency peaks are occurred at 490 nm, 580 nm and 690 nm as shown in the inset of Figure 2(d). According to the previous study,<sup>18</sup> the tunable resonant frequency of AuNPs arrangement responding in the visible light region fully matches the light emission of direct band-gap semiconducting  $\text{WS}_2$  crystal.

Apart from the PL enhancement on the edge sites of AuNPs/ $\text{WS}_2$  composite, it is interesting to investigate how the PL is varied on the defective sites of the composite. In order to study the influence of defects on Au nucleation, a solid-state laser with the wavelength of 488 nm and power of about 0.5 mW was irradiated on the sample for 10 min. Therefore, some defect sites may be induced on the bilayer  $\text{WS}_2$  due to potentially banishment of sulfur atoms.<sup>19</sup> Subsequently, we repeated the Au decoration on the new  $\text{WS}_2$  sample by the same experimental condition as the immersion of  $\text{HAuCl}_4^-$  solution process. Accordingly, the defective sites of 2D  $\text{WS}_2$  should favor the Au nucleation on those sulfur vacancies. Compared to the AuNPs- $\text{WS}_2$  composite before laser irradiation, Au arrangement of the irradiated sample is obviously denser from the SEM image as shown in Figure 3(a), we can observe the deposited AuNPs are occurred not only on the edge sites without laser treatment, but also in the central part of the  $\text{WS}_2$  triangle flake after the laser treatment. Therefore, AuNPs would be anchored mainly on the surface of  $\text{WS}_2$  via following the trace of laser irradiation, which is not limited to the edges sites. By counting on the number of AuNPs in the marked five regions of Figure 3(a), there are around 18 to 22 granules of AuNPs in each region. We have compared the light emission intensity of PL spectra from position 1 to 5 before and after Au decoration as shown in Figure 3(b). In Figure 3(b), it is apparent that PL enhancement factor varies in different positions and the maximum 8 folded intensity can be achieved in the position 5. It seems that there is weak relationship between the PL enhancement factor and density of AuNPs over the  $\text{WS}_2$  sample as previous reports.<sup>8,9</sup> Hence, other factors such as interspacing between

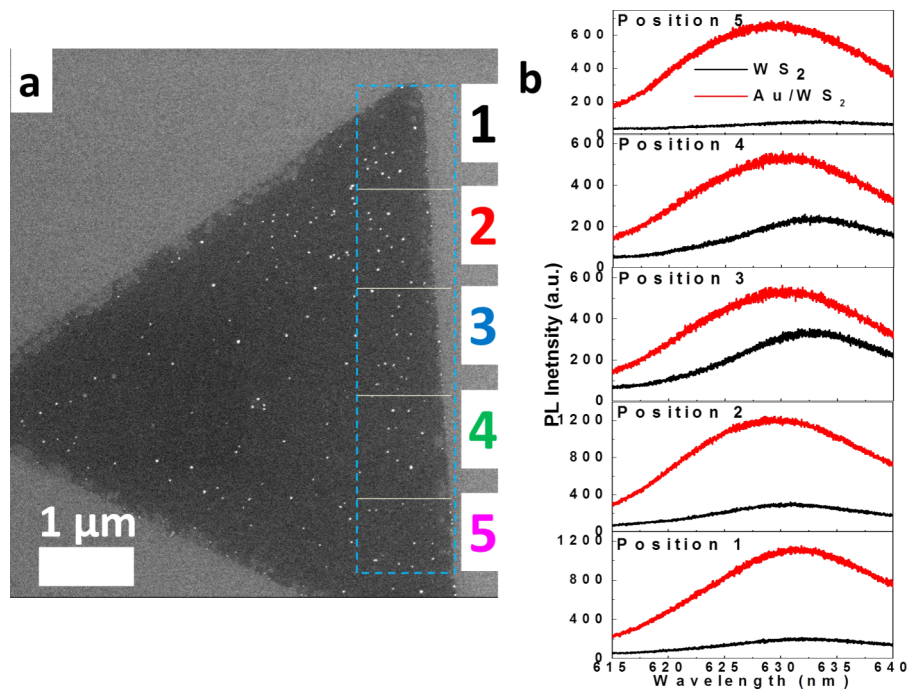


FIG. 3. (a) The SEM image with labelled position 1-5 corresponding to the PL spectra obtained. (b) PL spectra of position 1-5 before and after the decoration of AuNPs.



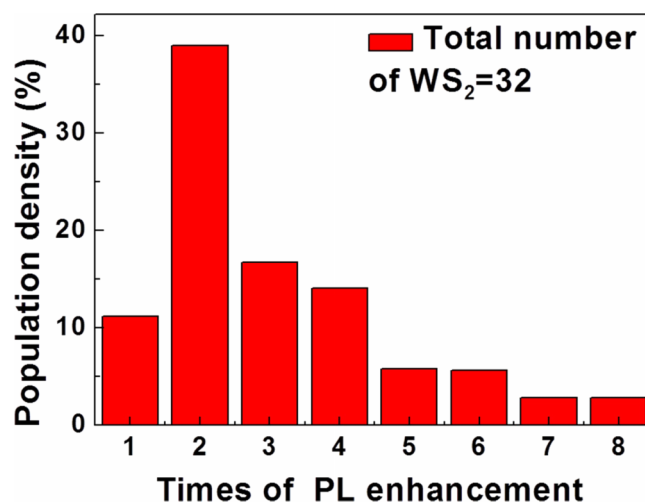


FIG. 4. The statistical distribution of average PL enhancement from total 32 Au-WS<sub>2</sub> flakes.

AuNPs may be responsible for the observed PL enhancement. In addition to the enhancement in PL intensity, a blue shift in PL spectra can be observed when decorating AuNPs on 2D WS<sub>2</sub>. Previous simulation implied that the pair of Au NPs configuration could give rise to a slight spectral blue shift due to plasmonic resonance.<sup>20</sup> Hence, it reveals that a blue shift in the PL emission wavelength in Figure 3(b) may correlate with the AuNPs arrangement.

Apart from the study of PL enhancement from the above described single triangle flake, we have measured PL variation from more triangle flakes. Figure 4 shows the average PL enhancement by decorating AuNPs on total 32 pieces of triangle WS<sub>2</sub> relevant to the same thickness. From the statistical analysis, we found that the most AuNPs/WS<sub>2</sub> induced PL enhancement is around two-folded on the whole, further supporting the feasibility of enhancing PL via the simple method of decorating Au NPs on few layer WS<sub>2</sub>.

#### IV. CONCLUSION

In conclusion, we have performed the synthesis, structural characterization and PL properties of Au-WS<sub>2</sub> nanocomposites. AuNPs can be selectively anchored on the surface of edge and defective sites of triangle atomic layered WS<sub>2</sub>. The conjugate provides an opportunity to modify PL features of 2D material due to increased optical absorption by plasmonic effect. We have demonstrated an enhancement and spatial distribution of PL in the Au-WS<sub>2</sub> nanocomposites. The simple method of Au NPs decoration may be generally expanded to the PL enhancement in a variety of 2D materials, which may provide a material platform to improve and exploit nanoscale photonic devices.

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