

PREPARATION AND CHARACTERIZATION OF AgNPs/MoS₂ NANOCOMPOSITES

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Silver nanoparticles/MoS₂ nanosheets (AgNPs/MoS₂) nanocomposites were prepared by a hierarchical assembly procedure. The functional 0D/2D nanocomposite will be a good candidate in many application fields, such as catalysis, antibacterial activity, energy storage, chemical and biological sensing. The obtained nanocomposites were characterized using X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and Raman spectroscopy. The results show that the AgNPs uniformly distribute on the MoS₂ nanosheets. The effects of silver nanoparticles with different weight ratio on the enhancing raman scattering of composites are discussed.

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1. Introduction

Two-dimensional (2D) nanomaterials have attracted great attentions because of their unique properties and promising applications. Among them, MoS₂ nanosheet is a typical 2D semiconductor and a graphene analogue constructed by stacking covalently bound S-Mo-S through weak van der Waals interactions which can be chemically intercalated and exfoliated using micromechanical cleavage or liquid phase exfoliation down to few layers or one layer thickness[1]. It has a similar structure to graphene, which attracts great attention in the fields of nanoelectronics[2], optoelectronics[3], catalysis, energy storage, solid lubrication, hydrogen storage, and lithium batteries[4]. The large surface area of MoS₂ nanosheet also allows it to be an excellent carrier and loaded with nanoparticles for the fabrication of 0D/2D multifunctional nanocomposites, offering a significant amplification in areas such as transparent conductive films, pH sensors, photothermal therapy and surface enhanced Raman scattering (SERS) electrochemical sensing signals[5-10].

Due to the quantum size effect, the metal nanoparticles have many unique properties. Silver nanoparticles have been intensively studied for a wide range of applications such as ultrasensitive (bio) sensing, nanomedicine, optoelectronics, and solar cells because of their distinctive electrical properties[11-13]. However, the unmodified metal nanoparticles are unstable and easy to lose excellent performance because of the oxidation and aggregation of the metal nanoparticles.

Here, we demonstrate a facile method for the preparation of AgNPs/MoS₂ nanocomposites with several advantages, including relatively low cost, high yields, and the capability to prepare metal nanostructures with controllable size and morphology. The distributions of AgNPs with different weight ratio on MoS₂ nanosheets are shown using TEM. The approach for high yields of AgNPs/MoS₂ nanocomposites opens up great possibilities for other potential applications.

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2. Experimental details

2.1 Preparation of AgNPs/MoS₂ nanocomposites

The procedures for exfoliating bulk MoS₂ into 2D materials were adapted from the previous studies[4]. The AgNPs were prepared via a mature route[14]. The process to load AgNPs onto MoS₂ nanosheets was briefly described as following. 36 mg AgNO₃ was dissolved in 200 ml deionized water and ultrasonic for 10 min. Then the solution was heated to boiling, and 4 ml 1 wt.% sodium citrate solution was quickly added. The boiling state was kept for 20 min to complete the reduction process. The obtained AgNPs with a weight ratio of 5% and MoS₂ nanosheets were mixed with a small amount of CuSO₄ aqueous solution. The mixed solutions were sonicated for 30 h to complete self-assembly, centrifuged at 10000 rpm for 80 min and dried in the vacuum oven. The 5wt.% AgNPs/MoS₂ nanocomposites with uniformly distribution of Ag nanoparticles on MoS₂ nanosheets were obtained.

2.2 Characterization methods

The X-ray diffraction (XRD) patterns were obtained using a D8 advance (Bruker-AXS) diffractometer with the 2θ range from 10 to 80°. The morphologies and structures of the samples were characterized by transmission electron microscopy (TEM) with a Japan JEM-100CX II transmission electron microscope. The SERS spectra were investigated by Raman laser spectrometer (DXR) at the excitation line of 632.8 nm.

3. Results and discussion

3.1 Structure and morphology characterization

AgNPs/MoS₂ nanocomposites were synthesized by a hierarchical assembly method. The crystalline structure of the obtained AgNPs/MoS₂ nanocomposites was confirmed by XRD, together with those of MoS₂ nanosheets, as shown in Fig. 1. In the XRD patterns, the (002), (100), (103), and (110) are the reflections of the structure of MoS₂ nanosheets. The evidence of crystalline AgNPs loaded on the MoS₂ nanosheets is shown by the additional peaks corresponding to the (111), (200), (220) and (311) diffractions, which confirms the successfully fabrication of the AgNPs/MoS₂ nanocomposites. However, the diffraction peaks of AgNPs are relatively weak, which may result from the low weight ratio of AgNPs in the nanocomposites. No other characteristic peaks were detected, indicating high purity of the sample.

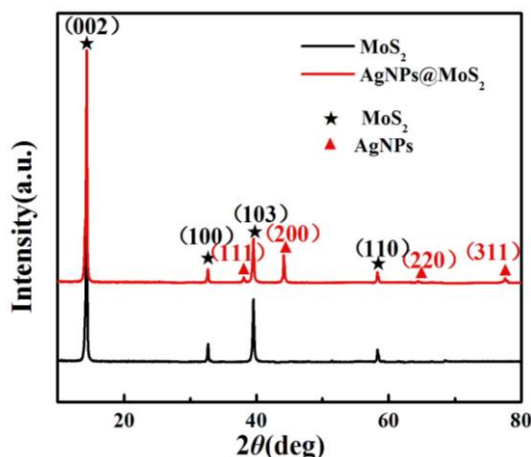


Fig. 1 XRD patterns of the as-prepared MoS₂ nanosheets and 5wt.% AgNPs/MoS₂ nanocomposites

The loading of AgNPs on MoS₂ nanosheets were studied by TEM (Fig. 2a and b). As shown in Fig. 2a and b, the sizes of MoS₂ nanosheets are ranging from 30 nm to 130 nm. Due to their ultrathin thickness, the MoS₂ nanosheets are entirely transparent to the electron beam. The AgNPs are uniformly dispersed on the surface of MoS₂ nanosheets with a diameter of 4 nm. Fig. 2c shows the HRTEM image of AgNPs/MoS₂ nanocomposites. The interfringe distance of 0.23 nm is consistent with the distance of the (111) lattice plane of AgNPs, which also confirms the successfully synthesis of AgNPs/MoS₂ nanocomposites.

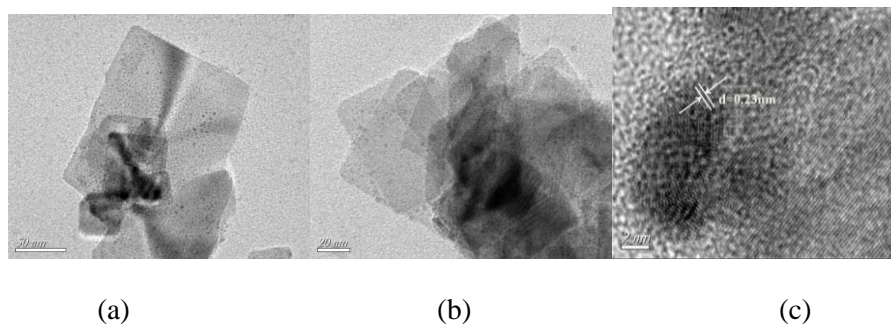


Fig. 2 TEM(a, b) and HRTEM images(c) of the 5wt.% AgNPs/MoS₂ nanocomposites

3.2 Characterization of AgNPs/MoS₂ nanocomposites with different weight ratio

The distributions of AgNPs with different weight ratio on the surface of MoS₂ nanosheets are also shown in Fig. 3 (the weight ratio is 5%, 10% and 20%, respectively) after a series of experiments have been performed. When the weight ratio of AgNPs is relatively low, the AgNPs are sparsely distributed on the MoS₂ nanosheets, as shown in Fig. 3a. The more silver particles are loaded, the denser distribution can be found (Fig. 3b). The assembled AgNPs are in high density and still uniformly disperse on the surface of MoS₂ nanosheets when the weight ratio is increased to 20%, as shown in Fig. 3c. It is obvious that the distribution of AgNPs on the MoS₂ nanosheets is becoming denser with the increasing weight ratio of AgNPs.

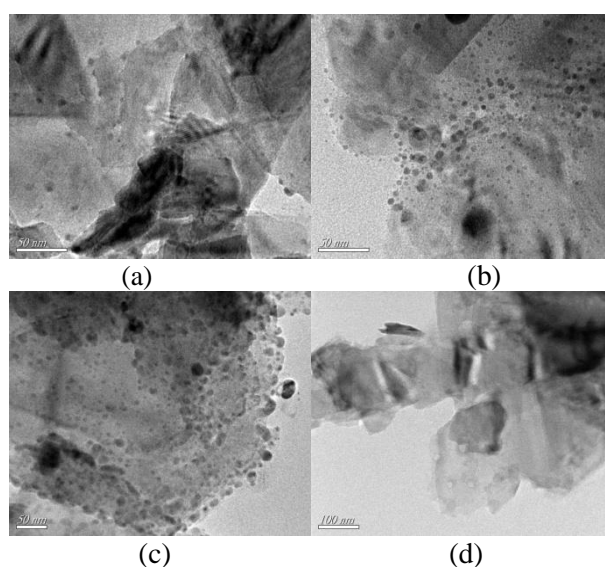


Fig. 3 (a), (b) and (c) TEM images of 5wt.%, 10wt.%, and 20wt.% AgNPs/MoS₂, respectively; (d) TEM images of 20wt.% AgNPs/MoS₂ without Cu(II) ions

It is noteworthy to find that there is no aggregation of AgNPs even with high weight ratio. When Cu(II) ions are absent, there are hardly any AgNPs deposited on the MoS₂ nanosheets surface due to the disappearance of electrostatic repulsion[15], as displayed in Fig. 3d. The adhesive force between the MoS₂ nanosheets and AgNPs is quite strong, and the interactions cannot be destroyed even after a long period of sonication during the preparation of TEM specimen.

SERS spectra of AgNPs/MoS₂ nanocomposites prepared at different weight ratios are measured and shown in Fig. 4. The Raman spectra of AgNPs/MoS₂ nanocomposites are excited by 632.8 nm line in air ambient environment. As shown in Fig. 4, the peaks of AgNPs/MoS₂ nanocomposites with different weight ratio are nearly consistent. The characteristic peaks of the 20wt.% AgNPs/MoS₂ nanocomposites are relatively stronger than those of other samples. The mechanisms for this enhancement can be attributed to the electromagnetic (EM) enhancement of the more AgNPs distribution onto MoS₂ nanosheet associated with larger local fields caused by the surface plasmon (SP) resonance of the 2D materials. Coupled SP is localized in the nanoscale junctions and interstices between AgNPs which play a main role of EM hot spots due to the uniformly distribution of more AgNPs that have intenser local EM fields, leading to the stronger Raman enhanced signals[1].

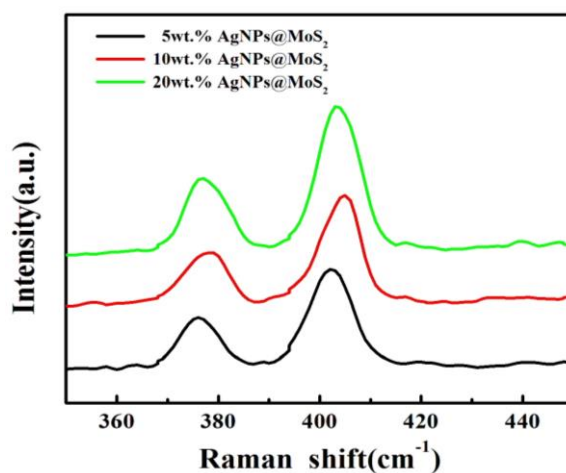


Fig. 4. Raman characterization of 5wt.%, 10wt.%, and 20wt.% AgNPs/MoS₂ nanocomposites

4. Conclusions

In conclusion, SERS-active AgNPs/MoS₂ nanocomposites have been successfully prepared via a self-assembly method. The distribution of AgNPs with different weight ratio on MoS₂ nanosheets are studied. When the weight ratio is increased to 20%, the distribution of AgNPs on MoS₂ nanosheets is already very dense. This facile method can be applied as a general method for the fabrication of 0D/2D nanocomposites especially transition metal dichalcogenides. This proposed approach will have great potential prospects for the development of 0D/2D materials-based devices.

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