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Facilitative effect of graphene quantum dots in MoS_2 growth process by chemical vapor deposition*

Lu Zhang(张璐), Yongsheng Wang(王永生), Yanfang Dong(董艳芳), Xuan Zhao(赵宣), Chen Fu(付晨), and Dawei He(何大伟)†

Key Laboratory of Luminescence and Optical Information, Ministry of Education, Institute of Optoelectronic Technology, Beijing Jiaotong University, Beijing 100044, *China*

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The substrate treatment with seeding promoter can promote the two-dimensional material lateral growth in chemical vapor deposition (CVD) process. Herein, graphene quantum dots (GQDs) as a novel seeding promoter were used to obtain uniform large-area MoS_2 monolayer. The obtained monolayer MoS_2 films were confirmed by optical microscope, scanning electron microscope, Raman and photoluminescence spectra. Raman mapping revealed that the MoS_2 monolayer was largely homogeneous.

Keywords: MoS_2, seed, graphene quantum dots (GQDs), continuous film

PACS: 81.07.–b, 81.07.Ta, 81.15.Gh, 81.10.–h **DOI:** 10.1088/1674-1056/27/1/018101

1. Introduction

Molybdenum disulfide (MoS_2), as a member of transition metal dichalcogenide (TMD) family, has attracted much attention due to their unique structures and remarkable properties.[1–3] The growth of MoS_2 has been extensively studied with chemical vapor deposition (CVD) and in this way triangular MoS_2 monolayer with tens of micrometers can be achieved.[4–6] However, the synthesis of thin larger-size MoS_2 layers is still a challenge.

It is reported that the edge,[5] scratches, stains, or rough surface of the substrate will provide nucleation sites and enable easier deposition for MoS_2 monolayer. Therefore the treatment process of the substrate has significant influence for the growth of two-dimensional MoS_2.[7,8] In Lee's report,[4,9] he dropped the reduced graphene oxide (r-GO) on the substrate and used r-GO as a seeding promoter, and systematically investigated perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt (PTAS), $F_{16}CuPc$, dibutyl phthalate (DBP), and 3,4,9,10-perylene-tetracarboxylic acid-dianhydride (PTCDA) on the role of the seeding promoter in synthesizing MoS_2 monolayers. He concluded that utilizing seeding promoters promotes the growth of a large-area, highly crystalline, and uniform MoS_2 monolayer at a relatively low temperature. Similar to the role of r-GO and aromatic molecules, the graphene quantum dots (GQDs) are also helpful for the nucleation of MoS_2.

In this work, we focused on the influence of GQDs as the seeding promoter to the growth of MoS_2. Using solid state precursors of MoO_3 and sulfur powder[8–10] which are simple and preferable for MoS_2 monolayer growth, we synthesize MoS_2 on sapphire substrate by CVD under atmospheric pressure. To characterize the samples, we used optical microscope, scanning electrical microscope (SEM), Raman spectroscope and photoluminescence (PL) spectroscope. A series of results indicated that GQDs can promote monolayer MoS_2 growth with a large area up to 670×500 μm^2.

2. Experimental section

2.1. Preparation of GQDs

GQDs were prepared from bottom-up carbonization of citric acid (CA).[11–13] 0.5 g CA was put into a round flask then placed into silicon oil bath. The oil bath was heated to 175 °C. About 5 min later, the CA was liquated. Subsequently, the color of the liquid was changed from colorless to pale yellow, and then orange in 30 min, implying the formation of GQDs. The obtained orange liquid for preparing GQDs was added drop by drop into 50 mL of 10 mg·mL^{-1} NaOH solution, under vigorous stirring. Subsequently, the solution was neutralized to PH 7.0 using dialysis bag (3000 Da) and the aqueous solution of GQDs was obtained.

2.2. Substrate treatment

Before the experiment, the sapphire substrate was purified with detergent solution under 60 min ultrasonication, then with deionized water and alcohol respectively under 20 min (3 times) ultrasonication. After the cleaning process, the substrate is preserved in alcohol solution. Prior to the CVD process, the substrate was blow-dried with nitrogen gas and then

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†Corresponding author. E-mail: dwhe@bjtu.edu.cn

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treated with oxygen plasma machine for about 2 min. Then, a certain concentration of GQDs solution was dropped onto the substrate and gently blow-dried with N_2 gas.

2.3. Synthesis of thin-layer MoS_2

Figure 1 schematically illustrates our experimental set-up. The MoO_3 powder (99.5%, 0.05 g) in a ceramic boat was placed in the center of the heating zone of the furnace and the sapphire substrate was faced down and mounted on the top of the boat. Also sulfur powder (99.5%, 0.5 g) loaded in a ceramic boat was placed in the low-temperature area, upstream relative to the gas flow direction. Prior to the growth, the furnace was purged with Ar for 30 min. Then, the MoO_3 container was heated to 700 °C and maintained at this temperature for 60 min. After this, the furnace was cooled down to room temperature naturally. For the entire process, Ar (100 sccm) was injected as a carrier gas.

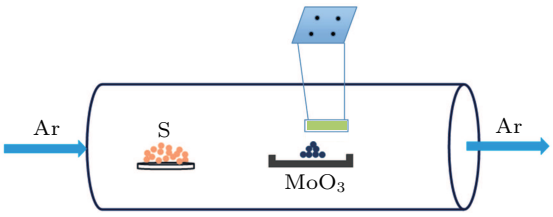


Fig. 1. (color online) Schematic illustration of MoS_2 CVD system.

3. Results and discussion

The GQDs were characterized by TEM shown in Fig. 2. The diameter mainly distributed between 1 to 5 nm (average diameter 2.35 nm).

We used deionized water to dilute prepared GQDs solution (10 mg/ml) into 1 mg/ml, 1.5 mg/ml, and 2 mg/ml GQDs solution. Figure 3 shows the obtained samples on substrates treated with different concentration GQDs solution.

The brighter-contrast area on the surface indicates the MoS_2 film, and the surrounding regions correspond to the substrate. Figure 3(a) shows the MoS_2 grown on substrate without adding GQDs, indicating that only a small area MoS_2 film with a lateral size about 150 μm was achieved. In Fig. 3(b), we also observe continuous film showed heterogeneous color and some isolated triangular parts. It is deduced that a comparative low concentration of seeding promoter provided less nucleation sites on the substrate. However, it can be seen that the sample in Fig. 3(c) is flat and homogeneous in color with a lateral size up to 500 μm. In Fig. 3(d), the density is too high to form a continuous MoS_2 film. Comparisons carried out in Figures 3(b)–3(c) suggest that the optimizing density of GQDs will facilitate a large-area, uniform and highly crystalline MoS_2 monolayer deposition on the substrate.

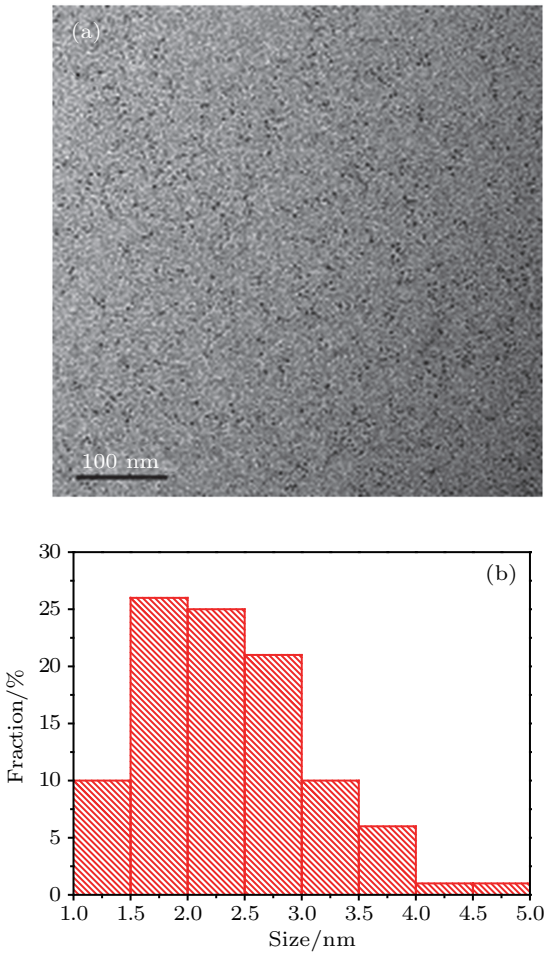


Fig. 2. (color online) (a) TEM image of GQDs. (b) Diameter distribution of GQDs.

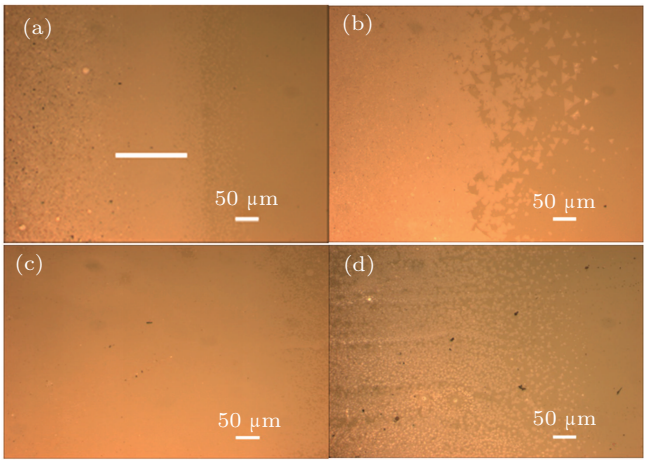


Fig. 3. (color online) Optical microscope images of MoS_2 samples on substrates treated with different concentration of GQDs solution. (a) MoS_2 films that are directly grown on the sapphire. MoS_2 films with GQDs at (b) 1 mg/ml, (c) 1.5 mg/ml, and (d) 2 mg/ml.

The sample with 1.5 mg/ml GQDs was further examined using SEM, Raman, and PL characterization.

Figure 4 show the SEM images for the sample. The brightness of scratches in the picture is obviously different from other areas. We can conclude that a large-area continuous

MoS_2 deposited on the substrate pre-treatment with 1.5 mg/ml GQDs, which is at least 200 μm in lateral size.

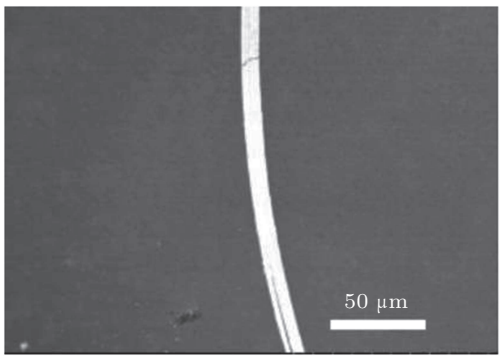


Fig. 4. Scanning electron microscope images of MoS_2 film.

The results demonstrate that Raman and PL spectra of the sample show good consistency with MoS_2 film synthesized on bare substrate and GQDs did not affect film thickness. In Fig. 5(a), two pronounced peaks were observed in MoS_2 due to the out-of-plane vibrational modes of the sulfur atoms (A_{1g}) and the in-plane vibrational modes of the molybdenum and sulfur atoms (E^1_{2g}). The frequency between the E^1_{2g} and A_{1g} Raman modes depends on the number of layers of the MoS_2 sample, which is about 20 cm^{-1} for monolayer MoS_2 and about 26 cm^{-1} for bulk MoS_2.[14,15] In our case, the E^1_{2g} and A_{1g} modes in the synthesized MoS_2 samples occurred at the 386.4 cm^{-1} and 406.0 cm^{-1}, and the frequency difference between the two modes is 19.6 cm^{-1} (Fig. 5(a)). This value agrees well with the values observed in previous studies[5,16,17] and indicates that we obtained monolayer MoS_2 by using 1.5 mg/ml GQDs as the seeding promoter. The black line in Fig. 5(b) shows the PL spectra of the sample. A remarkably high PL intensity was observed at 669 nm (1.85 eV) and this emission peak is known as direct excitonic transition.[18,19] In contrast, there is nearly no PL intensity for bulk MoS_2. The emission intensity obviously decreases with the layer number, because the optical bandgap transforms from indirect to direct one when the dimension of MoS_2 is reduced from a bulk form to a monolayer.[20] The PL result displayed by the black line is consistent with a direct bandgap of monolayer MoS_2, which further identifies high quality of obtained MoS_2 film.

We took $14 \times 14 = 196$ points from the center region (covers an area of 20 μm×20 μm) in Fig. 3(c) to make a Raman mapping scanning of E^1_{2g} and A_{1g}. Figure 6(b) reveals a frequency difference in Fig. 6(a) mainly distributed between 19.6 cm^{-1} to 20.4 cm^{-1}, suggesting that the thickness variation is negligible and shows a high uniformity of the MoS_2 film.

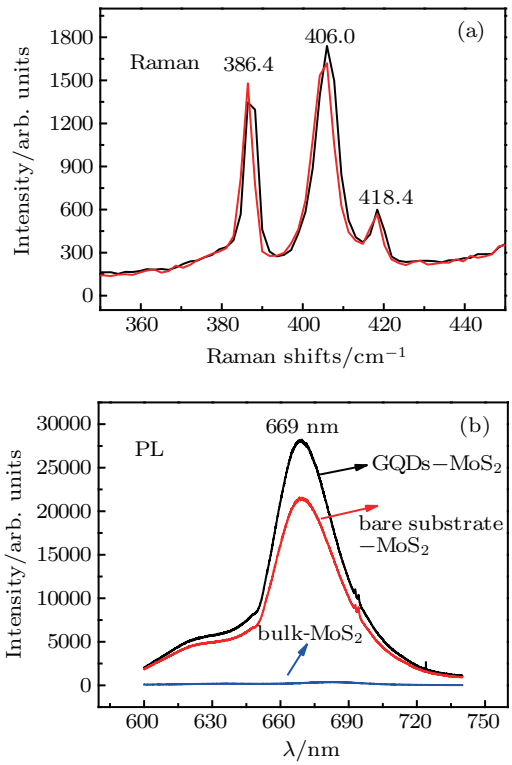


Fig. 5. (color online) Raman and photoluminescence spectra of MoS_2 monolayer with (black line) and without (red line) using GQDs as seeding promoter.

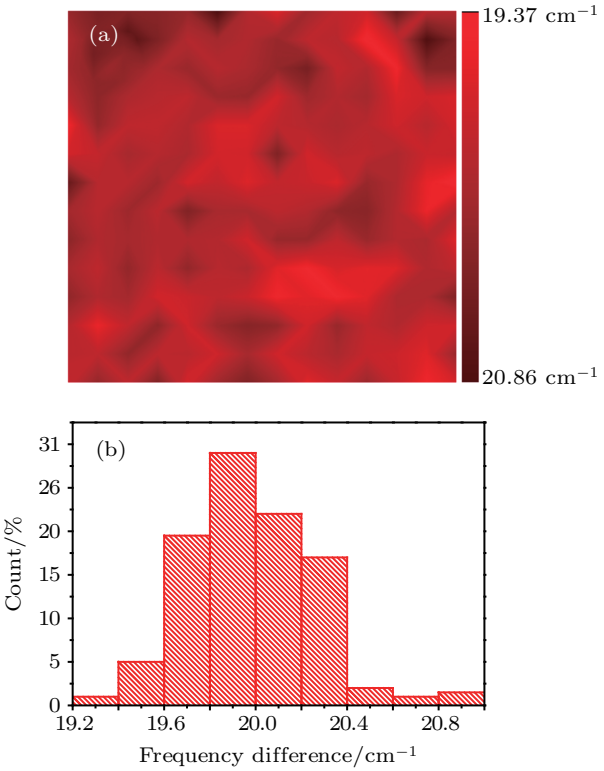


Fig. 6. (color online) (a) Raman mapping of the frequency difference E^1_{2g} and A_{1g}. (b) Distribution of frequency difference E^1_{2g} and A_{1g}.

4. Conclusion

In this work, we prepared GQDs and investigated the influence of GQDs in facilitating the growth of MoS_2 on sap-

phire substrate. Comparing the growth results with different concentration and without using the GQDs seeding promoter, it is clear that a large-area, continuous, and high-quality MoS_2 monolayer can be obtained under relatively low temperature (700 °C) conditions using 1.5 mg/ml GQDs as a seeding promoter. An optimum concentration of GQDs provided proper nucleation distance and played the same role as r-GO which will increase the surface adhesive force and promote the layer growth of MoS_2. Moreover, the film growth properties were further characterized by optical microscopy, SEM, Raman and PL measurements.

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