Research Article

Facile Hydrothermal Synthesis of Monodispersed MoS₂ Ultrathin Nanosheets Assisted by Ionic Liquid Brij56

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Monodispersed MoS₂ ultrathin nanosheets have been successfully fabricated by a facile hydrothermal process assisted by ionic liquid Brij56. The effect of Brij56 on the morphology and structure of MoS₂ has been obviously observed. XRD shows that the as-prepared MoS₂ assisted by Brij56 has the weak and broad peak of (002) planes, which implies the small size and well dispersed structure of MoS₂ nanosheets. TEM and SEM images reveal that MoS₂ ultrathin nanosheets have small size and few stacking layers with the adding of Brij56. HRTEM images prove that MoS₂ appears to have a highly monodispersed morphology and to be monolayer ultrathin nanosheets with the length about 5–8 nm, which can provide more exposed rims and edges as active sites for hydrogen evolution reaction. Brij56 has played a crucial role in preparing monodispersed MoS₂ ultrathin nanosheets as excellent electrocatalysts. The growth mechanism of monodispersed MoS₂ has been discussed in detail.

1. Introduction

Hydrogen as a promising sustainable energy carrier has attracted much attention owing to the increasing environmental pollution and the limited fossil fuel [1]. The ideal fashion of hydrogen production is to adopt photoelectrochemical [2] or electrochemical [3] route. However, Pt as highly active electrocatalyst for hydrogen evolution reaction (HER) [4] has a high price and limited resources, which largely prevent the wide utilization of HER. Therefore, replacing the novel metals with earth-abundant elements represents future development of the electrocatalysts for HER [5].

MoS₂ has been widely investigated as a promising substitute for Pt due to its unique properties and abundant reserve [6]. Recent research has shown that the active sites of MoS₂ for HER are highly dependent on the exposed defects of the rims and edges [7]. However, as a typical two-dimensional (2D) transition-metal sulfide, MoS₂ has analogous layered structure of graphene, which results in severe stacking owing to the high surface energy and interlayer van der Waals attraction [8]. Moreover, the unsaturated sulfur atoms of MoS₂ can improve the discharge reaction and form S–H bonds, thus

leading to hydrogen evolution easily [9]. Hu's group prepared the amorphous MoS₃ particles with catalytically active S^{2–} and superior catalytic activity [10]. Therefore, designing highly active MoS₂ with more rims and edges sites has been a challenge by a facile process [11].

The ionic liquids have been used as structure-directing agent or dispersion solvents to prepare novel nanomaterials including the 2D nanosheets [12, 13]. The most exposed basal planes of MoS₂ are the thermodynamically stable (002) planes, which have poor activity for HER [14]. In our previous work, ionic liquid Brij56 [C₁₆H₃₃–(OCH₂–CH₂)₁₀OH] has been used to synthesize MoS₂ nanoflowers [15]. However, the severe stacking and large size of MoS₂ nanoflowers would decrease the exposed active sites for HER, which may be attributed to the Na₂MoO₄ as precursor. Thus, preventing the growth along (002) plane by changing reactants and experimental conditions can be expected to improve the exposure of the active sites of MoS₂ for HER [16].

In this work, ammonium thiomolybdate (ATTM) has been chosen as precursor owing to its in situ decomposition [17] in comparison to sulfidation from Na₂MoO₄. And suitable pH and reductant HONH₃Cl have also been used to

FIGURE 1: XRD and selected area electron diffraction (SAED) of MoS_2 under different concentration of Brij56: (a) XRD of MoS_2 assisted by 0 mL, 1 mL, and 5 mL Brij56, respectively; (b, c, and d) SAED images of MoS_2 assisted by 0 mL, 1 mL, and 5 mL Brij56, respectively.

control the structure of MoS_2 . Therefore, monodispersed MoS_2 ultrathin nanosheets have been prepared by a facile hydrothermal synthesis assisted by ionic liquid Brij56. The effect of Brij56 concentration on the structure and size of MoS_2 has been investigated in detail. The growth mechanisms of monodispersed MoS_2 under the conditions of ATTMM and Brij56 are also discussed.

2. Experimental

ATTMM were synthesized according to the previous literature [18]. Then 1 mL or 5 mL Brij56 and 0.550 g ATTMM were added to 20 mL of deionized water at about pH 10 under stirring for 3 h. Then, an appropriate amount of HONH_3Cl was added. The obtained solution was transferred into a Teflon stainless steel autoclave. Hydrothermal reaction was carried out at 240°C for 24 h. The as-prepared samples were washed and dried at 80°C for 24 h in a vacuum oven. Compared with the absence of Brij56, MoS_2 was also synthesized under otherwise identical conditions.

Crystallographic information of all samples was investigated with X-ray powder diffraction (XRD, X'Pert PRO MPD, Cu KR). The morphology of the samples was examined with scanning electron microscopy (SEM, Hitachi, S-4800) and high-resolution analytical transmission electron microscopy (HRTEM, JEM-2100UHR, 200 kV). Selected area electron

diffraction (SAED) was used to examine the samples' crystallinity.

3. Results and Discussion

XRD patterns of the as-synthesized MoS_2 under different concentration of Brij56 are shown in Figure 1(a). MoS_2 without Brij56 has strong peaks corresponding to (002), (100), (103), and (110) reflections, respectively, consistent with the standard diffraction file of MoS_2 (JCPDS 37-1492). With the using of Brij56, the peaks of (002) and (103) of MoS_2 decrease remarkably (1 mL Brij56) and almost disappear (5 mL Brij56), which indicates that Brij56 strongly prevents the growth of (002) and (103) planes. And MoS_2 with the absence of (002) implies the low crystallinity and monolayer structure of MoS_2 [19]. The slight right shift of (002) peak could be attributed to the distortion of lattice in MoS_2 . The (100) and (110) planes keep stable, indicating the good stability of MoS_2 , which can be confirmed by the selected area electron diffraction (SAED). As shown in Figures 1(b), 1(c), and 1(d), the SAED patterns show clearly more and more invisible rings corresponding to (002) and (103) with the adding of Brij56, which well agrees with the results of XRD.

The size and morphology of as-prepared MoS_2 have been observed by SEM and TEM (Figure 2). Figures 2(a) and 2(d) show that MoS_2 assisted by 0 mL Brij56 has large aggregation

FIGURE 2: SEM and TEM images of MoS_2 with different concentration of Brij56: (a, b, and c) SEM images of MoS_2 assisted by 0 mL, 1 mL, and 5 mL Brij56; (d, e, and f) TEM images of MoS_2 assisted by 0 mL, 1 mL, and 5 mL Brij56.

and severe stacking, which imply less rims and edges of MoS_2 . Figure 2(b) shows that the large aggregation of MoS_2 decreases and MoS_2 has some loose microstructure (in Figure 2(e)) when using 1 mL Brij56. The effect of Brij56 on morphology of MoS_2 has been proved. Next, as shown in Figure 2(c), MoS_2 assisted by 5 mL Brij56 became smaller with the size of about 20 nm. And porous structures of MoS_2 have been observed. Figure 2(f) confirms the loose porous structure and smaller size of MoS_2 , indicating less stack layers and more rims and edges sites of MoS_2 with the increasing of concentration of Brij56.

HRTEM images with higher magnification prove the change tendency of monodispersed MoS_2 (Figure 3). Figure 3(a) shows that MoS_2 assisted by 0 mL Brij56 has the length of more than 100 nm and very severe stacking, indicating less rims and edges. Figure 3(b) shows that MoS_2 assisted by 1 mL Brij56 has obviously decreasing length of about 20–30 nm and less stacking layers with the larger interlayer

spacing. The results indicate that Brij56 has prevented the rapid growth along (002) planes and the severe stacking of MoS_2 . Figure 3(c) shows that monodispersed MoS_2 assisted by 5 mL Brij56 has the length of about 5–8 nm and appears to have monolayer structure, which is corresponding to the more porous structure of MoS_2 (in Figure 2(c)). The decreasing size and less stacking of MoS_2 would provide more defects sites. In addition, monodispersed MoS_2 ultrathin nanosheets are usually curly and bent to some extent on the rims and edges, which means more active sites [20].

The formation mechanisms of monodispersed MoS_2 assisted by Brij56 have been discussed in Figure 4. Firstly, non-ionic surfactant Brij56 as a dispersant will form a stable spherical micelles system for homogeneously dispersing MoS_4^{2-} under stirring. The size of the micelles will decrease with the increasing of the concentration of Brij56. The micelles could provide nucleation domains for in situ decomposition of MoS_4^{2-} , which may be helpful for size controlling and the

FIGURE 3: HRTEM images of MoS_2 with different concentration of Brij56: (a) 0 mL, (b) 1 mL, and (c) 5 mL.

FIGURE 4: Schematic illustration of the formation mechanism of monodispersed MoS_2 .

growth along (002) direction of MoS_2 . During the hydrothermal process, Brij56 micelles tend to be hydrophobic and increase the viscosity of micellar solution, which favors the monodispersed growth of MoS_2 [20]. MoS_2 with more monodispersed structure under the high concentration of Brij56 could provide rich active sites.

4. Conclusions

Monodispersed MoS_2 ultrathin nanosheets with more active sites for HER have been fabricated by a facile hydrothermal process assisted by Brij56. MoS_2 assisted by Brij56 has weak and broad peak of (002), indicating small size and well

dispersed structure. SEM and TEM images reveal that highly dispersed MoS₂ nanosheets have been obtained with the increasing of the concentration of Brij56. Monodispersed MoS₂ assisted by 5 mL Brij56 has the length of about 5–8 nm and a monolayer structure, which provide more rims and edges sites. The curly structure of monodispersed MoS₂ ultrathin nanosheets would also expose more active sites. The facile hydrothermal synthesis assisted by Brij56 has been a good route for excellent MoS₂ electrocatalysts for HER.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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