Monodispersed MoS$_2$ 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 MoS$_2$ has been obviously observed. XRD shows that the as-prepared MoS$_2$ assisted by Brij56 has the weak and broad peak of (002) planes, which implies the small size and well dispersed structure of MoS$_2$ nanosheets. TEM and SEM images reveal that MoS$_2$ ultrathin nanosheets have small size and few stacking layers with the adding of Brij56. HRTEM images prove that MoS$_2$ 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 MoS$_2$ ultrathin nanosheets as excellent electrocatalysts. The growth mechanism of monodispersed MoS$_2$ 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].

MoS$_2$ 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 MoS$_2$ 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, MoS$_2$ 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 MoS$_2$ can improve the discharge reaction and form S–H bonds, thus leading to hydrogen evolution easily [9]. Hu’s group prepared the amorphous MoS$_2$ particles with catalytically active S$^2$ and superior catalytic activity [10]. Therefore, designing highly active MoS$_2$ with more rims and edges sites has been a challenge by a facile process [11].

Monodispersed MoS$_2$ 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 MoS$_2$ has been obviously observed. XRD shows that the as-prepared MoS$_2$ assisted by Brij56 has the weak and broad peak of (002) planes, which implies the small size and well dispersed structure of MoS$_2$ nanosheets. TEM and SEM images reveal that MoS$_2$ ultrathin nanosheets have small size and few stacking layers with the adding of Brij56. HRTEM images prove that MoS$_2$ 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 MoS$_2$ ultrathin nanosheets as excellent electrocatalysts. The growth mechanism of monodispersed MoS$_2$ has been discussed in detail.
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 ATTM and Brij56 are also discussed.

2. Experimental

ATTM were synthesized according to the previous literature [18]. Then 1 mL or 5 mL Brij56 and 0.550 g ATTM were added to 20 mL of deionized water at about pH 10 under stirring for 3 h. Then, an appropriate amount of HONH$_3$Cl 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.
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 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.
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 MoS$_2$ nanosheets have been obtained with the increasing of the concentration of Brij56. Monodispersed MoS$_2$ 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 MoS$_2$ ultrathin nanosheets would also expose more active sites. The facile hydrothermal synthesis assisted by Brij56 has been a good route for excellent MoS$_2$ 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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References


