Preparation Of WS_2 Nanosheets By One-step Hydrothermal Method

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Abstract. In this work, a modified hydrothermal method has been developed and employed for synthesis of few layers Tungsten disulfide-nanosheets(WS_2-NS). Using of sodium cholate as a surfactant and changing in raw materials were the main changes which were applied in the modified method with respect to the orginal procedure. As-prepared WS_2 samples were characterized by XRD, TEM, and Raman spectrum. The results showed that the obtained WS_2-NS are consist of 1-10 atomic layers. The influence of surfactant on the formation of WS_2-NS was investigated. A possible growth mechanism is proposed to explain the formation of WS_2-NS.

Introduction

During the past years, tremendous attention has been paid to Two-dimensional layered materials. In addition to graphene[1], layered graphene-like materials also received quite a few interest, such as Transition metal dichalcogenides(TMD)[2] and Topological insulators. The element layer of the TMD consists of transition metal atoms sandwiched between the upper and lower layers of sulfur atoms. The atoms are connected by strong covalent bonds, while the layers are weakly held together by Van Der walls forces[3]. WS2 that is a representative TMD can be processed by chemical and physical methods[4,5] into a Two-dimensional nanosheet structure. WS2-NS with atomic scale thickness may exhibit special and interesting properties in contrast with those of their bulk compounds[6]. Due to the peculiar electron configuration and high specific surface area of WS2-NS,it has potential application in catalytic hydrogen production[7], electrode devices[8] andenergy storage devices[9].

To date, many methods have been reported to prepare the WS2-NS, including mechanical exfoliation, chemical exfoliation, chemical vapor deposition and hydrothermal method. Late[10], obtained the few layers WS2-NS by repeatedly folding a piece of adhesive Scotch tape with WS2 powder. Coleman et al[11], developed a reliable surfactant-assisted liquid exfoliation method to produce WS2-NS. In order to meet the requirements of WS2-NS in various fields, a one-step hydrothermal method was proposed to stably and efficiently prepare WS2-NS in this paper.

Experimental

Synthesis of WS_2 nanosheets:

All chemicals were analytical and used without further purification.

In a typical process,0.003 mol of tungstic acid(H2WO4) and 0.008 mol of sulfourea were dissolved in 60 ml deionized water, and then different surfactants was added into the above solution under continuous stirring. Hydrochloric acid and ammonia water were add into the above solution to adjust PH value to 6. The final solution was transferred into a 100 ml Telflon-lined stainless steel autoclave and sealed tightly, heated at 180 °C for 10 h and then naturally cooled down to room temperature. The black precipitates were retrieved from the solution by centrifugation and washed with distilled water and ethanol for several times, finally dried in vacuum at 60 °C for 12 h. To better distinguish the samples, the precipitates using no surfactants was named sample Ⅰ,while precipitates obtained with the addition of cetyltrimethyl ammonium bromide(CTAB, 0.008 g) and sodium cholate(0.012 g) were named as sample Ⅱ and sample Ⅲ.

Characterization:

The X-ray diffraction(XRD) patterns were recorded using German Bruker-AXS D8 X-ray diffract to meter with Cu Kα radiation(λ=0.1546 nm).The morphology of the as-synthesized products were examined by transmission electron microscopy(TEM, Hitachi, H-7650).Raman spectroscopy measurements were performed on a Lab RAM HA Evolution.

Results and Dscussion

In order to confirm the composion of the samples, the XRD patterns of WS2-nanosheets were shown in Fig.1.Allsamples present representative peaks indexed to be the hexagonal WS2 structure(JCPDS card No.87-2417).Whatever the surfactants are CTAB, sodium cholate or no surfactant is added three curves in Fig.1 are practically similar show that the surfactants which added to the system have no effect on crystallization of WS2-NS.

The morphology and structure of WS2-NS have been characterized using TEM, which are show in Fig.2, It is well known that crystal growth mechanisms and crystallization process in solution are very complicated, We mainly discuss the influence of surfactants on the above process. According to previous researches, the surfactant usually has a hydrophilic head and a hydrophobic tail, it will be self-assemble and formed micelles when the surfactant in the solution reaches a certain concentration and Nano materials will nucleate and grow with these micelles as templates. in our experiment, the reaction routes for the synthesis of WS2 could be expressed as follows:

$$4H_2WO_4+15CS(NH_2)_2+6H_2O \rightarrow 4WS_2+(NH_4)_2SO_4+6NH_4CSN+16NH_3\uparrow+9CO_2\uparrow \quad (1)$$

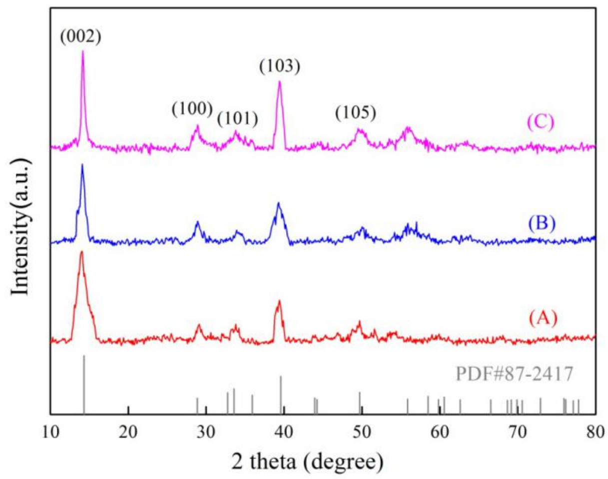

Figure 1. XRD patterns of (A) sample I , (B) sample II and(C) sample III.

As shown in Fig.2a,the sample Ⅰ is irregular shape with diameters ranging from 300 to 500 nm, it can be seen clearly for the special layered structure of WS_2, but the reaction produced WS_2 are still bulk phase without surfactants added. However, as show in Fig.2b and Fig.2c, when CTAB is added, A plate-like structure composed of nanorods appeared and the length of the nanorods or plate is 400 to 800 nm. First of all, CTAB is self-assemble and forms rod-like micelles in solution, of which external are hydrophilic group and internal are hydrophobic group. Then WS_2 uses rod-like micelle as template to nucleate and grow for one dimensional rod structure, finally WS_2 rods gather together and self-assembly to be a plate-like structure for keep the low energy of the system.

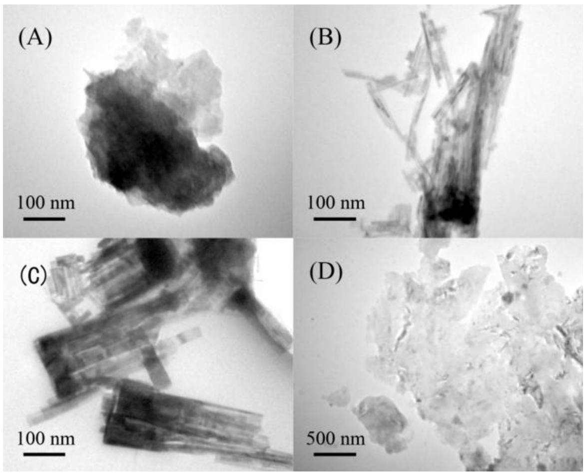

Figure 2. TEM images of (A) sample I , (B and C) sample II and(D) sample III.

Furthermore, Crystallization intactWS2-NS are obtained with surfactant sodium cholate while other experimental conditions are same as shown in Fig.2d. One of the important features of sodium cholate, unlike other surfactants, is that it doesn't have a fixed critical micelle concentration(CMC), but rather a gradual aggregation process, the CMC decreases with the increase of temperature. Therefore, we can get the lamellar micelles by adjusting the temperature(180°C) to control the CMC of surfactants. At the same time, sodium cholate reduces the free energy of the system and provides a suitable microenvironment for the stable existence of WS2-NS.

Raman spectroscopy was further applied to characterize the layered structure of the WS2.According to previous reports, the bulk crystal WS2 shows two Raman peaks at 355 and 421cm-1 corresponding to the well know active Raman modes in-plane E12g and out-of-plane A1g ,with the decrease of the number of crystals layers, the two peaks are red-shifted and blue–shifted respectively and close to each other. As show in Fig.3，the two peaks of sample Ⅰ appeared at 355.1 and 420.2cm-1, and this is consistent with bulk crystal WS2. The sample Ⅱ is a plate-like structure composed of regularly arranged nanorods and it still has specified thickness as compared with few layer nanosheets, so these two peaks appeared at 359.1 and 420.2cm-1 respectively. The E12g peak and A1g peak of sample Ⅲ appeared at 362.1 and 417.2cm-1 respectively and Raman shift between these two peaks is 55.1cm-1. Referring to Late et al[10], the thickness of sample Ⅲ is 1-10 atomic layers. Hence, independently of the TEM measurements, These results provide an additional confirmation of the few layer character of sample Ⅲ.

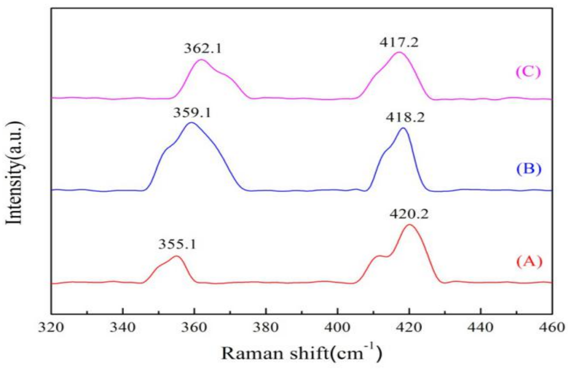

Figure 3. Raman spectra of (A) sample I , (B) sample II and(C) sample III.

Conclusion

In summary, WS_2-NS were successfully prepared by a simple one-step hydrothermal process. The thickness of the prepared nanosheets was confirmed to be 1-10 atomic layers by TEM images and Raman spectra. The experimental results of samples with different surfactants added suggest that the surfactants played an important role in the growth of WS_2-NS. Furthermore, a possible growth mechanism was proposed to explain the formation of WS_2-NS. Considering the simple synthetic process and thinness of WS_2-NS, we believe this work will open up an avenue for industrial production of WS_2-NS.

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