

Hydrothermal synthesis and controlled growth of tungsten disulphide nanostructures from one-dimension to three-dimensions

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Three kinds of tungsten disulphide (WS₂) such as nanospheres, nanowires and nanobelts have been synthesised using cetyltrimethyl ammonium bromide (CTAB) as a surfactant. The structural features of the as-prepared WS₂ were characterised by X-ray powder diffraction and scanning electron microscopy. The CTAB surfactants played a critical role in producing different WS₂ nanostructures. The growth mechanism of WS₂ nanostructures is proposed in detail and the schematic representation of the formation mechanism is also shown. Also, the optical absorption property of the WS₂ nanostructures was investigated. This reported work may be helpful to investigate structurally other metal chalcogenide materials with different morphologies.

1. Introduction: Recently, there has been much interest in the synthesis and study of transition metal chalcogenides (MX₂) compounds with a layered structure, where M=W or Mo (in particular) and X=S or Se [1–5]. As one of the very promising semiconductor materials for various applications, tungsten disulphide (WS₂) nanomaterials with novel three-dimensional (3D) hierarchical architectures have attracted considerable attention [6, 7]. Compared with WS₂ bulk materials, microscale or nanoscale WS₂ materials also always show unique properties. It has been shown that the WS₂ micro–nanomaterials can be applied in the fields of catalysts [8–11], solid super-lubricants [12–18], lithium batteries [19–21], electrochemical hydrogen storage [22–24], photocatalysts [25, 26] and so on. So far, various synthetic methods of generating micro–nanoscale WS₂ with specific morphologies and unique properties have been explored, including the mechanical activation method [24], magnetron sputtering [27], thermal decomposition [28], laser ablation [29], chemical vapour deposition [30, 31], solid–gas reaction [4] and so on. However, much time and expense are associated with the above methods, which has resulted in the limitation of widespread use. Owing to its low temperature, convenient and simple fabrication process, and high product purity [32–36], the hydrothermal process has been considered the most promising route.

In the work reported in this Letter, WS₂ with different morphologies was prepared successfully by cetyltrimethyl ammonium bromide (CTAB)-assisted hydrothermal synthesis. The possible growth mechanism of the different WS₂ nanostructures is discussed in detail. Furthermore, the optical absorption property of the WS₂ nanostructures are investigated.

2. Experimental

2.1. Synthesis: All chemical reagents were of analytic purity and used directly without further purification. The experimental procedure was designed as follows. 0.003 mol Na₂WO₄, 0.006 mol NH₂OH•HCl, 0.01 mol CH₄N₂S and appropriate CTAB (0.2; 0.4; 0.75 mmol) were dissolved in 50 ml deionised water. The pH value of the solution was adjusted to 6 by the addition of 2 mol/l HCl. The final mixed solution was under vigorous

magnetic stirrer for 4 h, then transferred into a 100 ml Teflon-lined stainless steel autoclave and sealed. The autoclave was maintained at 160–200°C for 12–24 h. After the reaction was completed, the autoclave was cooled to room temperature naturally. Black products were centrifuged for 1 min at 10 000 rpm and washed with distilled water and absolute ethanol several times, then dried in air at 60°C for 10 h.

2.2. Characterisation of WS₂ samples: The as-prepared samples were characterised using X-ray diffraction (XRD), a Rigaku D/Max-1200X diffractometer with Cu Kα radiation and a Nova 400 Nano field emission scanning electronic microscope.

3. Results and discussion

3.1. XRD analysis: Fig. 1 shows the XRD patterns of the as-prepared samples with different concentrations of CTAB. All diffraction peaks were perfectly consistent with the standard values (JCPDS No. 08-0237), which demonstrated that the as-prepared samples were WS₂. As shown in the XRD analysis, the addition of CTAB had little effect on the crystal structure under the present synthetic conditions.

3.2. SEM analysis: Three different morphologies of WS₂ nanospheres, nanowires and nanobelts are shown in Fig. 2. As shown in Fig. 2a, the obtained WS₂ nanospheres are of uniform size and shape. They are nearly spherical with diameters ranging from 100 to 150 nm. Meanwhile, from Fig. 2A, we note that these nanospheres are solid, not hollow. As shown in Fig. 2b, the net-like WS₂ structure is composed of numerous nanowires. A large scale of nanowires with a length of about 250 nm and diameters of about 10 nm joined together and formed a net-like structure. From Fig. 2B, we see that these nanowires' cross-sections are circular and solid. As shown in Figs. 2c and C, bunches of WS₂ nanobelts with a width of 30–50 nm and a length ranging from 300 to 500 nm are obtained. One can see that bunches of WS₂ nanobelts with a thickness of <10 nm are smooth and straight. The above results demonstrate that the desirable WS₂ nanomaterials from 1D to 3D have been synthesised successfully. Therefore, based on the above

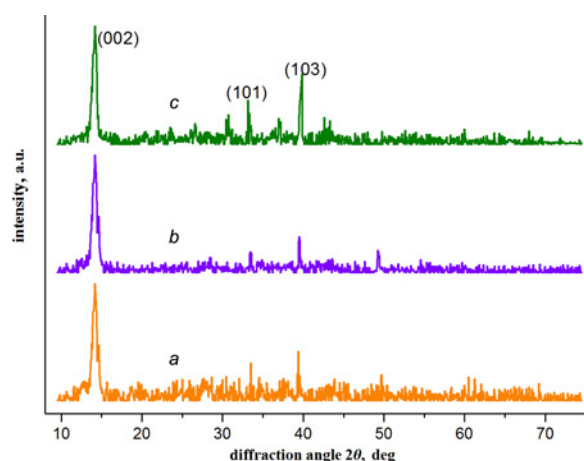


Figure 1 XRD patterns for the WS_2 products: a, 0.2 mmol CTAB; b, 0.4 mmol CTAB; and c, 0.75 mmol CTAB

experimental results, the CTAB had a crucial influence on the formation of different morphologies of WS_2 in our experiment.

3.3. Growth mechanisms: According to the above experimental results, the surfactant CTAB played an important role as a

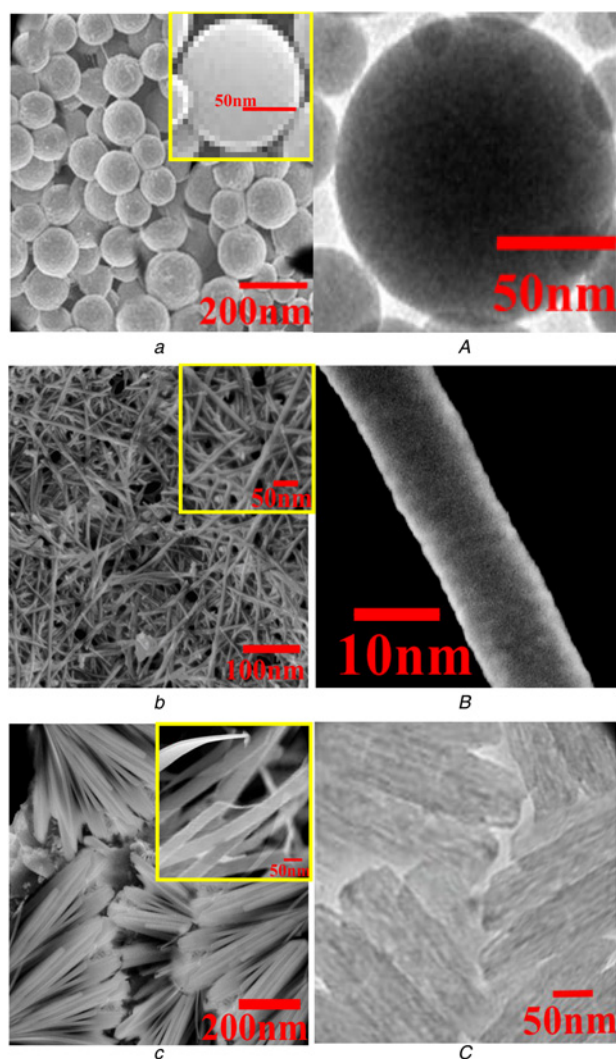


Figure 2 SEM images (a, b, c) and TEM images (A, B, C) of the WS_2 products: a and A, 0.2 mmol CTAB; b and B, 0.4 mmol CTAB; c and C, 0.75 mmol CTAB

template in the formation process of different WS_2 nanostructures. The surfactant CTAB had a hydrophilic head and a hydrophobic tail. As the surfactant concentration or temperature of the aqueous solution changes, hydrophilic groups spontaneously assemble into micelle structures with various shapes so that it can minimise the energy of the aqueous solution system [37, 38].

The formation mechanisms of the different prepared WS_2 nanostructures are illustrated in Fig. 3. When the volume of CTAB was adjusted to 0.2 mmol, the WS_2 nanospheres were obtained. On the basis of previous studies [39], the formation of the WS_2 nanospheres may result from the formation of sphere-like micelles. When the concentration was low, CTAB surfactant molecules assembled into numerous spherical micelles [40]. It can be discovered that WS_4^{2-} ions tended to gradually gather around the spherical micelles due to the electrostatic interaction of $CTA^+-WS_4^{2-}$ [41]. With the extension of reaction time, WS_4^{2-} ions were ultimately coated with CTA^+ ions, with the tail hydrophobic pointing outwards. With the help of hydroxylamine hydrochloride, WS_4^{2-} ions were reduced and WS_2 crystal nuclei were formed. In the meantime, hydrophobic interaction between the surfactant CTAB makes WS_2 crystal nuclei evenly disperse [33]. The formation process of WS_2 nanospheres is schematically illustrated in Fig. 3a.

When the volume of CTAB was adjusted to 0.4 mmol, WS_2 nanowires were obtained. On the basis of the literature [38], CTAB surfactant molecules assembled into rod-like micelles with WS_4^{2-} anions intercalating into the interspaces between the head groups of the CTAB to form $CTA-WS_4$ ion pairs. The CTAB took effect as a shape controller and stabiliser in the growth process of the WS_2 nanowires. It was widely believed that the growth process undertook an initial nucleation process, oriented aggregation, and Ostwald ripening using the procedure described in [42]. The formation process of WS_2 nanowires is schematically illustrated in Fig. 3b.

With the increase in concentration of CTAB surfactant, when the volume of CTAB was adjusted to 0.75 mmol, WS_2 nanobelts were obtained. On the basis of the literature [36, 43], if the concentration comes up to a critical micelle concentration of the lamellar micelles, CTAB molecules will incline to assemble to form lamellar micelles, as shown in Fig. 3c. In the meantime, the lamellae assemblies acted as the template of the crystal nucleus and a tiny reactor of crystal nucleus growth [43]. Hence, WS_2 crystals gradually grew, and the WS_2 nanobelts were obtained. The formation process of WS_2 nanobelts is schematically illustrated in Fig. 3c.

3.4. The optical absorption property: Fig. 4 displays the different UV–visible spectra of the as-prepared WS_2 nanostructures. As shown in Fig. 4, it was very significant that the WS_2 nanostructures with different morphologies had similar absorption

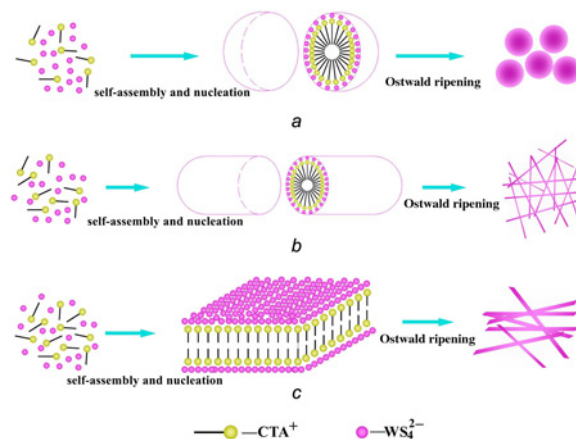


Figure 3 Schematic representation of the formation mechanisms of different WS_2 morphologies

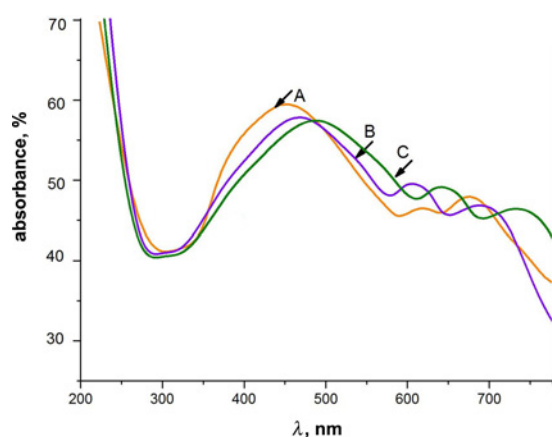


Figure 4 UV-vis light spectra of as-prepared samples (A, 0.2 mmol CTAB; B, 0.4 mmol CTAB; and C, 0.75 mmol CTAB)

spectra. The absorption spectra had two absorption peaks at about 450 and 650 nm, respectively. We also noted that the two absorption peaks connected to each other led to a wide absorption in the visible light region from 400 to 700 nm. Moreover, it has been reported that bulk WS₂ has absorption edges at 920 nm (1.35 eV bandgap) [44]. Combined with the above SEM analysis, UV-visible absorption for all WS₂ nanostructures underwent a substantial blue shift compared with the bulk WS₂. This may be because the quantum size effects that increased the bandgap in nanoscale WS₂ also shifted the redox potentials of the conduction and valence bands in advantageous ways. Therefore, as a result of this confinement, the bandgap of the WS₂ nanostructures increased, and its redox potentials accordingly changed [45]. The large blue shifts indicated the presence of a strong quantum confinement effect in the new photocatalysts, such as a visible photocatalyst.

4. Conclusions: We have described the solution-phase syntheses of WS₂ nanostructures with different morphologies under hydrothermal conditions. The surfactant CTAB had an important effect on different morphologies of WS₂ nanostructures. The WS₂ nanostructures exhibited wide and excellent absorption in the visible light region. This straightforward, solution-phase route can be applied as a low-cost and general method for the synthesis of other transition metal sulphide nanomaterials with different nanostructures.

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