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Shape-controlled synthesis of tungsten oxide nanostructures and characterization

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Abstract

Synthesis of tungsten oxide nanorods and nanodisks were reported here using hydrothermal method. Our study is focusing on the role of hexadecyltrimethyl-ammonium bromide (CTAB) and silver ions in tungsten oxide nanostructure formation comparing with typical methods. The sodium tungstate dehydrate was used as a precursor. We found that optimum concentration of CTAB and silver ions can provide a rod-like structure. Meanwhile, nanodisks were observed at the absence of silver ion. In addition, concentration of silver ions introduced to growth solution plays an important role in obtained nanostructure dimension. All prepared nanostructures were characterized by X-Ray diffraction (XRD) for crystalline structures examination. Moreover, field emission scanning electron microscopy (FE-SEM) was performed to determine morphology.

1. Introduction

Tungsten oxide nanostructures have increasingly attracted a great deal of attention due to their unique properties in physical, optical and electronics [1,2]. With a low band gap, tungsten oxide is dominant in n-type semiconductor which has been used in various applications including in electrochromic devices [3,4], lithium-ion batteries [5,6], smart window [7,8], bioimaging contrast agent [9], platform for photothermal therapy [10], photocatalyst [11,12] and gas sensors [13,14]. Taking an advantage of chemical stability, low cost and non-toxicity, tungsten oxide nanomaterials is promising for photocatalyst and sensing. To synthesize tungsten oxide nanostructures, high temperature reaction and annealing process were generally required. For example Shankar et al. [15] synthesized tungsten oxide nanorods under diamond growing conditions in a hot-filament chemical vapor deposition system using carbon nanotubes at templates. The deposition was carried out at a substrate temperature of 850°C for 30 min. The nanorods have an almost uniform diameter of 30-80 nm and length of 200-300 nm. Another report from Le Houx et al. [16] WO_3 nanoparticles in the diameter range of 5-30 nm have been prepared by solvothermal treatment of tungsten chloride in benzyl alcohol up to 210°C followed by annealing in air. Meanwhile, Yangchun et al. [17] reports the preparation of different dimension of tungsten oxide nanostructures using autoclave at 160°C for 16 h. Another report related to sol-gel, Ghasemi et al. [18] prepared tungsten oxide nanopowders using calcination of resin precursor at temperature 550ºC. Morphological evolution indicated rod-like and spherical shapes, depending on amount of complexing agent and polyethylene glycol in the reaction. Their nanopowders have an average particle size of 58 nm. Moreover, Yong et al. [19] prepared monoclinic tungsten oxide nanowire arrays on a tungsten substrate by thermal

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evaporation of tungsten oxide powder at elevated temperature in a tube furnace. They have found that the presence of tungsten oxide powder is crucial in producing tungsten oxide nanowires at high temperature.

In this work, we study shape controlled synthesis of tungsten oxide nanostructures using hydrothermal process because of being simple, low cost, reaction at low temperature and efficient way to obtain monodispered nanostructures. Here, sodium tungstate dehydrate was used as a precursor and the effect of different surfactants were studied under the same condition. The formation of tungsten oxides nanorods was studied at the different concentration of CTAB and silver ions. We found that changing the surfactant from oxalic acid to CTAB can regulated the shape from nanoplate to nanodisk-like structures.

2. Experimental

2.1 Materials

Sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$), hexadecyltrimethylammonium bromide (CTAB), and silver nitrate ($AgNO_3$) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl) was purchased from RCl Labscan. Oxalic acid ($H_2C_2O_4$) was purchased from CARLO ERBA Reagents. All the reagents were used without further purification.

2.2 Synthetic procedures

2.2.1 Synthesis of Tungsten oxides nanoplates

Tungsten oxides nanoplates were synthesized under an aqueous condition. In brief the mixture containing 100 ml of 2 mM of $Na_2WO_4 \cdot 2H_2O$ solution until pH=2. The mixture was stirred at room temperature for 10 min. After that, 20 ml of 0.1 M of oxalic acid was added into the solution and mixture was vigorously stirred at 90°C for 30 min. The solution turns green indicating formation of tungsten oxide nanoplates. Then, the obtained particles were washed with distilled water and absolute ethanol for several times to remove excess chemicals. Tungsten oxides nanopowder was dried at 60°C for 10 min.

2.2.2 Synthesis of Tungsten oxides nanodisks

Tungsten oxides nanodisks were synthesized by mixing 100 ml of 2 mM of $Na_2WO_4 \cdot 2H_2O$ solution with HCl until pH=2. After 10 min stirring at room temperature, 20 ml of 0.1 M of CTAB was added into the solution and mixture was vigorously stirred at 90°C for 30 min. The solution turns yellow indicating formation of tungsten oxide nanodisks. Then, the obtained particles were washed with distilled water and absolute ethanol for several times to remove excess chemicals. Tungsten oxides nanopowder was dried at 60°C for 10 min.

2.2.3 Synthesis of Tungsten oxides nanorods

Tungsten oxides nanorods were prepared by mixing 100 ml of 2 mM of $Na_2WO_4 \cdot 2H_2O$ solution with HCl until pH = 2. After 10 min stirring at room temperature, mixture containing 20 ml of 0.1 M of CTAB and 5 ml of $AgNO_3$ with varying concentration from 0.1 mM to 0.5 mM was added into the solution. The mixture was vigorously stirred at 90°C for 30 min. The solution turns dark green indicating formation of tungsten oxide nanorods. Then, the obtained particles were washed with distilled water and absolute ethanol for several times to remove excess chemicals. Tungsten oxide nanopowder was dried at 60°C for 10 min.

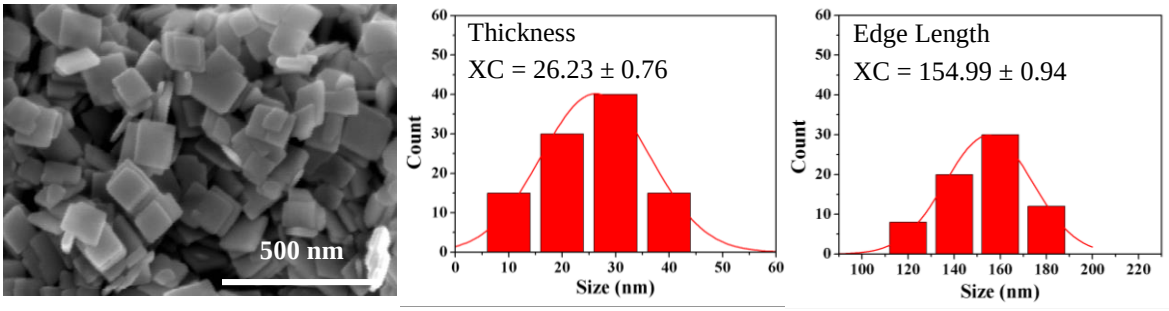

Figure 1. FE-SEM images and size distribution of tungsten oxide nanoplates synthesized at 90°C for 30 min.

2.3 Characterizations

The crystallization of tungsten oxide powder was determined by X-ray diffraction (XRD) using a Rigaku, Japan/ TTRAX III diffractometer with Cu K1 (λ= 1.5406 Å) radiation in a 2θ range of 10-80° and cutoff 15 min at room temperature. The morphology and size of tungsten oxide nanocrystal were characterized by field emission scanning electron microscopy (FE-SEM), Hitachi SU-8030 with power of electron beam 5 kV.

3. Results and discussion

In general, preparation of tungsten oxide nanoparticles has done using oxalic acid in the reaction. Li et al. [20] reported the preparation of tungsten oxide nanoplates by heating precursor in oxalic acid at temperature 90°C for 3 h in total solution volume of 100 ml. They found that their obtained tungsten oxide nanoplates have thickness of 25 nm and edge length of 150 nm. However, we here also demonstrate that the plate-like structure can be observed and stabilized in only 30 min of incubating time. We also observed the negligible change in morphology for more times. Our short time synthesis provides the nanoplates with thickness of 26.23 ± 0.76 nm and edge length of 154.99 ± 0.94 nm, as shown in figure 1.

To study the role of surfactant, CTAB was introduced to growth solution instead of using oxalic acid. The cation surfactant CTAB has been known as a soft template for gold nanorods formation for a decade [21-23]. The bromide ions preferentially adsorb on the low-index surface of gold nanocrystal leading to symmetry break [24,25]. Therefore, different crystallographic facets have different growth rate resulted in asymmetric shape formation.

However, spherical micelles of CTAB are generally found at the critical micelle concentration (CMC) ~1 mM [26]. Here, we performed the synthesis above CMC to see the morphology change of tungsten oxide nanocrystals. The yellow solution of tungsten oxide nanodisks was observed. The growth mechanism was written in Fig 2. Previously Asim et al. [27] reported synthesis of different size of WO_3 nanoparticles using different concentration of CTAB at different reaction temperature. Their results reveal that the CTAB is a good template in preparing small tungsten oxide nanoparticles, for example, in the size range of 3-15 nm. Similarly, we found here that CTAB can also provide a good template for obtaining nanodisks at an optimum concentration. The FE-SEM image of as-prepared tungsten oxide nanodisks in the presence of 0.1 M of CTAB at temperature 90°C for 30 min is demonstrated in figure 3, with mean diameter at 100 ± 1.60 nm.

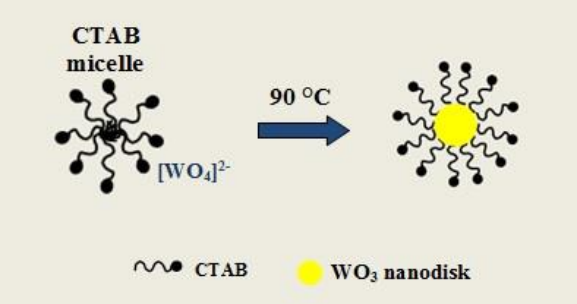

Figure 2. Growth mechanism of tungsten oxide nanodisks in the presence of CTAB.

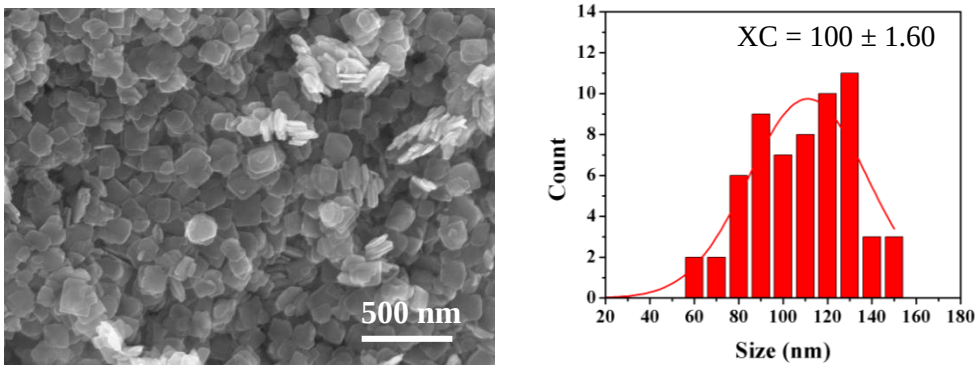

Figure 3. FE-SEM images and size distribution of tungsten oxide nanodisks synthesized at temperature 90°C for 30 min.

In addition, CTAB can provide rod-like template with a need of small concentration of silver ion. To explain this phenomenon, there are reports from many groups in understanding role of surfactant and impurities. One of widely accepted mechanism called the underpotential deposition (UPD) [28] in gold nanorods synthesis silver ions prefer to form silver monolayer in certain facets, i.e. Au {110}. This theory is compatible with report of AgBr adsorption on specific region directing asymmetric growth and also improve yield of rod formation [21,29]. Figure 4 shows selective adsorption of CTAB micelle in the presence of silver ions. Therefore, the crystal is able to grow in the both end, while the side of crystal is fully packed with CTAB molecule resulting in elongated growth. Although gold nanorods require undisturbed incubation process to from nice cylindrical crystal, our tungsten oxide nanorods can be formed in the vigorous stirring condition. The green solution was observed indicating tungsten oxide nanorods formation.

We further studied different concentration of silver ions. All study was done at temperature 90°C for 30 min. Figure 5(a)-(f) shows FE-SEM images in the presence of silver ions at concentration of 0.1, 0.2, 0.3, 0.4 and 0.5 mM, respectively. We found that nanorods have diameters of 33.26 ± 1.02, 34.71 ± 1.23, 39.99 ± 0.98, 53.85 ± 1.12 and 60.94 ± 0.81 nm respectively and length of 503.65 ± 11.12, 548.43 ± 11.51, 679.91 ± 10.98, 745.18 ± 10.12 and 805.02 ± 9.91 nm respectively. Therefore, the more silver ions introduced to the system, the larger tungsten oxide nanorods were obtained. We here observed that the more silver ions introduced to the system, the larger tungsten oxide nanorods were obtained. This result is corresponding to the UPD theory, addition of Ag ions generating longer rods. However, exceed amount of Ag ions or beyond optimal values leading to negative impact on nanorods formation [30].

Color of dried nanopowder of our prepared tungsten oxide comparing to the commercial tungsten oxide nanopowder are shown in figure 6. With this protocol, we can easily obtain high-yield production with monodispered structure.

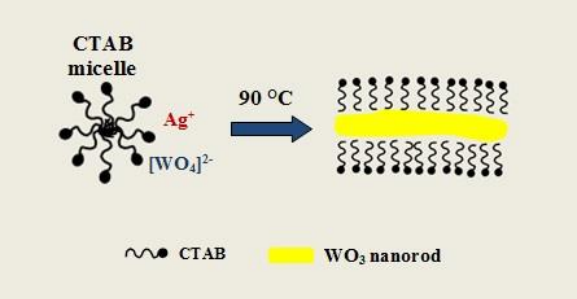

Figure 4. Growth mechanism of tungsten oxide nanorods in the presence of CTAB and silver ions.

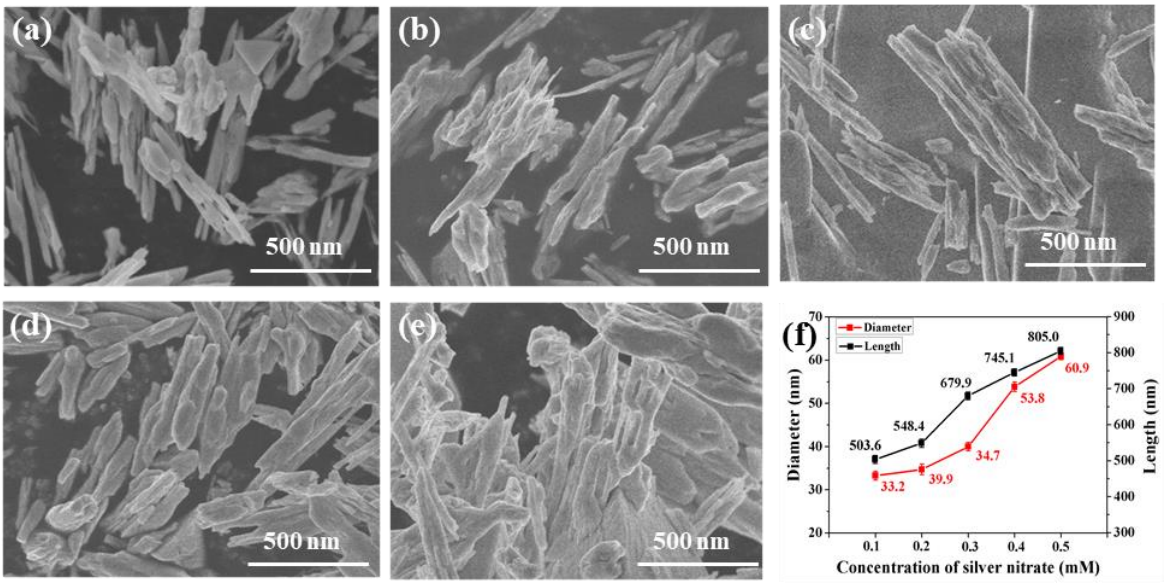

Figure 5. FE-SEM images of tungsten oxide nanorods with different concentration of silver ions (a) 0.1 mM (b) 0.2 mM (c) 0.3 mM (d) 0.4 mM and (e) 0.5 mM and (f) size distribution of obtained tungsten oxide nanorods.

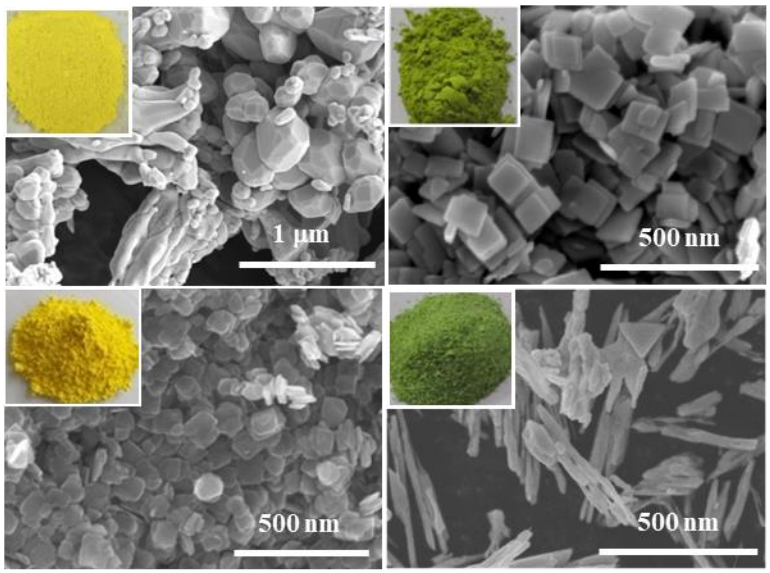

Figure 6. FE-SEM images of (a) commercially available tungsten oxide, (b) our prepared tungsten oxide nanoplates (c), tungsten oxide nanodisks and (d) tungsten oxide nanorods.

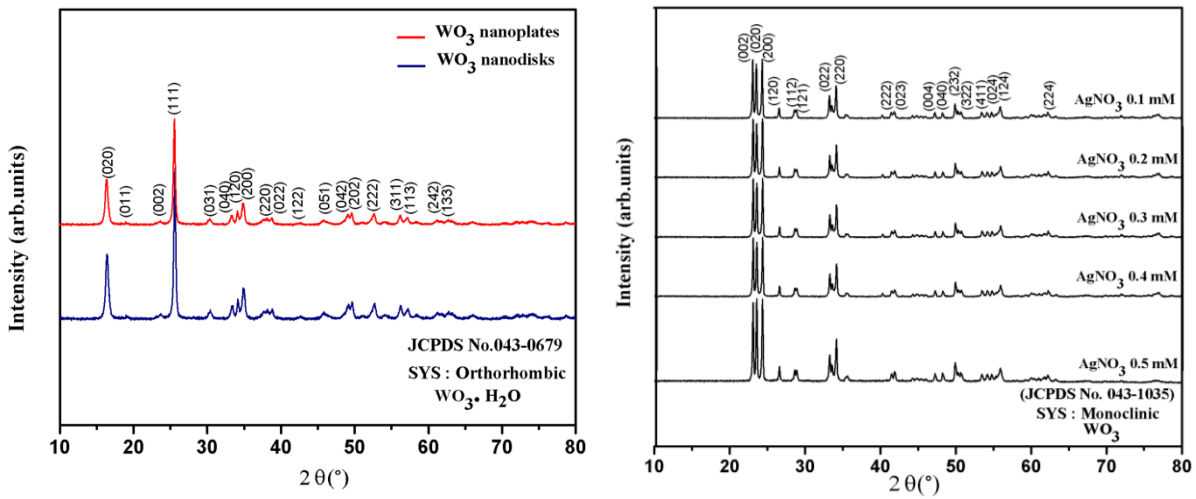

Figure 7. XRD patterns of (a) tungsten oxide nanoplates, nanodisks and (b) nanorods.

The XRD patterns of the tungsten oxide nanoplates and nanodisks prepared with oxalic acid (red line) and CTAB (blue line) are shown in Figure 7(a). We found that the peaks were indexed and perfectly matches with the orthorhombic phase of tungsten oxide structure (JCPDS No. 043-0679), i.e., corresponding to the (020), (111) and (002). While, the XRD patterns of the tungsten oxide nanorods are matched with monoclinic phase of tungsten oxide structure (JCPDS No. 043-1035). Different concentration of AgNO3 introduced to growth solution provides no differences in XRD patterns, as shown in Figure 7(b). The diffraction peaks are corresponding to the (002), (020) and (200) [31-32]

4. Conclusions

In summary, tungsten oxide nanoplates were synthesized using oxalic acid as a surfactant in 30 min of incubation. We found here that hexadecyltrimethylammonium bromide (CTAB) plays an important role in shape regulation. With CTAB, tungsten oxide nanodisks were observed. In addition, we found silver ions can control the morphology and provide nanorods. Concentration of silver ions also affects size of rods, i.e. high concentration of silver ions produces larger rods.

5. Acknowledgements

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