Large scale and controllable preparation of W_2C nanorods or WC nanodots with peroxidase-like catalytic activity

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W_2C nanorods or WC nanodots are prepared via an easy, shape-controllable and large-scale preparation technique. Results reveal that each of the W_2C nanorods and WC nanodots has a peroxidase-like activity. Besides, the peroxidase-like activity of W_2C is the first time to be demonstrated. The catalytic efficiency of W_2C nanorods is much higher than that of WC nanodots and chemical condition range of W_2C can be wider than that of WC, which indicates that W_2C is likely to be used as artificial mimetic peroxidase or in-situ amplified colorimetric immunoassay.

Keywords: W_2C nanorods, WC nanodots, peroxidase-like activity, mesoporous carbon

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1. Introduction

Due to the platinum-like behavior in surface catalysis,[1] excellent physical property and chemical stability,[2] tungsten carbide has been considered as an excellent green catalyst in hydrogenolysis, isomerization reaction, fuel cell, hydrogen evolution and catalytic oxidation.[3] What is more, tungsten carbide was supposed to have the various potential applications in biology,[4] especially to be used as artificial enzymes.[5] However, the peroxidase-like activity of tungsten carbide has seldom been reported.[5] Furthermore, the peroxidase-like performance of W_2C has never been reported as far as we know.

As is well known, natural enzymes have been studied and used in industrial, environmental and medical fields since they possess high substrate specificity and catalytic activity under relatively mild condition.[6] However, the natural enzymes have fatal weaknesses such as difficul preparation, unstable catalytic activity and low operational stability.[7] All of these drawbacks restrict its applications on a large scale and in varying conditions. Fortunately, due to its easy preparation, low cost, high stability and easy storage, the artificial enzyme has been considered as an ideal substitute for natural enzyme.[8] An important kind of enzyme is peroxidase as oxidation is a universal biochemical reaction. For now, since the first reported artificial nano-sized peroxidase-like Fe_2O_3,[9] kinds of peroxidase mimics have been reported, such as metal oxidizes or noble metal based materials (Au, Ag and CeO_2), and carbon based materials (carbon nanotubes or nanodots),[8] etc. Among the studied peroxidase mimics, tungsten carbide is the most promising one because of its excellent propertiesmentioned above.

The tungsten carbides including crystalline phases like W_2C and WC have been reported.[3] And it was shown that W_2C possesses higher catalytic efficiency than WC.[10,11] However, W_2C was considered as metastable phase of tungsten carbide and always synthesizes together with plenty of WC or other tungsten carbides.[12] And WC or W_2C was prepared by intermittent microwave heating,[13] electron beam induced deposition,[14] eutectic solidification,[15] electro-discharge,[16] chemical synthesis,[17] temperature-programmed carburization,[18] dc arc discharge plasma CVD,[19] or carbothermal reduction,[20] etc. However, large scale, nano-sized, ingredient and shape-controllable WC or W_2C is still hard to prepare.

On the one hand, due to its relatively high chemical and thermal stability, the low density, high strength, large surface area, uniform particle size,[21] nanostructured carbon with hollow macroporous core/mesoporous shell (NC-HMC/MS) is shown to have great potential applications in fields like supercapacitors,[22] drug delivery,[23] battery,[24] electromagnetic wave and microwave absorption materials,[25] metal/nonmetal nanoparticles encapsulation,[26] etc. Therefore the NC-HMC/MS is a kind of important support for catalysts.[27] On the other hand, the unique hollow-core and mesoporous-shell structure not only lowers its density[28] but also allows NC-HMC/MS to encapsulate materials in the hollow core via mesoporous in the shell. Hence, the materials could be effectively encapsulated without destroying its shell. Here in this work, we controllably prepare W_2C nanorods and

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WC nanodots via a simple synthesis method in which tubular NC-HMC/MS (TNC-HMC/MS) is used as support and template. The peroxidase-like activities of W_2C nanorods and WC nanodots are demonstrated. Most importantly, the peroxidase-like activity of W_2C is detected for the first time as far as we know.

2. Experiment

2.1. Preparations of W_2C nanorods and WC nanodots

Hydrophilia groups modified TNC-HMC/MS was dispersed into ammonium metatungstate (AMT) aqueous solution and then stirred for 24 h. The solid-liquid mixture was separated by filtration and the black powder was dried in oven.

The as-obtained black powder was the encapsulated AMT in TNC-HMC/MS, which was the precursor for W_2C or WC. The dried precursors were reduced in H_2 at 650 °C and then heat treated at 1200 °C under vacuum. Most importantly, the W_2C was obtained under a lower H_2 flow rate (0.1 sccm) reduction condition, and WC was obtained under a higher H_2 flow rate (0.3 sccm) condition. The phase and morphology of each of the obtained products were analyzed by x-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM).

2.2. Peroxidase-like activity

Both of the TMB (tetramethylbenzidine) and OPD (o-phenylenediamine) were catalytic oxidized in acetate buffer whose pH values were 4, 6, and 8. The buffer contained W_2C nanorods 0.2 mg/ml or WC nanodots 0.5 mg/ml. Then H_2O_2 (40 ml, 30% (v/v)) was added into the buffer.

Color changes were observed immediately after adding the substrates. The photographs and UV absorbance (recorded by UV-vis spectrophotometer (U-3900H from HITACHI Co.)) of OPD were recorded 20 min after the reaction had began. While for TMB, the UV absorbance was recorded 10 min after the reaction had began, and photos were taken almost as soon as the reaction (pH = 4) began. The recording adsorption spectra of OPD and TMB were at 450 nm and 654 nm respectively.

To detect the peroxidase-like activities of W_2C nanorods and WC nanodots in more detail, samples were detected in changed TMB and H_2O_2 conditions. That is, TMB varied from 1mg to 50 mg and H_2O_2 varied from 1 M to 10 M. The buffer has pH = 4 and contained W_2C nanorods of 0.2 mg/ml or WC nanodots of 0.5 mg/ml. Besides, for the TMB concentration changed samples, 10 M H_2O_2 was added; and for the H_2O_2 concentration changed samples, the TMB was maintained at 10mg. Results were also obtained by UV-vis spectrophotometer and recorded 10min after the reaction had began.

3. Results and discussion

As shown in Fig. 1, BET/BJH result (Fig. 1(b)) reveals that the TNC-HMC/MS belong in the N_2 adsorption-desorption-type IV and H4 hysteresis, which means that it contains mesoporous. What is more, according to the BJH and TEM result (Figs. 1(b) and 1(e)), the mesoporous size is about 4 nm. Mesoporous in the shell of TNC-HMC/MS is very important, since AMT cannot be encapsulated into the hollow core of TNC-HMC/MS without the mesoporous. Due to capillarity of the mesoporous, AMT is encapsulated into the hollow core of TNC-HMC/MS and forms nanorods (Figs. 1(c) and 1(d)).

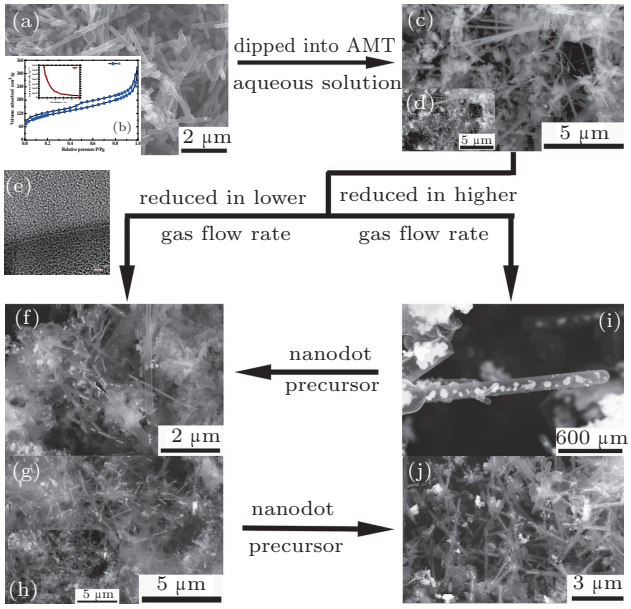


Fig. 1. FESEM imaging scheme of how the tungsten carbide precursors are formed, showing (a) the original TNC-HMC/MS, (b) the BET/BJH result of TNC-HMC/MS, (c) controllably encapsulated AMT, (d) the corresponding back scattering image of panel (c), (e) the TEM image of mesoporous in the shell, (f) and (h) encapsulated AMT reduced in lower H_2 flow rate which results in nanorod precursor, (g) the back scattering image of panels (h), (i) and (j) encapsulated AMT reduced in higher H_2 flow rate which results in nanodot precursor.

On the other hand, it has been reported that H_2 flow rate could influence the reduction product morphology of tungsten oxide,[26] and the tungsten oxide will certainly appear in the AMT reduction process. Because WO_3 reacts with $H_2O_{(g)}$ and forms gaseous W compound,[27] according to the mechanism of chemical vapor transportation which is a common mechnism for crystal growth,[29–31] lower H_2 flow rate in the AMT reduction process will yield nanorods/nanowires product, while higher H_2 flow rate will yield nanodot product. Hence, in the lower H_2 flow rate (0.1 sccm) reduction condition, nanorod precursor is obtained (Figs. 1(f)–1(h)), and in

the higher H_2 flow rate (0.3 sccm) condition, nanodot precursor is generated (Figs. 1(i) and 1(j)).

The reduction product is tungsten nanowires and nanodots (Figs. 1(f) and 1(i)). After heat treatment in vacuum at 1200 °C, W_2C nanorods and WC nanodots are formed, which are shown in Fig. 2. As the nanorod precursors provide more W elements than nanodot precursor, so the nanorod precursor is converted into W_2C and nanodot precursor is converted into WC. As shown in Fig. 3, the value of W:C decreases from the center of the nanorods (point 1) to the margin of the nanorods (point 2), and the shell is still of carbon (point 3). The graded composition reveals that the reaction of W with C takes place in the way of carburization. In addition, the generated W_2C in WC (Fig. 2(g)) should come from the precursors, which is because some areas contain more tungsten elements (see the areas marked by arrows in Figs. 1(j) and 2(i)).

From the FESEM and TEM images in Figs. 2(b)–2(f) and 2(h)–2(l), we can see that each of WC and W_2C has a diameter of about 50 nm, which is corresponding with the hollow core diameter of TNC-HMC/MS (circa 50 nm). This indicates that the TNC-HMC/MS not only provides carbon for the products but also acts as template for them and confines the growing of products. As is well known, nanomaterial has a severe weakness of agglomeration, but the obtained nanomaterials here are dispersed very well in the hollow core of TNC-HMC/MS (Figs. 2(h)–2(k)), which indicates that the TNC-HMC/MS also plays an important role of buffer.

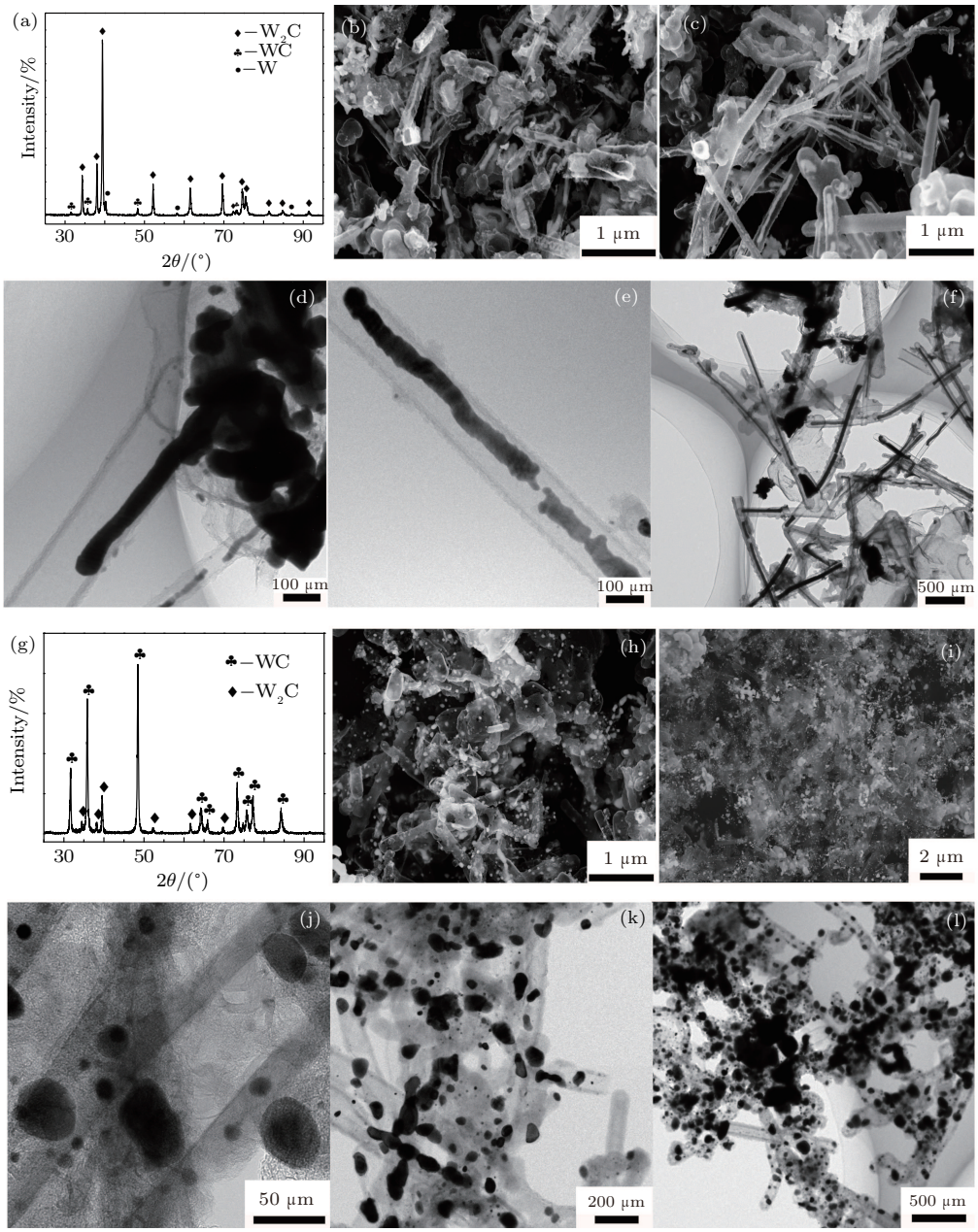


Fig. 2. (a) and (g) The XRD results of the as-obtained W_2C and WC, (b) and (c) FESEM images of W_2C nanorods, (d), (e), and (f) TEM images of W_2C nanorods, (h) and (i) FESEM images of WC nanodots, (j), (k), and (l) TEM images of WC nanodots.

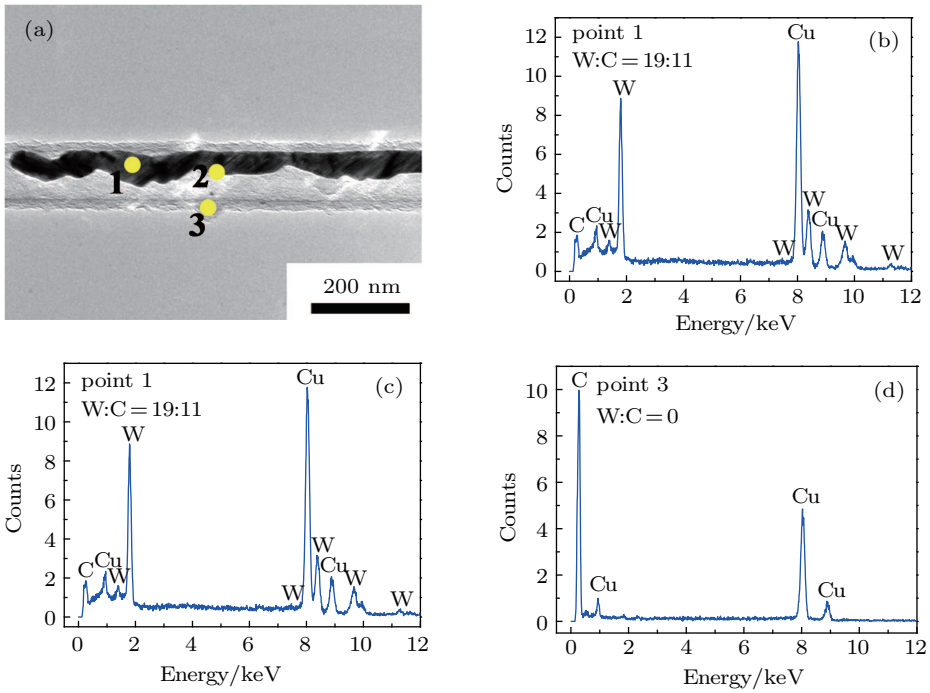


Fig. 3. (color online) (a) TEM image of the W_2C nanorod and EDS results of (b) point 1, (c) point 2, and (d) point 3 in panel (a).

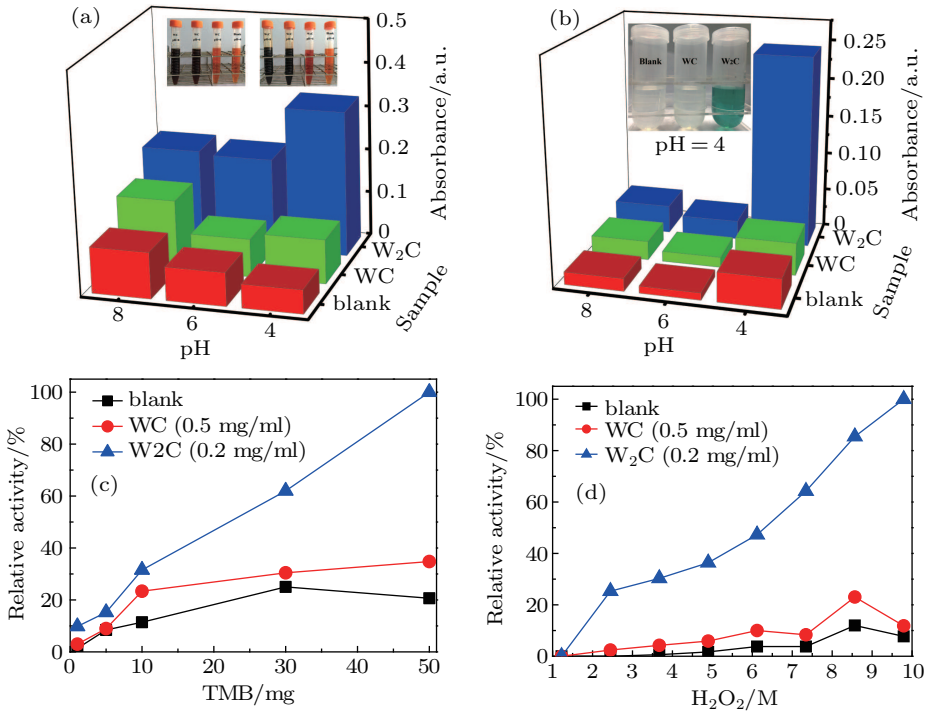


Fig. 4. (color online) Peroxidase-like activities of the as-obtained W_2C nanorods and WC nanodots. Panels (a) and (b) show UV-vis absorption spectra and photos for OPD and TMB, respectively. The left insert in panel (a) is the WC catalyzed oxidation of OPD and the right one the W_2C catalyzed oxidation of OPD. The insert photo in panel (b) is taken as soon as the reaction begins and the buffer is pH = 4. Panel (c) displays the variations of relative catalytic activity of W_2C nanorods and WC nanodts with TMB. Panel (d) exhibits the variations of relative catalytic activity of W_2C nanorods and WC nanodts with the quantity of H_2O_2.

The W_2C nanorods and WC nanodots are prepared respectively, and their peroxidase-like activities are also investigated. As can be seen from the inserts of Figs. 4(a) and 4(b), the chromogenic reaction of OPD with TMB indicates that both of WC nanodots and W_2C nanorods possess peroxidase-like activities. However, it is obvious that the catalytic efficiency of W_2C nanorod is much higher than that of WC, which is distinctly shown by the oxidation of TMB, especially at the moment when the oxidation begins (pH = 4), and the color changes in the W_2C catalyzed reaction (see the insert of Fig. 4(b)). Besides, it is another proof that all the UV-vis absorptions of W_2C catalyzed reactions are much higher than

those of WC catalyzed reactions in Fig. 4. In addition, for the catalyst, larger specific surface area means higher catalytic efficiency,[13] and nanodots possess larger specific surface area than nanorods. Hence the efficiency of WC nanodots should be higher than that of W_2C nanorods, however, efficiency of W_2C nanorods is higher than that of WC nanodots. As reported in Ref. [5] WC could be a perfect artificial enzyme, therefore, the results here reveal that W_2C nanorods could be the ideal artificial enzyme for biochemical oxidation reactions.

On the other hand, different pH values of buffer are demonstrated, which are shown in Figs. 4(a) and 4(b). Before the catalytic activities is measured, the as-obtained catalyzer has been incubated in the given pH buffer. Results reveal that the obtained W_2C nanorods and WC nanodots could catalyze reactions in varying pH (Figs. 4(a) and 4(b)).

As is well known, natural enzymes could be used in a narrow range of chemical conditions. However, as shown in Fig. 4, when the chemical conditions change, no matter whether it is the pH mentioned before, or how large the TMB and H_2O_2 concentrations are, both of the W_2C nanorods and WC nanodots show peroxidase-like activity, especially the W_2C nanorods show higher efficiency and probably could be used in a wider range of chemical conditions (Figs. 4(c) and 2(d)).

4. Conclusions

According to the mechanism of chemical vapor transportation, using AMT and TNC-HMC/MS as precursor and template/support, via controllable reduction at 650 °C, precursors of nanorod and nanodot are prepared. Then by means of heat treatment at 1200 °C, W_2C nanorods and WC nanodots are obtained respectively. The prepared nano-sized W_2C and WC each have a diameter of circa 50 nm, which are confined by the hollow core of TNC-HMC/MS. Most importantly, both of the obtained W_2C nanorods and WC nanodots show peroxidase-like activities. Furthermore, the catalytic activity of W_2C nanorods should be better than that of WC nanodots since the former present much higher efficiency and wider range of chemical conditions.

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