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# Synthesis of superconducting sphere-like $Mo_2C$ nanoparticles in an autoclave

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Sphere-like $Mo_2C$ nanoparticles have been synthesized through the reaction of sodium molybdate, anhydrous ethanol and sodium azide at 450 °C for 10 h in a sealed stainless steel autoclave. X-ray powder diffraction results indicated that the final product was $Mo_2C$. Transmission electron microscopy (TEM) and scanning elctron microscopy (SEM) were employed to characterize the as-prepared sample. The sample was mostly composed of sphere-like particles, which has a superconducting transition temperature of 9.5 K, and its calculated surface area is 30.859 $m^2/g$. The experimental parameters such as reaction temperature and reactants were studied to investigate the reaction mechanism. It was found that sodium azide and reaction temperature played key roles in the formation of sphere-like $Mo_2C$ nanoparticles.



## 1 Introduction

Molybdenum carbide ($Mo_2C$) has generated considerable interest in recent years because of its high melting point (2770 K), extreme hardness, superconductivity and catalytic performance [1,2]. As a catalyst, molybdenum carbide has been found to show similar catalytic behavior with noble metals in some cases [3]. And it has been reported that the superconducting performance of $Mo_2C$ was closely related to its structure [4,5].

Nanosturctured $Mo_2C$ has been well studied for its potiential uses in catalysis and superconductivity. For example, nanoscale $Mo_2C$ powders prepared by Suslic et al. via a sonochemical method were proved to be an excellent dehydrogenation catalyst, whose selectivity and activity was comparable to that of Pt [6]. It was also found that $Mo_2C$ nanowires with large surface and abundant nanoporosity exhibited good performance in the methanol decomposition reaction [7]. In the superconductivity test, $Mo_2C$ sample with 50-150 nm nanoparticles appeared to be strongly diamagnetic while samples with 2-4 nm nanoparticles were observed to be weakly diamagnetic.

Traditionally, bulk $Mo_2C$ have been synthesized by direct carburization of molybdenum powder or molybdenum oxide at high temperature (>1000 °C). In order to obtain $Mo_2C$ with nanoscale size, various methods have been employed, such as temperature-programmed reduction method [8-10], pyrolysis of molybdenum hexacarbonyl [11,12], solid state reactions [13-17], sonochemical synthesis [6] and solvothermal method [18]. Among the methods reported above for the preparation of $Mo_2C$ nanoparticles, solid state route has been widely employed owing to its simple manipulation process, low-cost instrument and diversity of starting materials. These advantages extend further explorations of new synthesis methods for $Mo_2C$ nanoparticles. However, the higher reaction temperature involved in solid state route usually leads to the production of larger $Mo_2C$ particles or impurities. Autoclave route is a developed promising method for the relative low temperature synthesis of carbide nanoparticles and nitride materials with regular shapes.

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Herein, we report the synthesis of sphere-like $Mo_2C$ nanoparticles in an autoclave at 450 °C. The required temperature is relatively low than that in solid state route. The majority of the as-prepared sample is composed of sphere-like nanoparticles with diemeters in the range of 50-100 nm. These sphere-like $Mo_2C$ nanoparticles have a superconducting transition temperature of 9.5 K, and the calculated surface area is 30.859 $m^2/g$. The route introduced in this work may be useful for the preparation of other carbide materials.

## 2 Experimental

**Materials** Sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$, analytical purity) was purchased from Tianjin Chemical Reagent No. 4 Plant. All the other reagents were of analytical purity and were purchased from Shanghai Chemical Reagent Co. Ltd. All the reagents were used without additional purification.

**Preparation of $Mo_2C$ nanoparticles** In a typical procedure, appropriated amounts of $Na_2MoO_4 \cdot 2H_2O$ (1.0 g), anhydrous ethanol (2 mL) and $NaN_3$ (2.0 g) was loaded into a 20 mL stainless-steel autoclave. The autoclave was sealed and heated to 450 °C from room temperature with an increasing rate of 10 K/min for 10 h, then cooled to room temperature. The black product was treated with absolute ethanol and hydrochloric acid solution (1 M) to remove byproducts. The product was then centrifuged in tribromomethane and washed with ethanol and water for three times. The final product was dried under vacuum at 60 °C for 10 h.

**Sample characterization** The X-ray powder diffraction (XRD) patterns of as-synthesized products were performed on a Bruker D8 advanced X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) at a scanning rate of 0.06 $°s^{-1}$ in the 2θ range from 20 to 80°. The structure and morphology of as-prepared samples were studied by transmission electron microscope (TEM, Hitachi H-600, 100 kV), field emission scanning electron microscope (FESEM, JSM-6700F), and high resolution transmission electron microscope (JEM-2100, 200 kV). Field-cooled and zero-field-cooled magnetization data were measured by employing a superconducting quantum interference device magnetometer (SQUID, Quantum Design MPMS-7). Micromeritics (Gemini 2375) surface area analyzer was used to measure the surface area of the as-prepared samples.

## 3 Results and discussion

Figure 1 shows the typical XRD pattern of the as-prepared sample. The diffraction peaks can be indexed as orthorhombic $Mo_2C$ (JCPDS card no. 31-0187). The calculated lattice constant $a$ = 4.732 Å, b = 6.006 Å, $c$ = 5.211 Å are in good agreement with the reported values (a=4.732 Å, b = 6.037 Å, c=5.204 Å). The strong and sharp peaks suggest that the as-prepared product is well-crystalline.

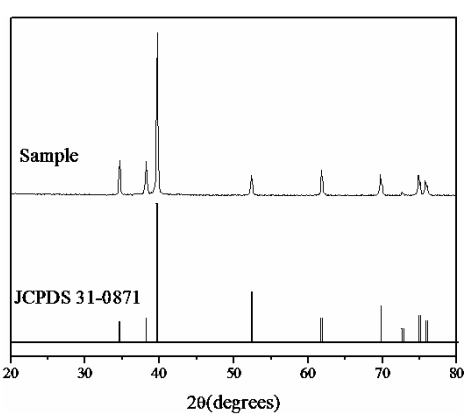


**Fig. 1** Typical XRD pattern of the as-prepared sample.

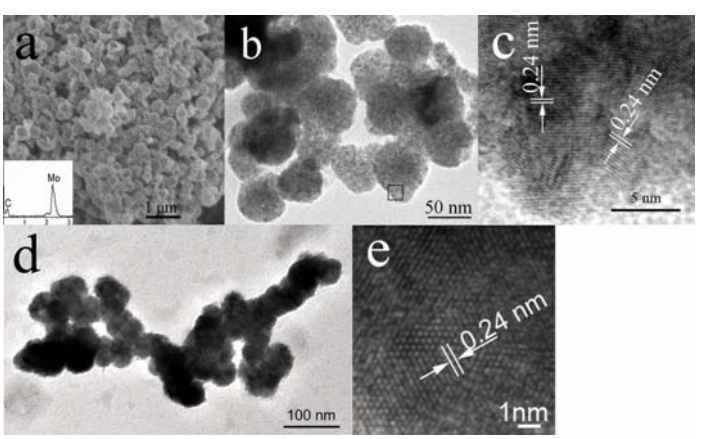


**Fig. 2** (a) Typical SEM image and EDS spectrum; (b) TEM image of sphere-like nanostructures; (c) corresponding HRTEM image of part of (b); (d) TEM image of branch-like nanostructure and (e) corresponding HRTEM image of part of particle in (d).

 

Figure 2a is a typical SEM image of the as-synthesized product. It is clear that the product is mainly composed of sphere-like nanoparticles. From the SEM observation, the diameters of most sphere-like particles are about 50-100 nm. The inset of figure 2a is the corresponding EDS spectrum, indicating that the surface chemical compositions of sphere-like nanoparticles are $Mo_2C$. Further structural analysis was carried out by TEM. Figure 2b is a typical TEM image of sphere-like nanoparticles. Their average diameter is about 50 nm. Figure 2c is the HRTEM image of part of a randomly selected sphere-like nanoparticle (marked with a black square in figure 2b). The calculated inter-planar spacing of 0.24 nm is consisted with the (200) plane of orthorhombic $Mo_2C$. It is interesting that a few branch-like nanostructures are observed under TEM, which can be seen in figure 2d. The profiles of sphere-like structures are easily found from the branch-like structure, indicating that the branch-like nanostructure is aggregation of sphere-like ones. The corresponding HRTEM image of branch-like structure shown in figure 2e reveals a interplaner spacing of 0.24 nm, which is consisted with the (200) plane of orthorhombic $Mo_2C$, also indicating the high crystallinity of the final product.

The zero-field-cooled (ZFC) and field-cooled (FC) magnetizations in a 10 Oe field of the as-prepared $Mo_2C$ are shown in figure 3. The ZFC and FC signals exhibit clear superconducting transitions, as evidenced by the strong diamagnetic response of the sample. The diamagnetic response of the ZFC signal is remarkably greater than that of the FC signal, which may be caused by the flux trapping in the superconductor under FC [19]. The $T_c$ value of the final product is 9.5 K, which agrees with the previous reported values of bulk and nanoscaled orthorhombic $Mo_2C$ [4,20].

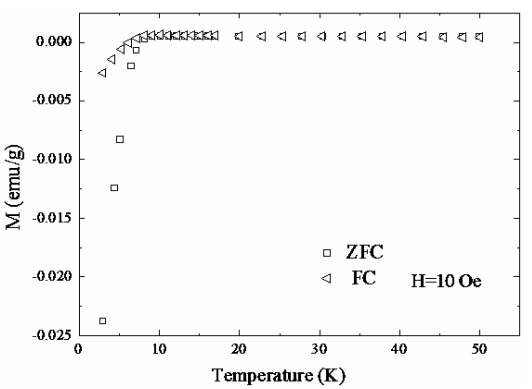


**Fig. 3** The zero-field-cooled (ZFC) and field-cooled (FC) magnetizations in a 10 Oe field of the as-prepared $Mo_2C$.

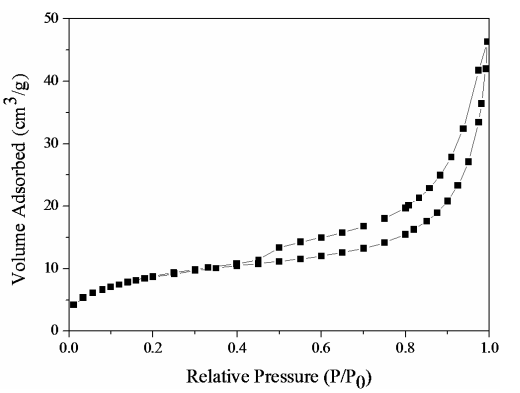


**Fig. 4** $N_2$ adsorption-desorption isotherm of $Mo_2C$ nanoparticles.

BET method was used to measure the surface area of the as-prepared samples. Figure 4 shows the $N_2$ adsorption-desorption isotherm of $Mo_2C$ nanoparticles. The BET surface area is calculated to be 30.859 $m^2/g$. To investigate the effects of reaction conditions on the formation of the final products, a series of relevant experiments were carried out. The results are listed in table 1. The reaction temperature and the reactants were found to be key factors for the formation of sphere-like nanoparticles. If the temperature was set below 350 °C, the products dissolved in water and no $Mo_2C$ was found. And the final products were big grains when the reaction temperature was higher than 500 °C. Besides the reaction temperature, the sodium azide plays an important role in the formation of the final products. When $NaN_3$ was replaced by magnesium powder or $NaBH_4$ with other conditions unchanged, no sphere-like nanoparticles were observed by TEM.

**Table 1** The summary of the final products prepared with different reaction conditions.

| Reaction system | Amount | T (°C) | Phases or morphologies |
|---|---|---|---|
| $C_2H_5OH+NaN_3+Na_2MoO_4$ | 2 mL; 2.0 g; 1.0 g | 450 | $Mo_2C$ sphere-like nanoparticles |
| $C_2H_5OH+NaN_3+Na_2MoO_4$ | 2 mL; 2.0 g; 1.0 g | 500 | $Mo_2C$ particles with irregular shape |
| $C_2H_5OH+NaN_3+Na_2MoO_4$ | 2 mL; 2.0 g; 1.0 g | 350 | No product |
| $C_2H_5OH+Mg+Na_2MoO_4$ | 2 mL; 1.0 g; 1.0 g | 450 | Irregular $Mo_2C$ particles |
| $C_2H_5OH+Mg+Na_2MoO_4$ | 2 mL; 0.5 g; 1.0 g | 450 | molybdenum oxides and carbides |
| $C_2H_5OH+NaBH_4+Na_2MoO_4$ | 2 mL; 2.0 g; 1.0 g | 450 | Mo and $Mo_2C$ |

Based on the experimental results, a brief formation process of the sphere-like $Mo_2C$ nanoparticles can be described as follows. $NaN_3$ decomposed when the temperature was near its thermal decomposition point [21], and the decomposed Na (as a strong reductant) will gradually react with $Na_2MoO_4$ and ethanol to form active molybdenum (Mo) and carbon (C) atoms through a thermal reduction process. The fresh Mo atoms and C atoms have higher activity than commercial molybdenum powder and graphite, and then they should react with each other to form $Mo_2C$ nanoparticles at elevated temperatures. The as-synthesized $Mo_2C$ nanoparticles tend to aggregate together to reduce surface energy, which may cause the self-assembled formation of sphere-like particles. And the ordered aggregation of sphere-like nanoparticles contributes to the formation of branch-like structures. However, owing to the complexity of the experimental process, the formation mechanism of these sphere-like $Mo_2C$ nanoparticles still needs further investigation.

## 4 Conclusion

In summary, sphere-like $Mo_2C$ nanoparticles have been synthesized using $Na_2MoO_4$, anhydrous ethanol and $NaN_3$ in a sealed autoclave at 450 ° C for 10 h. X-ray diffraction pattern shows that the final product is $Mo_2C$. Magnetization measurements indicate that sphere-like $Mo_2C$ nanoparticles have a superconducting transition at 9.5 K. It was found that a few branch-like $Mo_2C$ nanostructures were co-existed with the sperical $Mo_2C$ particles, which may be caused by ordered aggregation. Based on a series of experiments, a possible formation mechanism was also discussed. The route introduced in this work may be useful for the preparation of other carbide materials.

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