A “Chemical-Scissors-Assemble” Route to Titanium Carbide Nanorods

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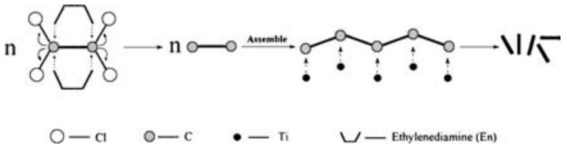
(Received April 23, 2002; CL-020357)

By using tetrachloroethylene (C_2Cl_4), metallic titanium powders and N-containing nucleophilic solvents, such as ethylenediamine (en), pyridine and diethylamine as raw materials, a new strategy, called “chemical-scissors-assemble” route, is explored to prepare TiC nanorods, in which nucleophilic solvent attacks at the carbon in tetrachloroethylene to remove the chlorine groups and produce free C_2, which can assemble into one-dimensional conjugate carbon chain clusters, and then react with Ti powders and result in a one-dimensional structure of TiC nanorods.

Nanomaterials have aroused remarkable interest because of their unique physical and chemical properties and very promising applications in the field of catalysis, sensor technologies, magnetic recording media and so on.[1] In particular, one-dimensional nanomaterials, such as nanorods, nanotubes, and nanowires with novel electronic and optical properties, have gained considerable attentions following the discovery of carbon nanotubes by Iijima.[2] Up to date, various methods have been developed to synthesize low-dimensional nanoscale materials, such as vapor-liquid-solid (VLS), solution-liquid-solid (SLS), laser ablation, carbon nanotube-confined reaction, electrochemical fabrication, and nonaqueous solution synthesis.[3–8]

Titanium carbide, an important non-oxide ceramic, has widely applications ranging from mechanical industries to chemistry and microelectronics,[9] due to its very high melting point (3260 °C), low density (4.93 $g \cdot cm^{-3}$), extreme hardness and high resistance to both corrosion and oxidation.[10] Several methods have been developed to obtain titanium carbide. The traditional industrial method for the preparation of TiC powders is carbon-thermal reduction of TiO_2 in a very high temperature range of 1900–2700 °C.[11] Thorne and co-workers reported that $TiCl_4$ reacts with H_2 and C to produce TiC by using an incandescent tungsten or carbon filament as the igniting agent.[12] Because of the corrosive effects of the by-product, HCl, special precautions have to be considered. Qian’s group reported a reduction method to prepare TiC nanocrystallites at 400–650 °C,[13] and all of the manipulations need to be carried out in a dry glove box filled with argon for the use of easily-volatile substance. And later, Qi[14] synthesized titanium carbide nanowires via the reaction of TiO gas with methane involving vapor-liquid-solid (VLS) growth mechanism at 1400 °C.

As for the preparation of nanorods, one famous synthetic route is to convert carbon nanotubes (CNTs) by reaction with a volatile chemical substance. For example, Dai et al.[15] have synthesized a series of metal carbide nanorods, e.g. TiC, by using carbon nanotube as a template in argon atmosphere at high temperature (1150–1750 °C). The experimental results suggest that CNTs act as a template during these reaction processes and the reaction is then confined to the local space around the CNTs. The template can be used as a constituent in the final products or be fully removed by oxidation, producing CO gas. However, preparation of TiC nanorods under relative mild conditions is still a challenge to both chemists and material researchers. Herein, we put forward a new strategy, called a “chemical-scissors-assemble” route, to synthesize TiC nanorods using tetrachloroethylene (C_2Cl_4), metallic titanium powders (Ti) and N-containing nucleophilic solvent such as ethylenediamine (en), pyridine and diethylamine as raw materials. This strategy can greatly decrease the reaction temperature. In the formation of one-dimensional conjugate carbon chain clusters, the nucleophilic solvents play a crucial role. Because of their strong nucleophilic ability, N-containing nucleophilic solvent attacking at the carbon atoms in tetrachloroethylene can lead to the removing of chlorine groups and producing free C_2. The newly formed free C_2 can assemble into one-dimensional conjugate carbon chain clusters, and then react with Ti powders to result in a one-dimensional structure of TiC. The whole process can be schematically described in Scheme 1.



Scheme 1. Schematic illustration of the proposed mechanism for the formation of the TiC nanorods.

In a typical experimental procedure, 2 ml tetrachloroethylene (excessive), 10 mmol (0.48 g) metallic titanium powder, and 1 mL ethylenediamine were loaded into an autoclave of 30 mL capacity. The autoclave was sealed and maintained at 500 °C for 10 h, and then naturally cooled to room temperature. The product was collected and treated by distilled water to remove the by-products, the free carbon in the product was removed by heating in air at 600 °C for 2 h. A dark gray product was obtained. The yield of the products based on the amount of Ti powders in the starting materials is over 95%.

The X-ray diffraction (XRD)[16] pattern of the nanorods is shown in Figure 1. All the reflections, to within experimental error, fit that of bulk cubic TiC.[17] No other impurities were detected in the XRD pattern, including Ti powders. Using the Scherrer formula on the (2*kl*) peaks (200) (220) and (222), the average diameter of the TiC nanorods is about 35 nm.

The structure and morphology of the sample were examined by transmission electron microscopy (TEM),[18] the typical TEM image shown in Figure 2A. The TiC crystals appeared to display short-rod-like morphology with diameters of 30–35 nm and length of 150–200 nm. The electron diffraction (ED) pattern shown in Figure 2B was obtained from a selected area of TiC nanorods shown in Figure 2A with a convergent beam, and revealed that the TiC nanorods were single crystals.

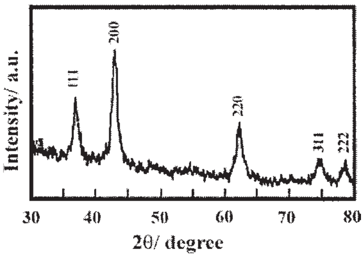


Figure 1. The XRD pattern of the product.

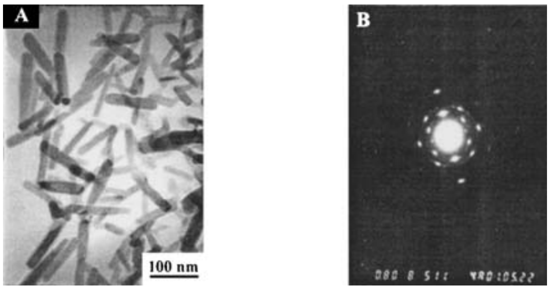


Figure 2. TEM image (A) and the electron diffraction pattern (B) of a TiC short nanorods sample.

The chemical composition of the product was determined using X-ray energy dispersion analysis.[19] The result of X-ray energy dispersion analysis reveals that the nanorods are composed of Ti and C, and the quantitative analysis indicates that the atomic ratio of Ti to C is approximately 1 : 1.

One of the chemical scissors — ethylenediamine has been confirmed as the nucleophilic attacking agent in our previous researches. For example, quantum-confined CdS nanowires have been successfully synthesized from cadmium bis(diethyldithiocarbamate) by removal of the thione groups with ethylenediamine. As a sequential research, a series of metal sulfides MS (M=Pb, Hg, Mn), Ag_2S, and $Cu_{1.8}S$ with spherical morphology were obtained by using ethylenediamine to attack at their metal diethyldithiocarbamate, respectively. The above results indicate that ethylenediamine only acts as the nucleophilic agent instead of the template for the further one-dimensional growth. As to the current preparation of TiC nanorods, the N-containing nucleophilic solvents, such as ethylenediamine, pyridine and diethylediamine, also act as the nucleophilic agent to remove the chlorine groups only. While in this process, it is the resulting one-dimensional conjugate carbon chain clusters that act as intermediate template to direct further growth of rod-like TiC. When Ti meets with the one-dimensional conjugate carbon chain clusters, TiC can grow along these chains and finally form the nanorods. From this point of view, such intermediate one-dimensional conjugate carbon chain clusters are very similar to the intermediate $[Cd_2S_2]$ cores in the above case of CdS nanowires. Therefore, we call it the "chemical-scissors-assemble" route. Meanwhile such phenomena is also supported by the fact that no rod-like metal sulfide MS can be obtained without the similar one-dimensional conjugate clusters, which is most probably caused by the characteristic structure of their respective precursor metal diethyldithiocarbanate. Thus, in the current approach, the ethylenediamine as well as pyridine and diethylamine only act as the nucleophilic solvents rather than the template for the further one-dimensional growth. Additionally, the existence of one-dimensional conjugate carbon chain clusters also have been detected in our previous work[20] on carbon nanotubes and nanorods, in which tetrachloroethylene was reduced by metallic potassium in benzene to form free C_2. But the formation mechanism of free C_2 in that paper is totally different from the presented process, in which free C_2 is produced via nucleophilic solvent cutting off the chlorine groups in tetrachloroethylene.

In the reaction process, the heating temperature had another important influence on the formation of TiC nanorods. If the temperature is below 400 °C, the reaction cannot take place; when the temperature is raised to 400–500 °C, pure phase TiC could not be detected by the XRD pattern; above the temperature of 500 °C, the reaction is rather complete.

In conclusion, a novel chemical reaction route was developed to prepare TiC short nanorods with the diameter of 30–35 nm and the lengths of 150–200 nm. In the process, ethylenediamine acts as a nucleophilic agent to cut the undesired chlorine groups, and one-dimensional conjugate carbon chain clusters as intermediate templates were used to direct the growth of rod-like TiC. We believe that the method can also be developed to synthesis other carbide nanorods at relative low temperature.

Financial support from the Chinese National Foundation of Nature Science Research and Chinese Ministry of Education are gratefully acknowledged.

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16 The XRD analysis was carried out with a Japan Rigaku D/max-γ rotation anode X-ray diffractometer, using Ni-filtered Cu $K\alpha$ radiation at 25 °C. A scanning rate of $0.05\,^{\circ}\cdot s^{-1}$ was applied to record the patterns in the 2θ range of 30–80 degree. The reflection data was collected at 25 °C.

17 JCPDS Card: File No 32-1383 for cubic TiC.

18 TEM images were taken with a Hitachi H-800 transmission electron microscope at the acceleration voltage 200 kV. The TiC powder was ultrasonically dispersed in absolute ethanol, and then one droplet of solution was adsorbed on the copper grid for measurement.

19 The X-ray energy dispersion spectrum was recorded by a hilips 9100/6 X-ray energy dispersion analysis equipment.

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