

## A Template-Interface Co-Reduction Synthesis of Hollow Sphere-like Carbides

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Hollow sphere-like carbides MC (M = Ti, V) with diameters of between 70 and 170 nm were synthesized via a template-interface co-reduction (TICR) route, in which  $\text{MCl}_4$  and hexachlorobuta-1,3-diene ( $\text{C}_4\text{Cl}_6$ ) were reacted with metallic sodium at 500 °C for 24 h. X-ray powder diffraction (XRD) patterns indicated the samples were single-phase NaCl-type

carbides. Transmission electron microscopy (TEM) photographs showed the hollow spheres consisted of nanocrystalline carbides. The possible formation mechanism of hollow sphere-like carbides is discussed.

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## Introduction

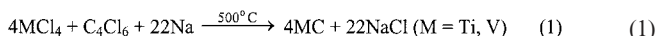
The transition-metal carbides of groups IV and V possess unusual properties that make them desirable and useful engineering materials in industry.<sup>[1]</sup> Nanosized TiC and VC powders have promising applications in mechanical and tribological fields.<sup>[2]</sup> Recent research work has proved that some transition metal carbides have similar catalytic properties to those of the platinum-group metals. For instance, vanadium carbide is an active  $\text{NH}_3$  decomposition catalyst.<sup>[3]</sup>

Hollow spheres consisting of nanoparticles are useful as fillers, coatings, catalysts, and encapsulating agents because of their low density, large specific surface area, and interesting optical properties.<sup>[4]</sup> Various hollow spheres including carbon,<sup>[5]</sup> polymers,<sup>[6]</sup> metals,<sup>[7]</sup> and inorganic oxides<sup>[8]</sup> have been synthesized by using spherical templates such as polystyrene beads or silica sol.<sup>[9]</sup> Several other methods have also been developed to fabricate hollow spheres, such as coaxial nozzle techniques,<sup>[10]</sup> microemulsion and reverse microemulsion methods,<sup>[11]</sup> exchange-resin methods,<sup>[12]</sup> self-organization,<sup>[13]</sup> and template-interface reactions.<sup>[14]</sup> Hollow sphere carbides may be promising materials in mechanical and catalyst fields. However, to the best of our knowledge, there are few reports on these compounds.<sup>[15]</sup>

Generally, transition metal carbides, including TiC and VC, are prepared by either direct element reaction,<sup>[16]</sup> carbothermal reduction,<sup>[17]</sup> self-propagating high-temperature synthesis (SHS)<sup>[18]</sup> or solid-state metathesis (SSM)<sup>[19]</sup> at el-

evated temperatures. Previously, we have developed a co-reduction method to synthesize nanocrystalline carbides by allowing  $\text{CCl}_4$  and  $\text{MCl}_4$  to react with metallic sodium at relatively low temperatures.<sup>[20]</sup>

Herein, we report a template-interface co-reduction (TICR) route to synthesize TiC and VC hollow spheres, using  $\text{TiCl}_4$  or  $\text{VCl}_4$  as the titanium or vanadium source,  $\text{C}_4\text{Cl}_6$  as the carbon source and Na as reductant.  $\text{TiCl}_4$  or  $\text{VCl}_4$  and  $\text{C}_4\text{Cl}_6$  are co-reduced by metallic Na at 500 °C. Metallic Na droplets generated in the co-reduction process may play a role as a template in the formation process of hollow sphere carbides. The formation of carbides can be expressed as shown in Equation (1):



## Results and Discussion

Figure 1 shows the XRD patterns of as-prepared samples. All the diffraction peaks in the XRD patterns can

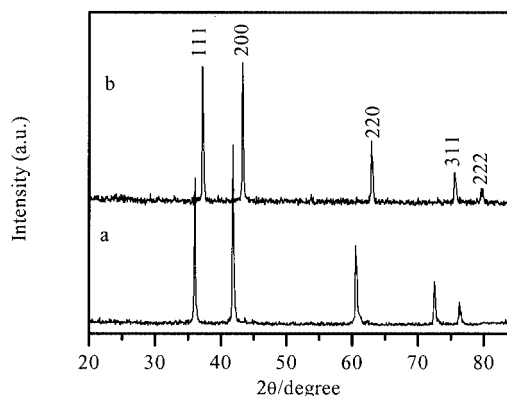


Figure 1. XRD patterns of as-prepared samples of (a) TiC and (b) VC

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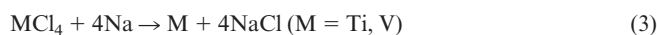
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be indexed as face-centered cubic (fcc) carbides. The shifts of the peak positions correspond to the different lattice constants of these two samples, due to the different ionic radii of Ti and V. The lattice parameters obtained from as-prepared products are  $a = 4.322 \text{ \AA}$  for TiC and  $a = 4.169 \text{ \AA}$  for VC, in good agreement with the values in the literature.<sup>[21]</sup>

The size and morphology of the carbides was studied by TEM. The TEM photographs and selected area electron diffraction (SAED) patterns of as-prepared carbides are shown in Figure 2a–d. From the TEM photographs it can be seen that there is an obvious contrast between the dark edge and the pale center of the samples, revealing that the core is hollow.<sup>[22]</sup> The hollow nature of the spheres is also supported by the observation of a TiC sphere with a broken shell [Figure 2a (inset)]. The as-prepared carbide spheres have diameters ranging from 70 to 120 nm; the thickness of the shell is about 10–20 nm for carbides. The SAED patterns of a single sphere of both samples show three clear ring patterns corresponding to the (111), (200) and (220)

reflections of cubic TiC (Figure 2b) and VC (Figure 2d). The cell constants calculated from the radii of the diffraction rings confirm the results from the XRD patterns. No diffuse rings of amorphous carbon are observable. These results indicate that the hollow spheres are mainly composed of polycrystalline carbides. From the HRTEM photographs (Figure 2e and 2f), it can be seen that the shells of the carbide spheres are composed of nanoparticles of between 2 and 5 nm. FESEM micrographs of both carbides are shown in Figure 3. Besides some irregular particles, the portion of spheres with sizes of about 70–170 nm in the products is above 60%. It can be seen that a big sphere is usually found with a broken shell (indicated by an arrow in Figure 3a).

Based on our previous experiment results,<sup>[20]</sup> the overall reaction [Equation (1)] might occur via a co-reduction route, which could be described by Equations (2)–(4):



Similar to the reaction between  $\text{CCl}_4$  and Na,  $\text{C}_4\text{Cl}_6$  could be reduced by Na to generate carbon [Equation (2)], which should be a thermodynamically spontaneous and exothermic process concluded from the very high Gibbs energy of formation and enthalpy of NaCl ( $\Delta_f G^\circ = -384.1 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta_f H^\circ = -411.2 \text{ kJ}\cdot\text{mol}^{-1}$ ).<sup>[23]</sup> The reaction in Equation (3) is highly exothermic ( $\Delta H^\circ = -881.6 \text{ kJ}\cdot\text{mol}^{-1}$  using  $\text{TiCl}_4$  as reactant;  $\Delta H^\circ = -1075.4 \text{ kJ}\cdot\text{mol}^{-1}$  using  $\text{VCl}_4$  as reactant).<sup>[23]</sup> The reaction in Equation (4), which produces TiC ( $\Delta H^\circ = -92 \text{ kJ}\cdot\text{mol}^{-1}$ ) or VC ( $\Delta H^\circ = -51 \text{ kJ}\cdot\text{mol}^{-1}$ ),<sup>[24]</sup> is also exothermic. Hence, the overall reaction in Equation (1) is highly exothermic.

In this synthetic system, metallic sodium may form droplets owing to reaction heat generated from the exothermic reactions, and these metallic Na droplets may act as templates in the formation process of hollow sphere carbides. This possible formation process is illustrated in Figure 4 and is similar to the mechanism of formation of CdS hollow spheres via a template-interface reaction.<sup>[14]</sup> In our experiment, upon increasing the reaction temperature to  $500^\circ\text{C}$  ( $\text{C}_4\text{Cl}_6$  (b.p.  $215^\circ\text{C}$ ),  $\text{TiCl}_4$  (b.p.  $136.4^\circ\text{C}$ ) and  $\text{VCl}_4$  (b.p.  $148^\circ\text{C}$ ) begin to vaporize.<sup>[23]</sup> Strongly exothermic reactions then take place on the surface of the fused sodium (m.p.  $97.82^\circ\text{C}$ ),<sup>[23]</sup> raising the local temperature near the surface

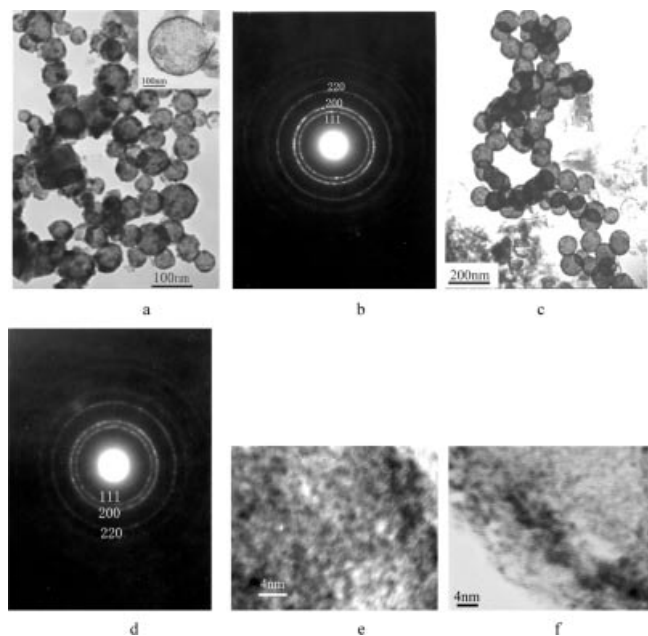


Figure 2. (a) (b) TEM micrograph and SAED pattern of TiC [(inset in a) single TiC hollow sphere with broken shell]; (c) (d) TEM micrograph and SAED pattern of VC; (e) HRTEM micrograph of the sphere shell of TiC; (f) HRTEM micrograph of the sphere shell of VC

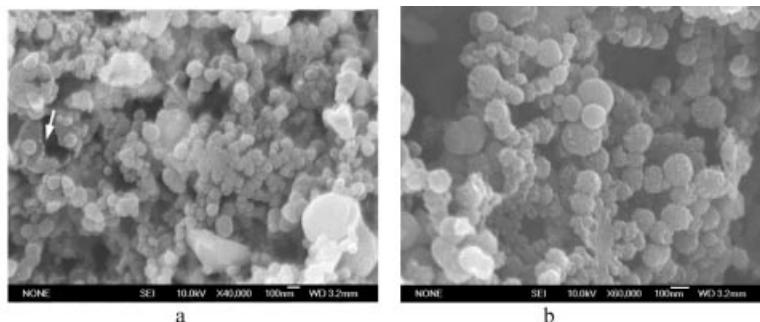


Figure 3. (a) FESEM micrographs of TiC; the arrow indicates a broken sphere; (b) FESEM micrographs of VC

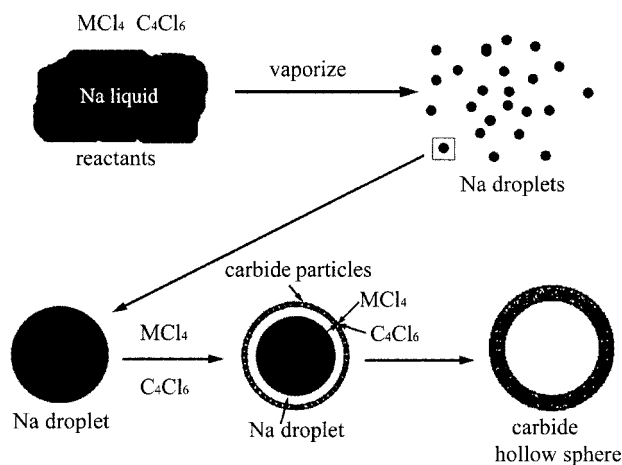


Figure 4. The formation mechanism of hollow carbide spheres

and hence causing the sodium to vaporize (b.p. 881.4 °C).<sup>[23]</sup> This sodium vapor could form many small droplets in the autoclave. Subsequently, the co-reduction reactions could occur on the surface of the Na droplets in the atmosphere of  $C_4Cl_6$  and  $MCl_4$ , which may result in the formation of a carbide shell around the Na core. This is an important step in the formation of hollow spheres. Analogous to the synthesis of hollow spheres using emulsion droplets as templates,<sup>[25]</sup> the produced carbide shell could stabilize the sodium droplets, thus preserving the spherical shape. As the reaction continues the amount of sodium becomes depleted and the shell gradually thickens, resulting finally in hollow spheres with a polycrystalline carbide shell. In this co-reduction procedure the sodium droplets may serve as a template with the carbide shells being formed near the liquid-gas interface. We have therefore called it a template-interface co-reduction (TICR) route. We have not observed sodium encapsulated in carbides by TEM directly due to the high reactivity and air sensitivity of sodium. However, the formation of broken spheres may be ascribed to the presence of unconsumed sodium in the hollow sphere, which could react with water to blow out the hollow spheres due to gas evolution. This may be a supportive evidence for the proposed mechanism. In order to understand the formation process of hollow sphere carbides, further extensive studies are underway.

## Conclusion

We have successfully prepared TiC and VC hollow spheres via a template-interface co-reduction (TICR) route. The TiC and VC hollow spheres have potential applications in catalysis and mechanical fields. A possible template-interface reaction mechanism for the formation of carbide spheres has been proposed. This TICR route may be applied to produce other carbide hollow spheres.

## Experimental Section

All manipulations were carried out in a dry glovebox under  $N_2$ . In a typical synthetic procedure for TiC, 0.02 mol of  $TiCl_4$  and 0.005 mol of  $C_4Cl_6$  were syringed into a stainless steel autoclave of 50 mL capacity, and 0.12 mol of granular metallic Na was added. The autoclave was sealed and maintained at 500 °C for 24 h, then allowed to cool slowly to room temperature. The product was collected and washed successively with absolute ethanol, 1 M hydrochloric acid and distilled water. After drying in vacuo at 60 °C for 4 h, 0.98 g of black powder was obtained. Substitution of  $VCl_4$  for  $TiCl_4$  gave VC.

The samples were characterized by X-ray powder diffraction (XRD) on a Japan Rigaku Dmax- $\gamma A$  X-ray diffractometer with graphite-monochromated  $Cu-K_\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Transmission electron microscopy (TEM) photographs and selected area electron diffraction (SAED) patterns were taken with a Hitachi Model H-800 transmission electron microscope. High resolution transmission electron microscopy (HRTEM) was carried out using a JEOL-2010 transmission electron microscope. Field-emission scanning electron microscopy (FESEM) images were taken with a JEOL JSM-6700F scanning electron microscope.

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