

# Synthesis of carbon hollow spheres and particles from $\text{CCl}_4$ and Mo

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## Abstract

Carbon materials with different morphology were prepared by reacting  $\text{CCl}_4$  and Mo at 873–1173 K. At 873–973 K, hollow spheres (diameter: 1–3  $\mu\text{m}$ , shell thickness: 50 nm) were obtained. At 1073 K, particles (diameter: 50–100 nm) encapsulated in spherical shells (diameter: 1–5  $\mu\text{m}$ ) were collected. At 1173 K, formation of particles (diameter: 200–300 nm) was observed. Mo acted as a reagent to remove chlorine atoms from the carbon source and a template for the formation of the spherical structures. We propose that reaction temperature and polymerization of chlorinated species formed from the pyrolysis of  $\text{CCl}_4$  affect the morphology of carbon products greatly.

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**Keywords:** Powder technology; Carbon hollow spheres; Electron microscopy

## 1. Introduction

Carbon hollow spheres and particles have been synthesized by a variety of methods, including direct pyrolysis of hydrocarbons, pyrolysis of hydrocarbons in carbon arc, impregnation and carbonization of organic precursors in mesoporous silica templates, pyrolysis of precursors on monodispersed cobalt nanoparticle template, polymerization of fullerene powders by shock-compression, and chemical vapor deposition (CVD) via mixed-valent oxide-catalytic carbonization (MVOCC) process [1–11]. In addition, recent reports have shown that carbon hollow spheres can be synthesized by reduction of chloroalkanes and alcohols with active metals in autoclave [12–16]. In this paper, we describe an interesting new reduction reaction process to form carbon hollow spheres by reacting  $\text{CCl}_4$  with Mo powders at high temperatures. We report our observations below.

## 2. Experimental procedure

In typical experiments, Mo powders (1–3  $\mu\text{m}$ , Riedel-deHaën) in a quartz boat were placed in a 30 mm diameter quartz tube in a

furnace. At 1 atm 873–1173 K,  $\text{CCl}_4$  (Fisher) at 298 K under a flow of Ar (10 sccm) was bubbled into the reactor for 1–4 h to produce black powders. The black powders were characterized by scanning electron microscopy (SEM, JEOL JSM-6330F at 15 kV), transmission electron microscopic (TEM, Philips TECNAI 20 at 200 kV), X-ray diffraction (XRD, Bruker D8 Advance, Cu  $\text{K}\alpha$  radiation, 40 kV, and 40 mA) and Raman

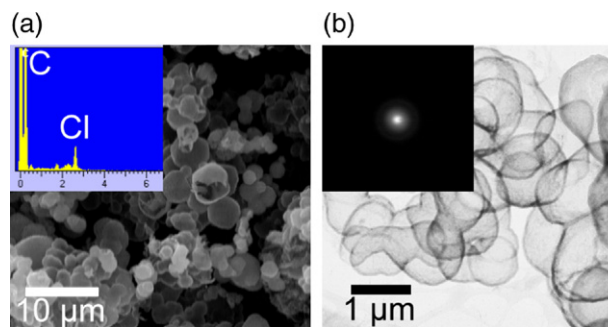


Fig. 1. (a) SEM and EDS (inset) images of powders prepared at 973 K for 4 h. (b) TEM and ED (inset) images of powders prepared at 873 K for 4 h.

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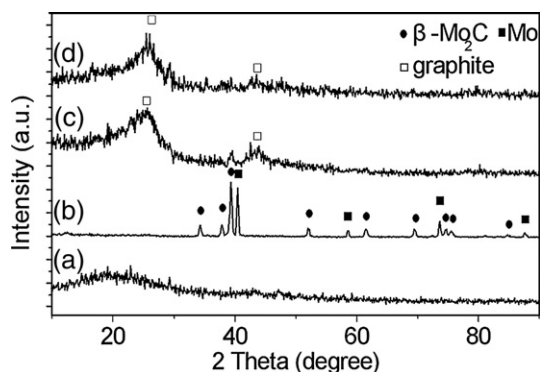


Fig. 2. XRD patterns of powders prepared at (a) 873 K for 4 h, (b) 1073 K for 1 h, (c) 1073 K for 4 h and (d) 1173 K for 1 h.

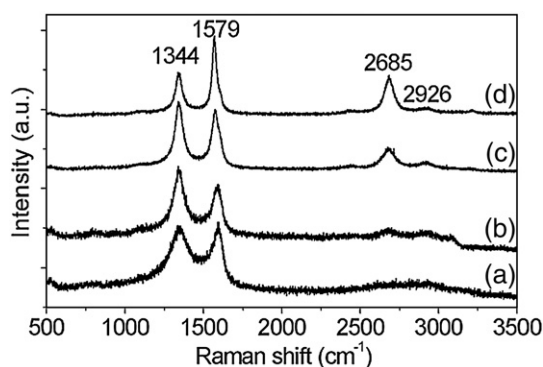


Fig. 3. Raman spectra of powders prepared at (a) 873 K for 4 h, (b) 973 K for 4 h, (c) 1073 K for 4 h and (d) 1173 K for 1 h.

spectroscopy (Jabin Yvon HR800 equipped with an  $\text{Ar}^+$  laser at 514.5 nm).

### 3. Results and discussion

Fig. 1 shows SEM and TEM images of the powder products. In Fig. 1(a), aggregated spherical particles with diameters 1–3  $\mu\text{m}$  are found in the sample prepared at 973 K. The spheres appear to be hollow because some broken thin shells with a wall thickness ca. 50 nm can be found in the image. An energy dispersive X-ray spectrum (EDX) of the sample shows that the major component is C while a

trace of Cl is also found. A TEM image of the sample prepared at 873 K is displayed in Fig. 1(b). This image confirms that the spheres are hollow. The diameter and the layer thickness shown in the image are compatible to the SEM observation. An electron diffraction (ED) pattern in Fig. 1(b) indicates these hollow spheres are amorphous. For reactions performed at 1073 K and 1173 K, the results were different. Instead of hollow spheres, particulate solids were produced. The sample prepared at 1073 K consisted of carbon particles (diameters 50–100 nm) inside carbon spheres (diameters 1–5  $\mu\text{m}$ ). When the reaction temperature was 1173 K, the product was carbon black-like particles with sizes of 200–300 nm.

Fig. 2 shows the XRD patterns of the samples. Fig. 2(a) suggests that all of the reactant Mo is completely consumed at 873 K for 4 h and the product prepared from the reaction is amorphous. This is comparable to the ED pattern shown in Fig. 1(b). Fig. 2(b) displays the XRD of the solid gathered from the reaction at 1073 K for 1 h. The pattern is indexed to a mixture of the reactant Mo and a product  $\beta\text{-Mo}_2\text{C}$  [17,18]. When the reaction time exceeds 4 h, the reflections from Mo and  $\beta\text{-Mo}_2\text{C}$ , as shown in Fig. 2(c), become insignificant while a pattern of graphite with broad peak widths appears. The pattern can be indexed to a less ordered graphitic material. The calculated  $d$ -spacing of (002) planes is 0.344 nm, which is larger than the reported value of graphite,  $d=0.33756$  nm [19]. The XRD data suggest that the product lacks the long-range orderness of graphite. The result is similar to the observations of other related carbon materials [12,15,16]. For the sample prepared at 1173 K for 1 h, the  $d$ -spacing of (002) planes, estimated from the pattern in Fig. 2(d), is 0.339 nm. This suggests that the particles synthesized at this condition are also graphitic but not well-ordered [19].

Raman spectra shown in Fig. 3 are further used to characterize the carbon products. Two strong scattering peaks near 1344 and 1579  $\text{cm}^{-1}$ , assigned to D and G modes respectively, are observed for the samples [20,21]. In some cases, overtones from these vibrations are also observed at 2600–3000  $\text{cm}^{-1}$  [20,21]. The intensity ratio of D peak to G peak,  $I_D/I_G$ , decreases as the reaction temperature increases. This implies that the degree of graphitization is lower for the carbon hollow spheres synthesized at 873–973 K than for the particles prepared at 1073–1173 K. This agrees with the XRD results well.

The reaction pathway between  $\text{CCl}_4$  and Mo powders is proposed in Fig. 4. It is known that  $\text{CCl}_4$  decomposes at high temperatures into many dechlorinated species, such as  $\text{CCl}_2$ ,  $\text{CCl}_3$ , and  $\text{CCl}_2=\text{CCl}_2$  [22]. These species could polymerize and dehalogenate further into various carbon containing products [13,23,24]. We propose that at 873–973 K, the Mo particle acts as a template for the initial carbon hollow sphere formation. As the reaction proceeds, the inner Mo core is etched away

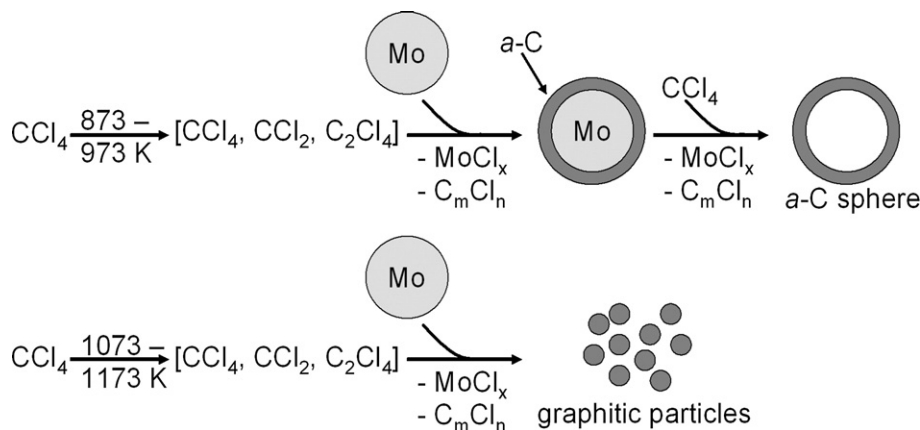


Fig. 4. Proposed reaction pathway.

by Cl atoms to form the amorphous carbon hollow sphere. At 1073 K, the surface of Mo particle is carbonized initially into a layer of Mo<sub>2</sub>C. As the reaction proceeds, the inner Mo core is also carbonized and etched. Prolonged reaction causes all of the Mo atoms to be etched away, leaving only carbon particles as the main product. Previously, Mo<sub>2</sub>C@*a*-C core-shell powders were prepared by reacting Mo particles with 1-chlorobutane (<sup>n</sup>BuCl) and hexachlorobenzene (C<sub>6</sub>Cl<sub>6</sub>) [25]. In the study, the Mo containing core was preserved. But in this study, the Mo metal was removed completely. The reason for this difference is attributed to the different Cl/C ratios of the chlorinated reactants. Apparently, the C/Cl ratio of CCl<sub>4</sub>, 4, is higher than the numbers of <sup>n</sup>BuCl and C<sub>6</sub>Cl<sub>6</sub>, 0.25 and 1, respectively. As more Cl atoms are supplied, more of the Mo containing cores can be removed by etching. Consequently, the carbon products formed are Mo-free.

#### 4. Conclusions

The reaction between CCl<sub>4</sub> and Mo at 873–1173 K is a combination of pyrolysis, polymerization, dechlorination and etching processes. The morphology of the carbon products is highly affected by the reaction temperature and the Mo size. At 873–973 K, carbon hollow spheres were obtained. The size of the spheres was influenced by the Mo diameter. We suggest that by employing smaller Mo metal particles, smaller carbon spheres can be fabricated by the same methodology. At 1073–1173 K, due to fast etching and carbonization of the Mo core, carbon particles were formed as the major product.

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