

PD Research Report for the 2016 year

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Research Theme Development of nanohybrid system between metal carbides and nanoporous carbons for high performance rechargeable batteries

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Research Results (about 2,500 characters in Japanese, about 65 lines times 90 characters in English)

At present, various carbon materials, such as active carbon, graphite, carbon nanotubes, and graphene, have been reported so far and extensively studied in energy storage fields. Nanoporous carbon materials with high surface areas are attractive, because they can enhance the performance of carbons in applications such as batteries, supercapacitors, and catalysis applications. Great efforts have been devoted towards the preparation of nanoporous carbons. For instance, highly-ordered nanoporous carbons have been prepared by using inorganic hard-templates including zeolites and mesoporous silicas. As another approach, inorganic–organic mesostructured hybrids have been recently demonstrated to be excellent precursors for making nanoporous carbons.

Currently, nanoporous carbon particles are mainly being prepared by carbonization of organic spheres. For instance, by using several polymer spheres, nanoporous carbon spheres with tunable nanopore sizes can be obtained. The generation of nanopores inside the polymer spheres is spontaneous during the carbonization. Nevertheless, formation of uniform pore sizes is not easy, the present method by using mesoporous silica nanoparticles as hard-templates includes several steps, which is somewhat complicated in the case of large-scale production. In order to overcome the above drawbacks, alternative ways for facile preparation of nanoporous carbons with controlled particle sizes are in much demand. Recently, porous metal–organic frameworks (MOFs), as typical inorganic–organic hybrids, have been used as precursors to prepare nanoporous carbons through thermal conversion. The obtained nanoporous carbons showed attractive features, including ultra-high specific surface areas, ultra-large pore volumes, and controlled pore structure. Here, I used a facile route for the preparation of monodispersed ZIF-8 crystals with controlled particle sizes ranging from the nanometer scale to the micrometer scale under various conditions. Then, the obtained starting precursors ZIF-8 crystals were converted into nanoporous carbons, retaining their original shapes.

Three sets of ZIF-8 samples with different particle

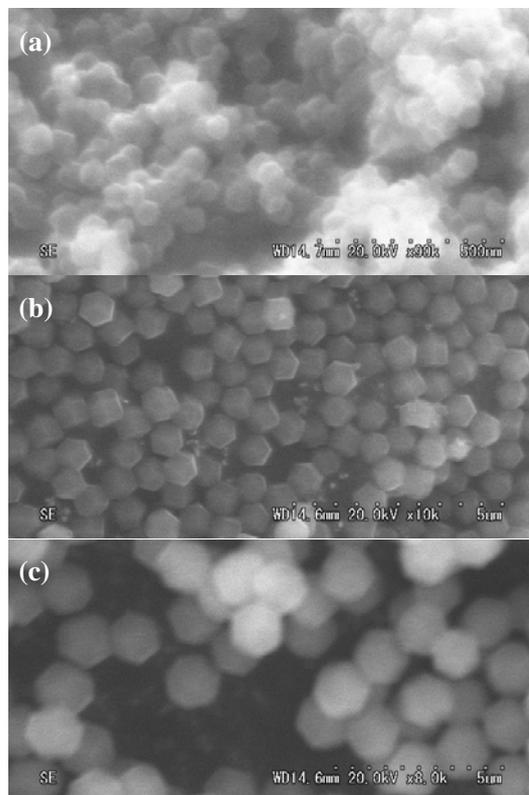


Figure 1. SEM images of ZIF-8 of (a)~50μm, (b)~700 nm, (c)~1.5 μm.

sizes within a wide range was synthesized according to the method described in the literature.¹ Figure 1 shows scanning electron microscopy (SEM) images of ZIF-8 crystals prepared under different conditions. The SEM images show that the well dispersed nanocrystals in polyhedral shape with sizes from 50 nm to 1.5 μm . In general, the particle size of ZIF-8 is determined by the speed of crystal nucleation and growth via coordination and deprotonation equilibria of ligands. A fast nucleation speed with a short reaction time leads to small nanoparticles, while a slow nucleation speed with a long reaction time tends to yield large crystals. SEM observations demonstrate the success of the size-controlled syntheses (for the uniform particle size distributions).

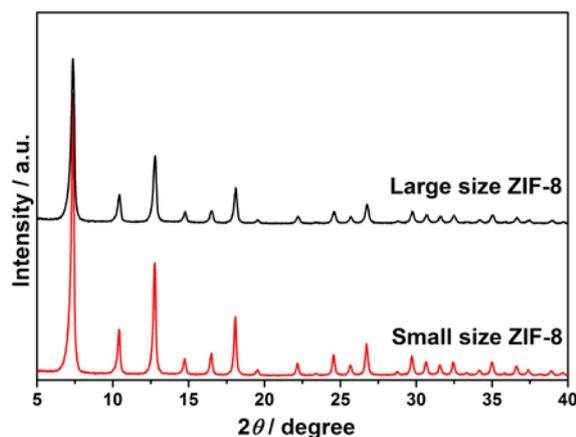


Figure 2. Powder XRD patterns of ZIF-8 with different particle size.

To examine the crystal structure of the three ZIF-8 samples with different particle sizes, powder XRD measurement was performed. All the samples exhibited pure crystals with cubic $I43m$ group, which matched with the well-known ZIF-8 crystal structure (Figure 2.). The obtained ZIF-8 crystals with different particle sizes as templates/precursors underwent pyrolysis at 900 $^{\circ}\text{C}$ under Ar gas to afford porous carbons. In this process, the generated ZnO was reduced by carbon to give evaporative Zn at such high temperature. Pure carbons with graphitic structure were obtained according to XRD patterns. The SEM observations illustrate that the obtained carbons are well dispersed and have retained sizes and morphology from their precursors, ZIF-8 crystals.

In conclusion, ZIF-8 crystals with controlled particle sizes ranging from the nanometer scale to micrometer scale have been successfully synthesized as templates/precursors. Then, the obtained ZIF-8 crystals were successfully converted into nanoporous carbons, retaining their original shapes. Compared to traditional approaches, this one-pot approach without any complicated steps is really simple. We will prepare hybrid materials between layered metal carbides and the nanoporous carbon for lithium ion batteries and supercapacitors.

References:

1, Nagy L. Torad, Ming Hu, Yuichiro Kamachi, Kimiko Takai, Masataka Imura, Masanobu Naito and Yusuke Yamauchi. *Chem. Commun.*, 2013, 49, 2521-2523.

Articles, presentations:

Preparation of gamma- LiV_2O_5 from polyoxovanadate cluster $\text{Li}_7\text{V}_{15}\text{O}_{40}$ and its battery performance as cathode active materials, H. Wang, J. Isobe, Takeshi Shimizu, D. Matsumura, T. Ina, H. Yoshikawa, paper in preparation.

Reaction mechanism and electrochemical performance of amorphous Vanadium polyoxovanadate cathode for Li-ion batteries, H. Wang, J. Isobe, Takeshi Shimizu, D. Matsumura, H. Yoshikawa, paper in preparation.