Preparation of Carbon Micro-beads via an Ethanol-thermal Route

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Carbon micro-beads (CMB) with regular and perfect shape, high yields, and narrow size distributions were obtained via an ethanol-thermal reduction process in a stainless steel autoclave at 500 °C. In this process, $LaNi_5$ alloy was used as a catalyst. The products were characterized with X-ray powder diffractometer (XRD), scanning electron microscopy (SEM) and Raman spectroscopy. There were two types of carbon micro-beads, spherical and spindle-like, in the sample. The spherical micro-beads have diameters ranging from 2 to 5 μm. The spindle-like micro-beads had diameters ranging from 2 to 4 μm and lengths ranging from 5 to 10 μm.

The discovery of a number of novel carbon materials with unique structures, such as carbon nanotubes,[1] carbon onions,[2] cone-shaped graphitic structures,[3] carbon micro-trees,[4] carbon hollow spheres,[5] and carbon micro-coils,[6] depending on the techniques and the carbon precursors used has led to a wide research interest. Micro-bead carbon materials attract many researchers due to their unique applications, which include high-density and high-strength carbon artifacts,[7,8] lithium-ion secondary battery,[9–14] and their unique spherical shape with a diameter of approximately 1 to 40 μm being appreciated. The preparation and properties of these carbon materials have attracted considerable attention, because their applications significantly depend on the shape and size of the particles.

Qiu et al.[15] reported a ball-like carbon material obtained by arc discharge evaporation of composite carbon rods made from coal and nickel particles. The carbon micro-balls were observed in various forms such as mono-dispersed individual balls, net-like and plate-like materials. It is well known that carbonaceous spheres or mesocarbon micro-beads (MCMB) can be prepared from pitch or polymeric materials in large quantities with various methods, such as direct polymerization from pitch,[16] emulsion method,[17,18] and suspension method.[19] In the present study, carbon micro-beads were fabricated with $LaNi_5$ alloy as a catalyst via an ethanol-thermal reduction process in a stainless steel autoclave at 500 °C. The yield of carbon micro-beads was estimated through SEM observations of the as-prepared samples to be about 95%.

All reagents of analytical grade were commercially available in our experiment. A lanthanum nickel alloy prepared by melting method was used as a catalyst to produce carbon micro-beads. In a typical experiment, an appropriate amount of $LaNi_5$ alloy (0.5 g), and absolute ethanol (50 mL) were put into a stainless steel autoclave of 60 mL capacity. The reactor was maintained at 400, 500, and 600 °C for 12, 24, 36, and 48 h, respectively, and then it was cooled to room temperature naturally. A dark precipitate was collected and washed with absolute ethanol, dilute HCl aqueous solution, distilled water and absolute ethanol, respectively. The obtained sample was then dried in a vacuum at 60 °C for 4 h.

Structure characterization was performed by X-ray diffraction (XRD) on a MSAL-XD2 X-ray diffractometer using Cu Kα radiation (40 kV, 20 mA, $\lambda = 1.54051$ Å). The morphologies of the sample were characterized with Philips XL-30 scanning electron microscopy. The Raman spectrum of as-prepared samples was recorded at ambient temperature on a Renishaw RM2000 Raman microspectrometer with an argon-ion laser at an excitation wavelength of 514.5 nm.

Figure 1 shows the X-ray diffraction pattern of the as-prepared samples. A scanning rate of $0.08^\circ\ s^{-1}$ has been used to record the pattern in the range of 20–55°. The XRD pattern shows that the presence of two peaks at $d = 3.4169$ Å and $d = 2.0249$ Å, which are reflections from the 002 planes and from the 101 planes, respectively. The peaks can be indexed to a hexagonal graphite lattice with cell constant $a = 2.448$ Å and $c = 6.834$ Å. The deviation was lower than 1% compared with the reported values $a = 2.470$ Å and $c = 6.790$ Å (JCPDS No.75-1621).

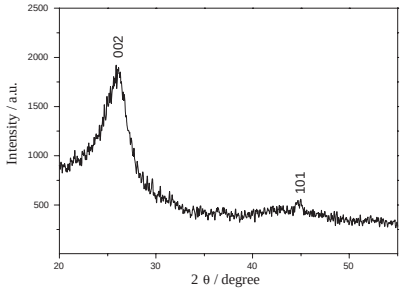

Figure 1. X-ray diffraction pattern of the products, using Cu Kα X-ray as radiation.

Figure 2a shows SEM image of $LaNi_5$ alloy catalyst. The catalyst have sizes ranging from 10 to 40 μm. Figure 2b shows many carbon micro-beads grown from the surface of $LaNi_5$ alloy. Low-magnification SEM image (Figure 2c) indicates that carbon micro-beads with large quantity, narrow size distributions, regular and perfect shape are achieved by this approach. Most of carbon micro-beads are spheres with diameters ranging from 2 to 5 μm. Furthermore, there are many spindle-like carbon micro-beads (Figure 2d), diameters ranging from 2 to 4 μm and lengths ranging from 5 to 10 μm. In addition, we could also observe some hemispheres in the sample via SEM observation (Figure 2c). All of them are mono-dispersed, and the surfaces seem to be rather smooth. Yamada et al.[8] separated mesocarbon micro-beads by solvent fractionation from heat-treated coal-tar pitch and from heat-treated asphalt at 430 °C. The shapes of the mesocarbon micro-beads are classified into lemon-like and spherical in their report. In our experiment, a particular period of reaction time (48 h) appears to be optimum to give a large quantity of the carbon micro-beads than other reaction times. The optimal reaction temperature is 500 °C. There is no carbon

micro-bead in the as-prepared sample when the temperature is lower than 400 °C or higher than 600 °C. $LaNi_5$ alloy may be play a catalytic role in producing carbon micro-beads, because no carbon micro-beads were obtained when there was not $LaNi_5$ alloy in the reaction process. A study of the growth mechanism of the carbon micro-beads is underway.

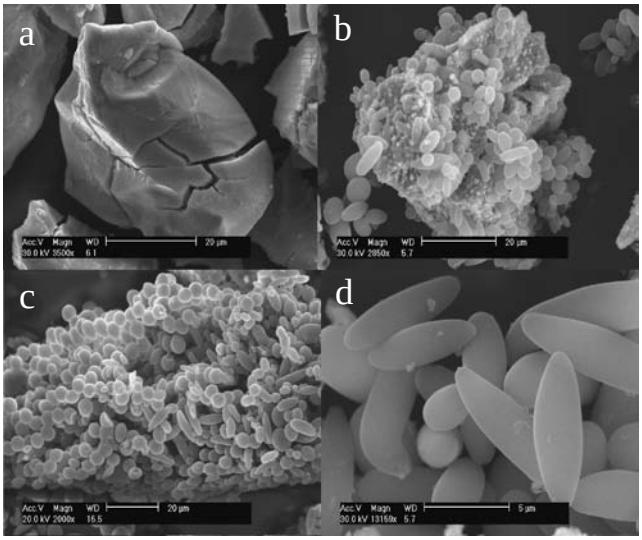

Figure 2. SEM image of sample: (a) LaNi5 alloy catalyst, (b) Carbon micro-beads grown from the surface of LaNi5 alloy, (c) Low-magnification SEM image of carbon micro-beads, (d) Spindle-like carbon micro-beads.

Raman spectroscopy is one of the powerful techniques for characterizing carbon materials. The carbonaceous products have been used directly to record the Raman spectrum (Figure 3) at ambient temperature. A strong peak at 1592 cm^{-1} as well as a relative weak peak at 1342 cm^{-1} can be clearly seen. The peak at 1592 cm^{-1} (G) corresponds to an E_{2g} mode of graphite and is related to the vibration of sp^2-bonded carbon atoms in a two–dimension hexagonal lattice, such as in a graphite layer. The peak at 1342 cm^{-1} (D) is associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite. The line at 2908 cm^{-1} is assigned to a combination of the graphitic and a disorder mode (G + D). It is well known that the graphitic degree of carbons is confirmed by the width of I_G peak and the value of I_D/I_G. The relatively large I_D/I_G (about 0.71) indicated the lower graphitic degree in the as-prepared carbon micro-beads prepared via ethanol-thermal route, compared with the sample prepared through the arc discharge method ($I_D/I_G = 0.25$) reported by Qiu et al.[15]

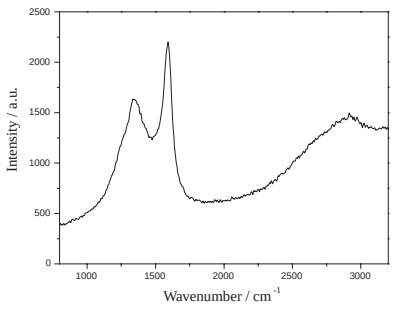

Figure 3. Raman spectrum of the as-prepared sample.

In summary, we have successfully synthesized carbon micro-beads on a large scale through an ethanol-thermal route. In this process, ethanol was used as the carbon source and solvent, and $LaNi_5$ alloy prepared by melting method was used as a catalyst. The optimal reaction time was 48 h, and the most favorable temperature was 500 °C. Two types of carbon micro-beads, spindle-like and spherical, are obtained by the approach. They have narrow size distributions, regular and perfect shape. Further studies along this line are in progress. Compared with other methods, this approach was simple and feasible. Furthermore, nontoxic and cheap ethanol was used as carbon source. Therefore, it may potentially be applied on the scale of industrial production.

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