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Agglomerates of amorphous carbon nanoparticles synthesized by a solution-phase method

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ABSTRACT

A novel solution-phase method is developed for preparation of agglomerates of amorphous carbon nanoparticles under ambient atmosphere by the reaction of ferrocene and ammonium chloride in diglycol at 200 °C. Samples are characterized by X-ray diffraction, field-emission scanning electron microscopy, transmission electron microscopy and N_2 adsorption–desorption isotherms. It is found that the nanoparticles are complete amorphous and agglomerate together due to the strong surface tension. The agglomerates of amorphous carbon nanoparticles with a diameter of 20–50 nm have a wide size distribution of mesopores with a Brunauer–Emmett–Teller surface area of 75.2 $m^2 g^{-1}$. It is proposed that the dissolved reactants uniformly dispersing in the solutions could react at a molecular level to form uniform carbon nanoparticles.

1. Introduction

Over the past few decades, porous nanocarbons with specific morphology have attracted much attention due to their distinctive properties, like sorption ability, chemical stability, low density, suitability for large scale production and wide variety of structural forms. These advantages bring a series of opportunities for the potential technological applications of the porous nanocarbons in hydrogen storage, electric double-layer capacitor, catalysis and drug delivery [1–4]. The morphology and structure of porous nanocarbons are very sensitive to the synthesis method, processing, carbonization and activation conditions [5]. Therefore, various synthesis methods, such as vapor-phase growth, carbonization of organic aerogels, template-assisted and solvothermal method, have been carried out for direct and controlled synthesis of porous nanocarbons without further activation.

Vapor-phase synthesis, such as chemical vapor deposition (CVD) and flame synthesis, is a powerful technique for large scale nanocarbon preparation with shape controlling. However these methods not only require complicated and expensive equipment, but also have difficulty in producing uniform samples. Carbon aerogel, consisting of interconnected uniform nanoparticles, is usually prepared by polycondensation of resorcinol with formaldehyde and carbonization of the resulting organic gel [6], which involves a time-consuming and costly supercritical drying step. The template-assisted method can be adopted to fabricate ordered porous carbon materials [7]. However, the complicated process makes it unsuitable for large-scale production for industrial applications. On the other hand, the synthesis temperature is still relatively high in these methods mentioned above. The solvothermal method can evidently lower the synthesis temperature, but the preparation should be completed in an autoclave with high pressure resistance and the reaction time is long [8]. All the methods cannot be carried out in ambient atmosphere because oxygen should be avoided during preparation in order to prevent oxidation of carbon. Considering the disadvantages in these methods aforementioned and the close relationship between the wide application and the efficient synthesis, a new strategy for porous nanocarbons is still worthy of investigation. In the present paper, a novel method is developed to synthesize amorphous carbon nanoparticles in solution under ambient atmosphere.

2. Experimental details

In a typical synthesis process, 20 g ammonium chloride was first dissolved in 500 ml of diglycol in a four-necked round-bottomed flask equipped with an air condenser, magnetic stir bar, dropping funnel, thermometer, gas inlet tube, heating and stirring mantle. Then the solution was heated to 200 °C, and 10 g ferrocene dissolved by 500 ml of ethanol was added drop by drop under strong magnetic stirring for 2 h with a 50 sccm air flow. Fig. 1 is the scheme of the experimental setup. After the resulting black homogeneous suspension was cooled down to room temperature, 2.14 g of amorphous carbon nanoparticles were collected by filtration, washed with HCl solution and deionized water for several sequential times, and finally dried in an oven at 100 °C for 12 h. Phase characterization was performed with an X'Pert PRO X-ray diffractometer (XRD) with Cu Kα radiation

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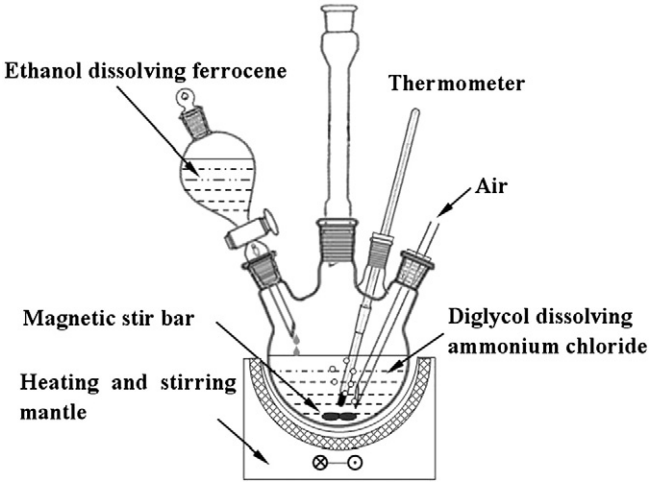

Fig. 1. Scheme of the experimental setup.

($\lambda = 0.15418$ nm). The microstructure analysis was conducted with a JEOL JSM 7500F field emission scanning electron microscope (SEM) and a JEOL JEM 2010 transmission electron microscope (TEM), operating at 5 and 200 kV, respectively. The N_2 adsorption and desorption isotherms were determined on a JW-BK-112 specific surface area and pore size distribution analyzer (Beijing JWGB Sci. & Tech. Co., Ltd.) at 77.4 K with a sample outgassed for 5 h at 200 °C. Surface areas were calculated using the Brunauer–Emmett–Teller (BET) equation and pore size distributions were obtained using the Barrett–Joyner–Halenda (BJH) method using the adsorption branch of the isotherms.

3. Results and discussion

Fig. 2 gives the XRD profile of the carbon nanoparticles in the as-prepared state. The broad peak around $2\theta = 26°$ can be assigned to the amorphous phase of carbon, representing the amorphous carbon nanoparticles prepared at low synthesis temperature by the present method.

For SEM observation, the as-synthesized powder was directly transferred to double sided adhesive conductive carbon tape without further coating. SEM micrographs are shown in Fig. 3. Fig. 3a at relative low magnification exhibits large amount of cotton-like agglomerates less than 200 nm in diameter. At high magnification in Fig. 3b, it is obvious that the agglomerates consist of nanoparticles

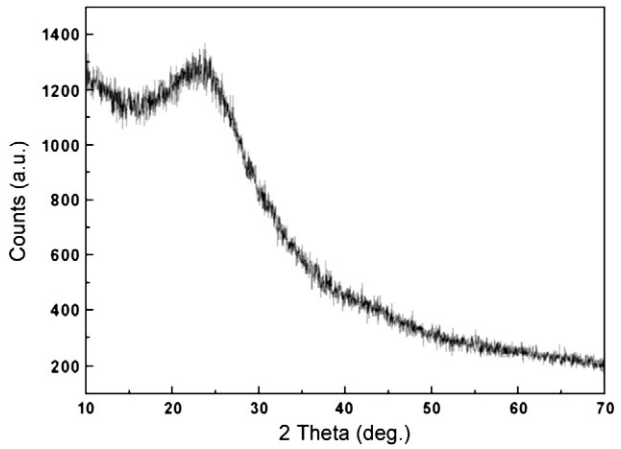

Fig. 2. XRD profile of the as-prepared amorphous carbon nanoparticles.

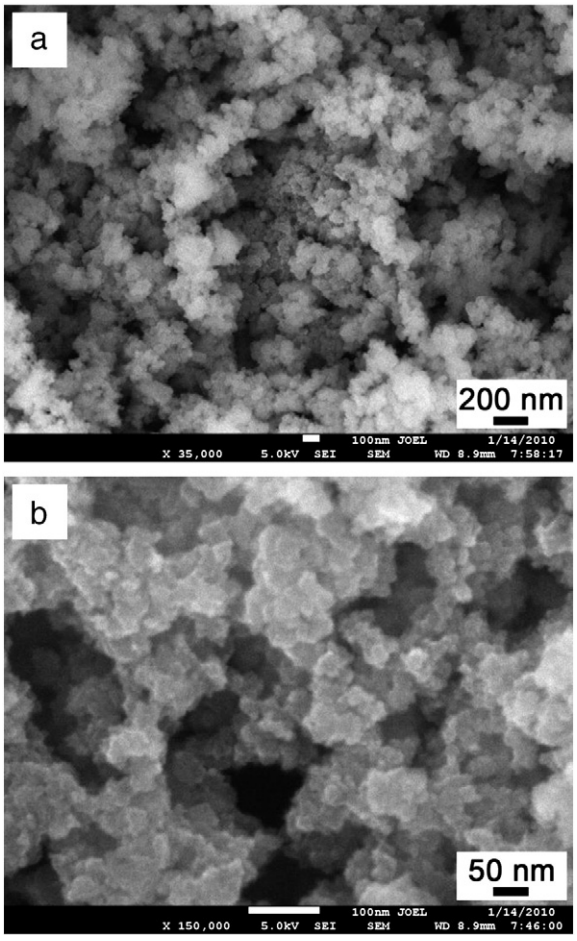

Fig. 3. SEM micrographs of the amorphous carbon nanoparticles at different magnifications.

with dimensions ranging from 20 to 50 nm. In fact, the as-prepared powder suffers greatly from shrinkage during drying due to strong surface tension, resulting in the formation of agglomerated carbon nanoparticles. Typical TEM bright field morphology of the amorphous carbon nanoparticles is shown in Fig.4. It is clear that the agglomerate consists of nanoparticles as shown in Fig. 4a, which is consistent with SEM micrographs. The shape of the nanoparticles is not regular and surface is not smooth either. The high resolution TEM image further proves the nanoparticles are completely amorphous, as shown in Fig. 4b.

Fig. 5 shows the nitrogen adsorption–desorption isotherm of the sample, which lies between a type II and type IV isotherm shape, suggesting the presence of both macro- and mesoporosity. The large hysteresis loop at a relative pressure between 0.4 and 1.0 is the characteristic of a wide distribution of slit-shaped mesopores [9], which matches very well the calculated pore size distribution by the BJH method in the insert of Fig. 5. The average pore diameter and BET surface area of the amorphous carbon nanoparticles is 9.8 nm and 75.2 $m^2\,g^{-1}$, respectively. The formation of mesopores should be mainly attributed to the spaces between the agglomerated nanoparticles, as well as the pores in the nanoparticles created by the generated gases druing the synthesis.

In our previous paper, we synthesized amorphous carbon nanotubes at 200 °C in air by the reaction of ferrocene and ammonium chloride [10]. The chemical reaction equations are also proposed as follows:

$$4(C_5H_5)_2Fe + O_2 + 4NH_4Cl \rightarrow 4(C_5H_5)_2FeCl + 4NH_3 + 2H_2O \quad (1)$$