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Simple synthesis of highly uniform bilayer-carbon nanocages

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ABSTRACT

A simple, highly scalable method of obtaining densely-packed, three-dimensional structures of interconnected, bilayer, hollow carbon nanocages, is reported. High-quality nanocages with well controlled wall thickness are synthesized via catalytic templating on densely-packed, mono-sized nickel nanoparticles, nucleating *in situ* during short, mid-temperature annealing of an inexpensive precursor obtained from nickel acetate and citric acid. Following nickel dissolution, large monolithic grains of densely packed networks of carbon nanocages are obtained and extensively characterized. *In situ* TEM experiments are conducted to elucidate the mechanism of nanostructure formation, and a geometrical model is proposed to explain the high specific surface area and its relation to the nanocages' diameter and wall thickness. These nanocages, with their bilayer structure, unimodal pore size distribution and pore size of ~2.5 nm, approach the theoretical capacity of undoped bilayer graphene when tested in an electrochemical double-layer capacitor system. Our synthesis approach provides a facile method for tuning nanocages' morphology and efficiently doping them, creating an effective enhancement of capacity and properties suitable for a broad range of new energy and environmental applications.

1. Introduction

Carbon, with its unrivaled ability to form different hybridization states, can exist in various allotropes, many of which show unique, often drastically different, sets of properties. Diamond and graphite are the best examples: diamond consists of tetrahedrally-coordinated sp^3 atoms, each covalently-bonded with its four nearest neighbors, and graphite of a highly anisotropic layer structure of honeycombed atomic planes of strongly-bonded sp^2 atoms, with weak π-type interlayer bonding. Among carbon allotropes, there are also: graphene - a single layer of graphite, and fullerenes - carbons at the nanoscale (whose family includes hollow spheres, ellipsoids, or single- and multi-wall nanotubes) [1]. Carbon nanocages (CNCs) are a particular type of carbon nanoshell, often interconnected and forming three-dimensional (3D) mesoporous structures with significant pore volume and high specific surface area. Recently, they have attracted notable attention due to their unique properties and prospects for applications in gas separation and storage [2,3], catalysts [4] and catalysts supports [5], as well as electrode materials for energy storage devices [6–8]. CNCs are particularly promising electrode materials for supercapacitors [6,7] - electrochemical storage appliances which exhibit high power capabilities and play a key role in several technologies [9,10], including electric transportation, energy management systems [11], and intelligent wireless sensor systems [10]. CNCs show comparable performance to other carbons used for supercapacitors [10], such as carbon nanotubes [12], activated carbon (AC) [13,14], mesoporous carbon [15,16], and graphene [17–19]. Because of their high specific surface area, CNCs are suitable for electrochemical double layer capacitors (EDLCs), which use an energy storage mechanism based on the physical adsorption of charges at the electrode-electrolyte interface. Doping and adding a pseudocapacity storage mechanism can further enhance the overall capacity.

Several methods have been proposed to produce CNCs; Ma et al. [20] has used laser-induction complex heating evaporation to

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create vapors of iron species to react them with methane and form iron nanoparticles coated with graphitic shells, Li et al. [21] have produced CNCs by the deposition of p-xylene over MgO-supported Co/Mo catalyst in supercritical CO_2, whereas Tsai et al. [22] have used the chelation of the Cu^{2+}-β-cyclodextrin complexes by carbonization at 573 K. Some studies [7,8,23] have also reported the use of a closed-system approach, with a precursor solution sealed inside a high-pressure autoclave and annealed at high temperature for several hours. Also recently, Wang et al. [5] have used spray pyrolysis of iron carbonyl and carbon precursors. However, the obtained CNCs showed broad size distribution and inhomogeneity. Most of the previous methods pose other challenges, such as long synthesis times, the use of expensive chemicals, scalability issues, or poor size and uniformity control, especially for small CNCs. Here, we report an alternative method that addresses most of these matters. In this approach, short duration synthesis, carried out at moderate temperatures, converts an inexpensive precursor into highly homogenous, densely-packed, interconnected bilayer CNCs. The approach is easily scalable and produces smaller CNCs than any other previously reported [5–8,10,20–29], as compared in Fig. 1. The highly-uniform, monomodal, 3D mesoporous structure of our CNCs makes this material attractive for applications as electrodes, adsorbents or membranes. Herein, we focus first on our CNC synthesis method. Systematic synthesis studies, using both *in situ* and *ex situ* experiments, are conducted, and the formation mechanism is discussed in detail. Samples are synthesized under various conditions and thoroughly studied regarding their morphology, structure, and composition. A proposed geometrical model gives the correlation with their morphological parameters. Finally, the potential of these CNCs for energy applications is demonstrated by preparing EDLCs with them, and measuring their electrochemical performance (which is comparable to undoped bilayer graphene).

2. Experimental section

2.1. Preparation of carbon nanocages

CNCs are synthesized by a novel *in situ* nickel template method. Initially, nickel acetate ($Ni(CH_3CO_2)_2 \cdot 4H_2O$) and citric acid ($C_6H_8O_7$) (Sigma-Aldrich) are dissolved in equal proportions (by wt %) in water. The solution is then dried in an oven at 80 °C, which leaves the precursor powder used for the synthesis of CNCs. The precursor powder, placed in a quartz crucible, is inserted into a horizontal tubular furnace and annealed in a continuous N_2 flow at a rate of 80 cm^3 min^{-1}. Five different materials are synthesized by heating the precursor at 50 °C min^{-1} from room temperature to 500 °C, 550 °C, 600 °C, 700 °C and 850 °C, respectively; annealing takes place for 10 min followed by a cooling period inside the furnace to room temperature, to avoid oxidation. The synthesized powders consist of dense structures of CNCs encapsulating nickel nanoparticles, which are treated with a dilute nitric acid solution to remove nickel, then washed with ethanol and distilled water.

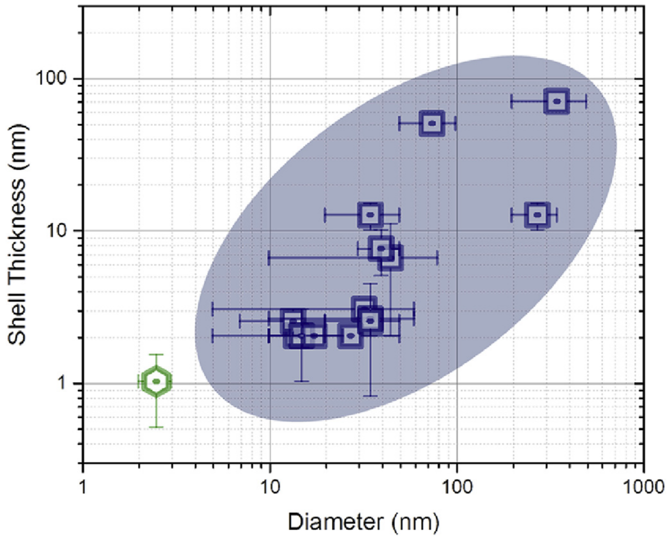

Fig. 1. A comparison of morphological parameters (diameter and shell thickness) of our CNCs (green hexagon) and CNCs reported in literature, obtained using other methods (blue squares) [After Refs [5, 7–9, 11, 21–30]]. (A colour version of this figure can be viewed online.)

2.2. Structural characterization and analysis

The microstructure and morphologies of the CNC samples are investigated using scanning electron microscopy (SEM) in a Carl Zeiss FE-SEM Supra 35VP and transmission electron microscopy (TEM) in a FEI Tecnai F20 operated at 200 kV. Several TEM-based techniques, including diffraction contrast imaging, high-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM) and selected area electron diffraction (SAED) are employed to analyze these samples. Nucleation and structural evolution of nickel nanoparticles, as well as the formation of CNCs, are studied *in situ* in TEM using a single-tilt Gatan heating stage. TEM specimens are prepared by dispersing the precursor powder onto gold grids-supported holey carbon films. During *in situ* heating experiments, specimens are heated at a rate of 50 °C min^{-1} to target temperatures (400 °C, 500 °C, 600 °C, 850 °C) and held for 10 min. In addition to SAED measurements, the phase composition and crystal structure are also analyzed using X-ray diffraction (Bruker D8 Discover) with nickel-filtered Cu-Kα radiation ($\lambda = 1.5418$ Å). The Brunauer-Emmett-Teller (BET) specific surface area is determined from nitrogen adsorption-desorption isotherms using a Micromeritics TriStar 3000 system. Two standard materials, alumina (~215 m^2/g) and activated carbon (AC) (~1200 m^2/g), were used to test the system and specific surface area values comparable to nominal ones were obtained.

2.3. Electrochemical characterization

Electrochemical measurements are carried out for use in a supercapacitor. Both electrodes are made using 85 wt % of active material (carbon nanocages synthesized at 600 °C, after the removal of nickel nanoparticles), 10% of carbon black (CB), and 5% of polytetrafluoroethylene (PTFE) binder distributed in ethanol. This paste, well-mixed, is coated onto nickel foam current collectors (a surface area of ~0.79 cm^2) and dried at 120 °C for 12 h under vacuum. Electrochemical performance is measured in a symmetric Swagelok® cell configuration system using a cellulose separator and 6 M KOH aqueous solution as the electrolyte. The charge/discharge measurements are carried out over a potential range between 0 and 0.9 V in a Pine Research Instrumentation WaveDriver 20 Bipotentiostat/Galvanostat System.

3. Results and discussion

3.1. CNCs formation mechanism

3.1.1. In situ studies

As shown schematically in Fig. 2a, the synthesis of CNCs consists of the following steps: (1) *in situ* formation of nickel nanoparticles, (2) catalytic growth of graphitic shells, and (3) removal of nickel nanoparticles through dissolution in HNO_3. *In situ* TEM heating