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Graphene-like carbon with three-dimensional periodicity prepared from organic-inorganic templates for energy storage application

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ABSTRACT

Free-standing, intergrown and covalently-bonded structures of three-dimensional (3D) graphene may have great advantages in electric and thermal transport properties for energy applications, but the desired symmetry and periodicity are rather hard to design and produce. Here we use an organic-inorganic template to grow an inverse.

opal graphene structure by chemical vapor deposition. The symmetry-controlling temperate is a porous polymethylmethacrylate (PMMA) opal, infiltrated with inorganic cation precursors that form an interfacial phase between spheres. A graphene-like inverse opal, comprising nanometer-thick porous carbon of few-layer graphene sheets, forms on the surfaces of the porous inorganic oxide (Al_2O_3, MgO, SiO_2) interfacial phase by templated CVD, and it remains free-standing after template removal. The three-dimensional ordered microporous and mesoporous graphene inverse opals are highly conductive with a low sheet electrical resistance of 0.35 Ω sq^{-1} and a large specific surface area of 972 m^2 g^{-1}. After N-doping, this inverse opal graphene exhibits a specific capacitance of 252 F g^{-1} that is stable over 5000 cycles, offering great potential for electrochemical energy storage applications.

1. Introduction

Artificial crystals such as photonic crystals with a unit cell that provides photonic band gaps may realize interesting physical and chemical properties. While most artificial crystals are made of oxides and polymers, amorphous carbon and graphite have also been used to obtain carbon-based photonic crystals. Artificial graphene crystals, however, has not been attempted, although several types of graphene foam with irregular packing and periodicity have already been reported. In addition to photonic properties, free-standing, covalently bonded graphene artificial crystals are expected to have outstanding electric and thermal conductivity for energy applications. If mesoporous porosity is further engineered into the building unit of graphene crystals, molecular selectivity in hosting and/or transporting may also be realized. In this work, we report an artificial graphene-like crystal that has remarkable electrochemical properties suitable for electrochemical energy storage [1–7].

Most porous graphene-based materials with a high specific surface area, *e.g.*, three-dimensional (3D) graphene with a micron-sized microstructure length scale fabricated by vacuum filtration of chemically modified graphene [8,9], suffer from poor electrical conductivity. In contrast, graphene obtained by chemical vapor deposition (CVD) has very high electrical conductivity, but its form is mostly limited to two-dimensional films. The first CVD 3D graphene grown on a nickel foam template has a rather coarse microstructure with a characteristic length scale of the order of several hundred micrometers [10–12]. However, recent work using mesoporous silica as the template has achieved nanometer sized porosity with a large percentage of pore volume and a high specific

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surface areas [13,14]. A natural extension of these templated CVD approaches is to construct an ordered, inverse-opal-like graphene structure with desired symmetry and periodicity, albeit with a repeat distance at a mesoscopic length scale. Such porous graphene structures may be ideal for electrochemical energy storage.

2. Experimental

The goal of this research is to demonstrate such graphene-like carbon "photonic crystals" and to investigate their structure, electrical conductivity and electrochemical properties. For template, we used the following hybrid: (a) Monodispersive polymethylmethacrylate (PMMA) microspheres packed into a cubic opal crystal, forming an organic template, and (b) cation (Al^{3+}, Mg^{2+}, Si^{4+}) containing slurry infiltrated into the intersticies of the PMMA crystal, forming an inorganic template. In addition, the CVD graphene grown onto this template will be doped by nitrogen to obtain a three-dimensional ordered macroporous (3DOM) structure. The final material having a large specific surface area will be tested for potential use as a supercapacitor electrode with superior reversible specific capacitance and ability to sustain cycling.

To fabricate supercapacitor electrode, the slurry, containing 1.0 mg electrode material and 0.5 mg polyvinylidenefluoride was homogeneously suspended in N-methyl-2-pyrrolidone and coated on a graphene foam substrate with an exposed surface area of 1 cm × 1 cm and dried at 120 °C under vacuum.

The sample morphology was observed by a Hitachi S-4800 field emission scanning electron (FESEM) microscope. Transmission electron microscope (TEM) images were investigated by JEOL 2100F. Raman spectra were collected on a thermal dispersive spectrometer using a laser with an excitation wavelength of 532 nm at a laser of power of 10 mW. X-ray photoelectron spectroscopy (XPS) analysis (Thermo VG Scientific) was undertaken under high vacuum on graphene using Al-Kalpha 1486.6 eV radiation at 400 W (15 kV). Nitrogen adsorption measurements were performed with ASAP 2020 M (Micromeritics) to obtain the specific surface area and pore size distribution. Electrochemical measurements were all carried out on a CHI 760E electrochemical workstation (Shanghai, Chenhua).

3. Results and discussion

Fig. 1 shows the schematic preparation process of our samples. PMMA microspheres (220 nm in diameter) were synthesized using an emulsifier-free emulsion polymerization approach [15]. The PMMA-containing liquid was centrifuged at 5000 rpm for 1 h. After decanting the supernatant and drying at 60 °C, a highly ordered PMMA opal was obtained. It was next soaked in a solution of aluminium nitrate (made from $Al(NO_3)_3 \cdot 9H_2O$ and alcohol), then drained and dried in a desiccator for 24 h. Calcination was performed in an Ar flow at 300 °C for 3 h, followed by heating to 1100 °C over 2 h under H_2 (50 sccm) and Ar (300 sccm), leaving an inorganic template. To grow CVD graphene, the sample was next placed in a gas flow of CH_4 at various flow rates and temperature for 60 min, then cooled to 400 °C at 10 °C min^{-1} before natural cooling to the room temperature. The inorganic template was removed by etching in a mixed acid solution to obtain the graphene-like carbon inverse opal. To improve the electrochemical performance, nitrogen doping was introduced by using a NH_3 flow during the CVD growth process. Other inorganics such as magnesium nitrate was also similarly used to form an inorganic template on which graphene-like carbon was grown.

Since PMMA is dissociated at ca. 290 °C, PMMA microspheres were at least partly removed following 300 °C calcination. After thermal treatment at 600 °C, an inorganic templates of Al_2O_3 appeared. Fig. 2 shows SEM and TEM images of this inorganic template, which is an inverse opal itself with a highly ordered micro- and mesoporous framework. The micropore size is about 180 nm, controlled by the size of PMMA, meanwhile, in the walls of the inorganic template, there are mesopores of the size of about 5 nm according to Fig. 2d. The inorganic template was polycrystalline as can be seen from the electron diffraction rings.

Inverse opal graphene adopted the structure of the inorganic template as shown in Fig. 3. Its constituent hollow spheres has a diameter of about 170 nm, and they are periodically arranged with excellent structural integrity (Fig. 3a). Further characterization by FESEM and TEM shown in Fig. 3b and c found the wall thickness of about 30 nm. The graphene/carbon layer (Fig. 3c and d) shows a few-layer structure of about 3–6 graphene sheets, in certain regions deformed and folded.

Raman spectra (Fig. 4a) reveal the characteristic 2D band of graphene in samples. In inverse opal graphene (3D G), from 2D band's peak position (2683 cm^{-1}) and full-width-at half-height-maximum (57 cm^{-1}), along with the intensity ratio of this band to the G band (~0.5), we deduce the graphene thickness is below five, which is consistent with the HRTEM observation. Interestingly, the intensity ratio of 2D band to G band (I_{2D}/I_G) decreases with the increase of CH_4 flow rate, indicating that the layer number of the corresponding graphene increases. The D band at ~1340 cm^{-1} is mainly derived from defects or edges of graphene, similar to the previously reported results [16].

Nitrogen adsorption/desorption measurements found a broad pore size distribution (Fig. 4b) centered around 2.0–8.0 nm for inverse opal graphene. Nitrogen adsorption–desorption isothermals of Inverse opal graphene and N-doped sample are shown in Fig. S1, which exhibit a typical Langmuir IV hysteresis, indicating the presence of well-defined mesopores in both samples. Among the two, N-doped sample exhibits a larger surface area (972 $m^2\ g^{-1}$) with a larger total pore volume of 1.06 $cm^3\ g^{-1}$ and average pore width (4.27 nm) due to the predominance of smaller pores.

XPS spectra in Fig. 4c have three characteristic peaks in the C 1*s* spectrum centered at 284.5, 285.4 and 286.5 eV, corresponds to sp^2 C without N, sp^2 C and sp^3 C bonded to N [17,18]. The N 1*s* spectrum of N-doped sample, may be fitted by two nitrogen species, pyridinic nitrogen (398.3 eV) and pyrrolic nitrogen (400.2 eV) [19]. The atomic percentage of N in N-doped sample, estimated by XPS, is about 5.6%.

In order to evaluate the electrochemical properties, we assembled three-electrode electrochemical cells (EC) in an aqueous electrolyte of 1.0 M H_2SO_4. The results in cyclic voltammetry (CV) experiments are shown in Fig. 5a. In comparison with commercial activated carbon (YP-50 from Kuraray), 3D G has an enhanced electrochemical performance with a nearly rectangular CV loop at a scan rate of 10 mV s^{-1}, which is indicative of nearly linear capacitive behavior. The CV profile still retains a rectangular shape at faster scan rates of 100 mV s^{-1}. In comparison, N-doped sample at 10 mV s^{-1} exhibits two additional Faradaic peaks which are nearly symmetric with a small peak separation (~59 mV), indicating the redox reaction has good reversibility and a fast charge transfer process [16]. These Faradaic peaks are maintained at 50 mV s^{-1} (Fig. S2), again indicative of fast charge transport in support of the pseudocapacitance. These results in H_2SO_4 electrolyte give, at a sweep rate of 10 mV s^{-1} (Fig. 5a), a specific capacitance of 252 F g^{-1} for the 3D NG electrode, which is higher than that of 3D G (145 F g^{-1}), and much higher than that of YP-50 (135 F g^{-1}). Furthermore even at the current density as high as 50 A g^{-1}, the nitrogen 3D NG electrode also shows good performance (Fig. S3). In addition, both 3D G and 3D NG electrodes display good cycling and stability behavior by maintaining >98% of the initial capacitance after 5000 cycles.