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Facile wick-and-oil flame synthesis of high-quality hydrophilic onion-like carbon nanoparticles

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HIGHLIGHTS

- Facile one-step flame synthesis of highly hydrophilic onion-like carbon in bulk quantity.
- Synthesis process does not require any catalyst or sophisticated instrumentation.
- The as-prepared product is not contaminated by any other allotropes of carbon.
- Fabricated binder-free flexible OLC electrodes show high supercapacitive performance.

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ABSTRACT

Because of their unique 0-D structure, small (<10 nm) diameter, high electrical conductivity and relatively easy dispersion, compared to 1-D nanotubes and 2-D graphene, onion-like carbon (OLC) has been shown to be ideal as an active material for supercapacitor electrodes. However, its implementation is fraught with lack of convenient methods for their high yield preparation and purification. Here we report a facile scalable and one-step "wick-and-oil" flame synthesis of OLC nanopowder from 'clarified butter' without contaminated by any other forms of carbon; thus eliminating the post processing purification procedure. Brunauer–Emmett–Teller (BET) specific surface area of as-prepared OLC was 218 m^2/g, which is higher as compared to other reported flame synthesis methods. The as-obtained OLC powder is highly dispersible and the suspension is stable for months indicating the presence of surface functional groups which is confirmed by Fourier transform infrared spectroscopy (FTIR). It is demonstrated that by suitable choice of a precursor material, very pure and hydrophilic OLCs can be prepared in bulk quantities by flame synthesis method. An effective and simple strategy was developed to prepare flexible, binder-free OLC electrodes on cotton fabrics and demonstrated their application in a flexible supercapacitor device. The capacitance of OLC is 102 F/g with a measured power density of 1224 W/kg and an energy density of 3.5 W h/kg in 1 M Na_2SO_4 as the electrolyte.

1. Introduction

Beginning with nanofibres, moving to carbon nanotubes, and most recently to graphene, carbon nanomaterials are widely studied and used in a range of applications including electronics, tribology and energy storage. Onion-like carbon (OLC) is a new addition to the nanostructured carbon materials. They are spherical and typically 4–25 nm particles, consisting of concentric shells of graphitic carbon [1–4]. Because of the unique shell-shaped physical form, OLC demonstrates a high specific surface area, high electrical conductivity and excellent tribological behavior. Therefore, OLC nanoparticles are being widely researched for applications in energy devices [5–7], catalysis [8], non-linear optical limiting [9], field emission, in solar cells [10] and in fuel cell electrodes [11] and solid lubricants [12]. To realize all these interesting applications, OLC must be prepared on an industrial scale. Since its first discovery by irradiating carbon soot with high-energy electron irradiation [1], many other methods like carbon arc discharge [13,14], carbon arc plasma [15], catalytic chemical vapor deposition [16], thermal annealing of nano-diamond [17,18] and catalytic cracking of methane [19] were developed. The drawback with high-energy electron irradiation is requirement of high energy input and it produced only minuscule amounts of carbon nano onions. Although thermal annealing of nanodiamond is scalable separation

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of OLCs from initial diamond source seems to be problematic. The size of carbon onions were limited by the size of the parent nano-diamond, and were typically of 3–10 layers with nano-diamond cores. Only after continued annealing did hollowed or caged cores form. OLCs from carbon arc plasma and catalytic chemical vapor deposition are always contaminated by undesired byproducts, e.g. catalyst particles encapsulated in carbon cages. Carbon arc discharges submerged in deionized water produced a mixture of OLCs and nanotubes. However, in all these methods purity is an issue, where the as-prepared product is usually contaminated with other forms of carbon formed as a byproduct or by the catalyst used. Further, they require sophisticated instrumentation and high vacuum. Therefore, a tedious post-processing purification procedure is sometimes required, which uses harsh chemicals. Such chemical treatment introduces more defects in the OLC and can decrease the actual yield [20]. Therefore, large-scale applications require a simple, continuous and energy-efficient method to synthesize carbon nano-onions.

A flame can naturally and easily produce an appropriate high-temperature environment with high radical concentrations required for the growth of OLCs. Therefore, flame synthesis is a continuous-flow and scalable method with a higher potential for considerably lower cost production of high-purity OLCs than the other methods now available. It does not require any sophisticated instrumentation such as vacuum chambers and has the potential to produce OLC in gram scale. Quite a few studies with emphasis on flame synthesis of OLCs using counterflow diffusion flames [21], flames modulated by acoustic excitation [22], flames irradiated with laser beam [10] and from cheap sources like camphor and polystyrene foam, plastic waste etc [23,24] have been reported. The disadvantages include a mixture of products, sophisticated set-up for laser irradiation/acoustic modulation, purification of raw soot to remove undesired byproducts, etc. The type of precursor used has a strong impact on the structure and properties of OLCs produced. High specific surface area and good surface wettability of OLC are very important, especially for electrochemical energy storage applications, as it promotes better adsorption of ions, transport of electrolyte and easy electron exchange at the electrode-electrolyte interface.

Herein, we report a new synthesis pathway for producing OLCs in gram scale by a one-step "wick-and-oil" flame synthesis method. The OLCs were prepared by burning clarified butter (also known as *ghee* in the Indian sub-continent region) under ambient condition [25]. Our OLCs are highly crystalline and not mixed with other allotropes of carbon or unburned precursor materials and hence do not need any further purification post synthesis. Furthermore, our method does not use any catalysts. The as-prepared OLCs are highly dispersible in polar solvents (i.e. hydrophilic). The electrochemical performance of the as-synthesized OLCs in aqueous electrolyte has been studied by cyclic voltammetry and galvanostatic charge/discharge analysis. The high surface area coupled with high surface wettability and high dispersibility results in a flexible, binder-free supercapacitor with a high specific capacitance of 102 F/g, power capability of 1224 W/kg and an energy density of 3.5 W h/kg.

2. Experimental

2.1. Flame synthesis of OLCs

OLC nanoparticles were prepared by a simple flame synthesis method by using clarified butter [25] (also known as *ghee* in Indian sub-continent region) as a precursor. In a typical setup (Fig. 1), a spirit lamp was filled with clarified butter. A pure cotton wick was used, whose one end was immersed in the clarified butter and the other end was exposed to the ambient condition through a nozzle

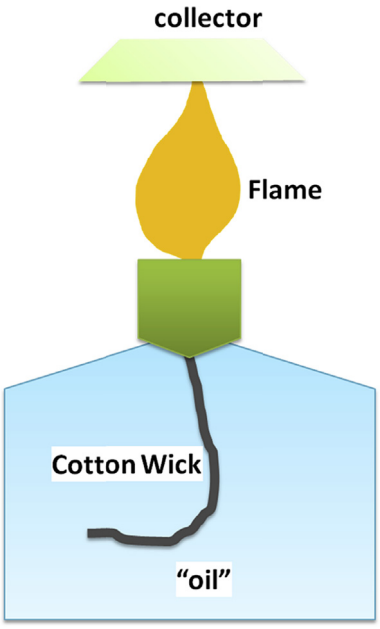

Fig. 1. "Wick-and-Oil" method for flame synthesis of OLC. The "oil" was clarified butter and the sample was collected on a thin bronze plate.

of 4–5 mm diameter. The exposed end of the wick was ignited. Clarified butter rises to the exposed end of the wick by capillary action, where it burns under ambient condition. To collect the soot, a clean, polished bronze plate was placed at the upper part of the flame. The as-prepared sample was used as it is, without any purification. The yield by this method depends on the duration of the collection and the amount of the "oil". The method is capable of producing OLC at a rate of the order of grams per hour.

2.2. Materials characterizations

The morphology of the product was examined using a Hitachi Model S-3400N field-emission gun scanning electron microscope (FEG-SEM) and a JEOL JEM-2100 high-resolution transmission electron microscope (HR-TEM) with 0.19 nm point resolution. X-ray powder diffraction (XRD) patterns were obtained in a Philips X-Pert PRO X-ray diffractogram (XRD) with Ni-filtered Cu Kα radiation (V = 40 kV, I = 50 mA). All the phases were identified by the International Center for Diffraction Data (ICDD) database. Raman spectra were collected between 100 and 4000 cm^{-1} in Horiba HR8000 spectrometer equipped with argon laser of wavelength 514.4 nm. Nitrogen adsorption and desorption experiments were carried out at 77 K on ASAP2020 V3.05 H volumetric adsorption analyzer. Prior to the collection of the isotherm, the sample was degassed at 300 °C for 20 h under a vacuum. The specific surface area was calculated by multipoint Brunauer Emmett Teller (BET) method. The pore-size distribution was obtained from the adsorption/desorption data by using the Barret-Joyner-Halenda (BJH) method. Zeta potential of the ethanol suspension of the as-prepared OLC was carried in Beckman Coulter Delsa™ Nano Version 2.21/2.03. X-ray photoelectron spectroscopy (XPS) data were taken on an AXIS Supra instrument from Kratos Analytical in the range of 1–1200 eV to investigate the surface chemical composition of the obtained OLC.

2.3. Electrochemical measurements

All the measurements were performed in a two electrode