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Nitrogen-containing ultramicroporous carbon nanospheres for high performance supercapacitor electrodes

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ABSTRACT

In this paper, we report a facile and novel synthesis of nitrogen-containing ultramicroporous carbon nanospheres (N-UCNs) for high performance supercapacitor electrodes. Phloroglucinol and terephthalaldehyde are polymerized to obtain polymer nanoparticles with a mean diameter of ~15 nm. Hexamethylenetetramine (HMTA) is utilized to substitute ammonia and formaldehyde to polymerize with resorcinol on the surfaces of the polymer colloids for the fabrication of carbon spheres under the Stöber condition. The introduction of phloroglucinol/terephthalaldehyde brings regular ultramicroporous (0.58 nm) to the typical N-UCNs. Besides, the polymerization of resorcinol and HMTA on the surfaces of polymer nanoparticles reduces the diameter of carbon nanospheres from submicrometer sizes to nanoscaled sizes (~36 nm). Furthermore, the NH_4^+ released from the hydrolysis of HMTA also acts a source of nitrogen in the carbon framework (1.21 at.%), which can improve the surface properties and electric conductivity of N-UCNs. The typical N-UCNs ($N\text{-}UCN_{4.50}$) with spherical geometry, high surface area (1439 $m^2 g^{-1}$), regular ultramicropores and nitrogen functional groups shows excellent electrochemical performance such as high specific capacitance (269 $F g^{-1}$ at 1.0 $A g^{-1}$), long-term cycle stability (90.3% retention after 10000 charge/discharge cycles) in 6 M KOH aqueous electrolyte. This finding provides new opportunities for well-designed carbon nanospheres to achieve advanced supercapacitor electrodes.

1. Introduction

In recent years, development of green, efficient and reusable energy storage and conversion systems, such as supercapacitors and lithium-ion batteries, have received considerable attentions [1–7]. Supercapacitors, also called electrochemical capacitors or ultracapacitors, show long cycle life, high power density, excellent pulse charge/discharge capability and product safety [8]. Besides, supercapacitors also exhibit the capability to bridge the power/energy gap between batteries/fuel cells and conventional electrostatic capacitors [9–12]. The US Department of Energy has designated supercapacitors to be as important as batteries for future energy storage systems because it can provide necessary power for acceleration and an additional function to recuperate brake energy [13]. Normally, based on the energy storage mechanism, supercapacitors could be classified into two categories: (1) electric double-layer capacitors (EDLCs) where the capacitance comes from the pure electrostatic charge accumulated at the electrode-electrolyte interface; and (2) Faradaic supercapacitors which store energy by a fast and reversible faradaic reactions (redox reactions) taken place on the electrode surface formed with electroactive materials [14–20].

Electrode is one of the most important factors to influence the performance of supercapacitors [21–24]. Carbon materials are the most widely used electrode active materials for EDLCs because of their excellent advantages, including abundance, non-toxicity, high specific surface area, good electronic conductivity, and high chemical stability [25–32]. Recently, carbon spheres are emerged as a kind of promising carbon materials used in catalysis, photonic crystals, and energy storage due to their merits of regular morphology, tunable porosity and particle size over other carbon powders or flakes [33–40]. Therefore, many efforts were conducted on the fabrication of micro- or nanometer sized carbon spheres with regular geometry and well-designed pore structure to achieve

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advanced electrodes for EDLCs [41–45]. The Stöber method is a well-known strategy to synthesize size controllable and uniform silica spheres by hydrolysis and condensation of tetraethyl orthosilicate using ammonia as catalyst in ethanol-water mixture system [46]. Liu et al. first extended the Stöber method to fabricate monodisperse polymer and carbon spheres with highly controllable and uniform sizes at submicrometer scale (200–1000 nm for polymer spheres and 150–900 nm for carbon spheres) [47]. After that, the modified Stöber strategy gives new opportunities for the synthesis of templated porous carbon spheres [48–50]. For example, Jaroniec group have reported that the Stöber-like recipe for the synthesis of carbon spheres can be extended and effectively used for the generation of micropores and mesopores, and additional mesoporosity can be formatted between smaller carbon spheres [51].

Generally, porous carbon spheres prepared by the extended Stöber strategy have micro- or submicrometer sizes. According to the energy storage mechanism of EDLCs, a high surface area is required to achieve a high double-layer capacitance. Therefore, reducing the diameter of carbon spheres to nanometer size to achieve higher surface area is a preferred choice for tailoring high performance EDLC electrodes. For example, Lei et al. reported the preparation of mesoporous carbon nanospheres with a diameter of ~65 nm by a chemical vapor deposition method involving mesoporous silica nanospheres as a template and ferrocene as a carbon precursor [52]. Zhao group demonstrated a very low-concentration (10^{-7} mol L^{-1}) hydrothermal synthesis of ordered mesoporous carbon nanospheres using F127 as the soft template and phenolic resol as the carbon source [34]. This method allows the decrease of the particle size of carbon nanospheres as low as 20 nm through simply varying the reagent concentration. However, it is still a great challenge to synthesize nanosized carbon spheres using a simple method.

Herein, we demonstrate a facile and novel synthesis of nitrogen-containing ultramicroporous carbon nanospheres (denoted as N-UCNs) for high performance supercapacitor electrodes. Phloroglucinol and terephthalaldehyde are polymerized to generate polymer colloidal particles (~15 nm). Hexamethylenetetramine (HMTA) which can release formaldehyde and ammonia by hydrolysis could be utilized to substitute ammonia to synthesize carbon spheres under the Stöber condition [53,54]. The polymerization of resorcinol and HMTA on the surfaces of polymer colloids reduces the diameter of carbon nanospheres from submicrometer sizes to nanoscaled size (~36 nm). Besides, without any template, the introduction of phloroglucinol/terephthalaldehyde brings regular ultramicropores (0.58 nm) for the final typical carbon nanospheres, which are accessible electrochemically for aqueous ions. Furthermore, the NH_4^+ released from the hydrolysis of HMTA also acts a source of nitrogen in the carbon framework (1.21 at. %), which can improve the surface properties and electric conductivity of N-UCNs. The resultant N-UCNs as electrode materials for supercapacitors exhibit excellent electrochemical performances such as high specific capacitance, high rate capability and excellent long-term cycle stability.

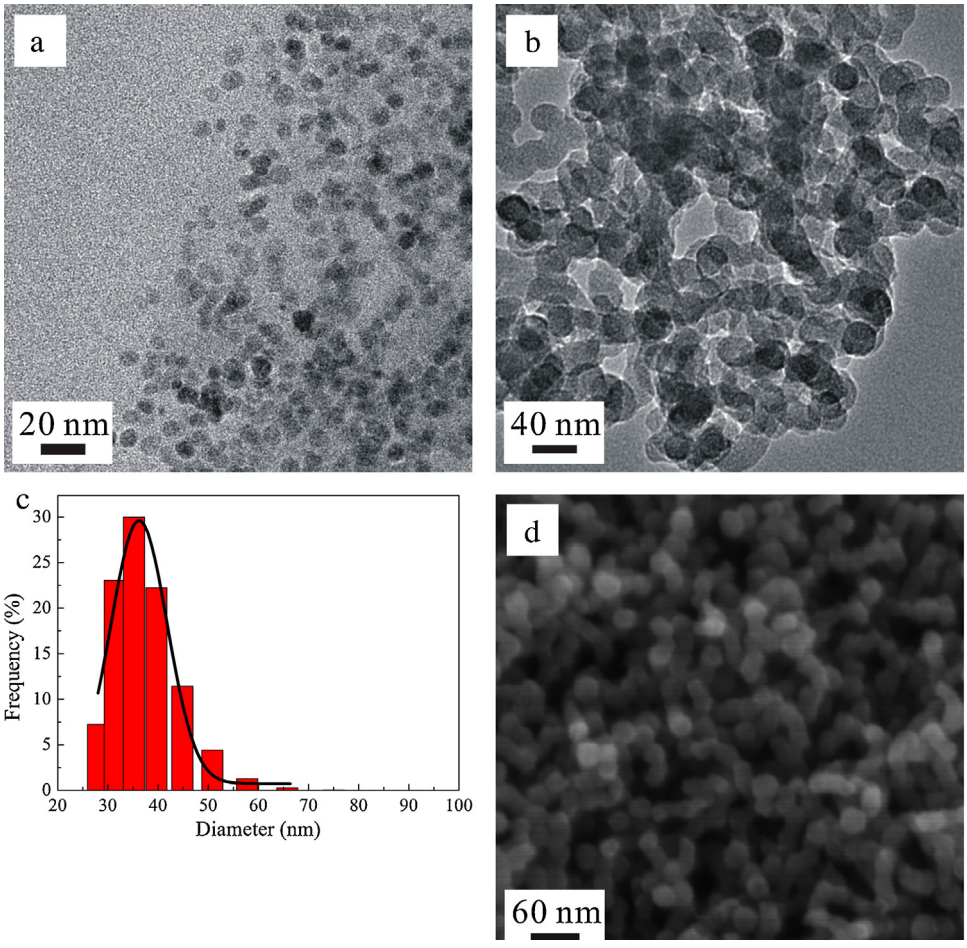

Fig. 1. TEM images of (a) phloroglucinol/terephthalaldehyde polymer colloids and (b) N-UCN$_{4.50}$; (c) DLS data of N-UCN$_{4.50}$; (d) a SEM image of N-UCN$_{4.50}$.