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Three-dimensional nanoporous N-doped graphene/iron oxides as anode materials for high-density energy storage in asymmetric supercapacitors

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ABSTRACT

There is considerable interest in developing novel electrode materials for storing/delivering more energy than carbonaceous materials at fast charge/discharge rates. Here we demonstrate nitrogen-doped graphene/iron oxide hybrid electrode with three-dimensional nanoporous architecture (NP NDG/FeO_x) as one of promising anode materials in asymmetric supercapacitors. Such NP NDG/FeO_x hybrid electrode simultaneously has low internal resistance (5.4 ohms) and high specific capacitance ($\sim$409 mAh g^{-1}) because of its unique architecture, in which the constituent FeO_x serves as electroactive material to improve the charge-storage density while the in-situ grown NDG facilitating the electron transport. This enlists the nickel-iron battery-like asymmetric supercapacitors (ASC), which are assembled with NP NDG/FeO_x and Ni/$Ni(OH)_2$ hybrid electrodes as anode and cathode, to exhibit durable pseudocapacitive energy storage in a wide voltage window of 1.7 V in aqueous electrolyte. The energy storage with maximum energy density of $\sim$142 Wh kg^{-1} is close to the values in lithium-ion batteries and much higher than that of lead-acid battery or Ni-MH battery, at the power delivery of 1.4 kW kg^{-1}. The impressive performance makes it promising candidate as an anode material in next-generation ASC devices.

1. Introduction

Electrochemical supercapacitors (SCs) are highly safe energy storage devices that bridge the gap between high-energy batteries and high-power dielectric capacitors, and show genuine potential in many important applications, including portable electronics, energy backup power devices and hybrid vehicles [1,2]. They can store/deliver charge by non-faradaic and faradaic mechanisms, relying on their electrode materials. The former usually occurs in high-surface-area carbonaceous materials (such as carbon nanotubes, graphene and active carbons) via electrostatic ion adsorption/desorption (electric double-layer capacitance, EDLC) [3], and the latter takes place at or near the surface of pseudocapacitive transition-metal oxides (TMOs) or conductive polymers through reversible redox reaction (pseudocapacitance) [4]. No matter which type of electrode materials is employed in SC devices, these surface processes enlist them to have many desirable electrochemical properties when compared with batteries, that are short charge/discharge time, high levels of power delivery and long-term stability. However, they suffer from a key limitation of low energy densities ($\sim$5–10 Wh kg^{-1}) [3–5], in particular for the devices with a limited area or volume. Therefore, the improvement of energy density is crucial for supercapacitor to meet future practical applications without sacrificing power density.

In general, the energy density (E) of SCs can be increased by exploring novel electrode materials with high specific capacitance (C) and extending their voltage window (V) according to the equation $E = CV^2/2$ [5–7]. Therefore, considerable research efforts have been devoted to asymmetric SCs (ASCs), which are assembled with two dissimilar electrodes as energy and power sources, respectively, in aqueous electrolytes. In view of the advantages of high ionic conductivity, non-flammability and safety for aqueous electrolytes, such devices are expected to be effective to realize more energy storage/delivery at fast charge/discharge rates through widening their voltage window [8,9]. Indeed, this has been demonstrated in traditional ASC devices, wherein numerous pseudocapacitive TMOs (such as RuO_2 [9,10], MnO_2 [11,12], TiO_2 [13], SnO_2 [14,15] and $Ni(OH)_2$ [16,17]) and carbonaceous nanomaterials [18,19] are employed as cathode and anode in environmentally friendly aqueous electrolyte. However, the anode in such ASC devices usually has capacitance much lower than the cathode, or $C_{anode} \ll C_{cathode}$, due to the intrinsically low EDLC of $\sim$5–15 μF cm^{-2} in carbon nanomaterials [18,20], where C_{anode} and $C_{cathode}$ are the capacitances of anode and cathode, respectively. This large mismatch

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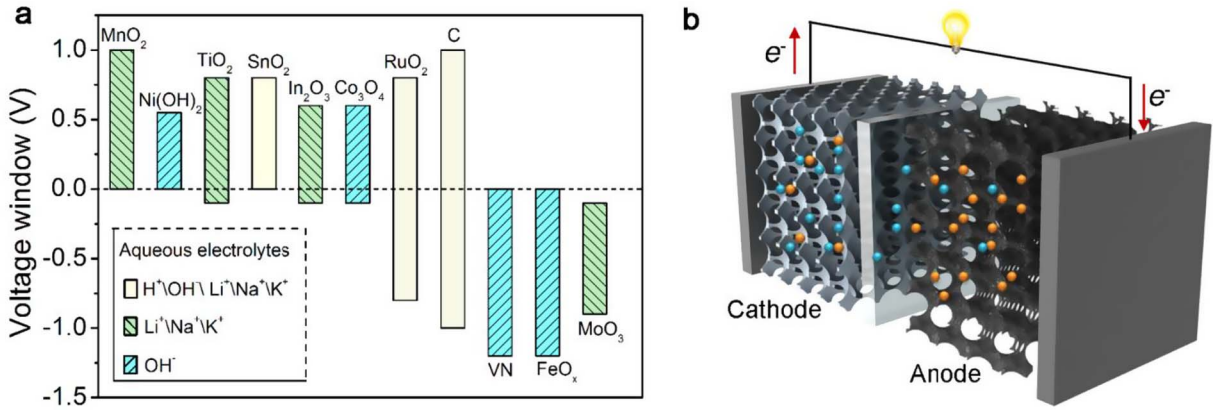

Fig. 1. (a) Cathode and anode materials for asymmetric supercapacitors with wide voltage windows in various aqueous electrolytes. (b) Schematic illustration showing for asymmetric supercapacitors consisting of cathode and anode electrodes with three-dimensional bicontinuous nanoporous architectures.

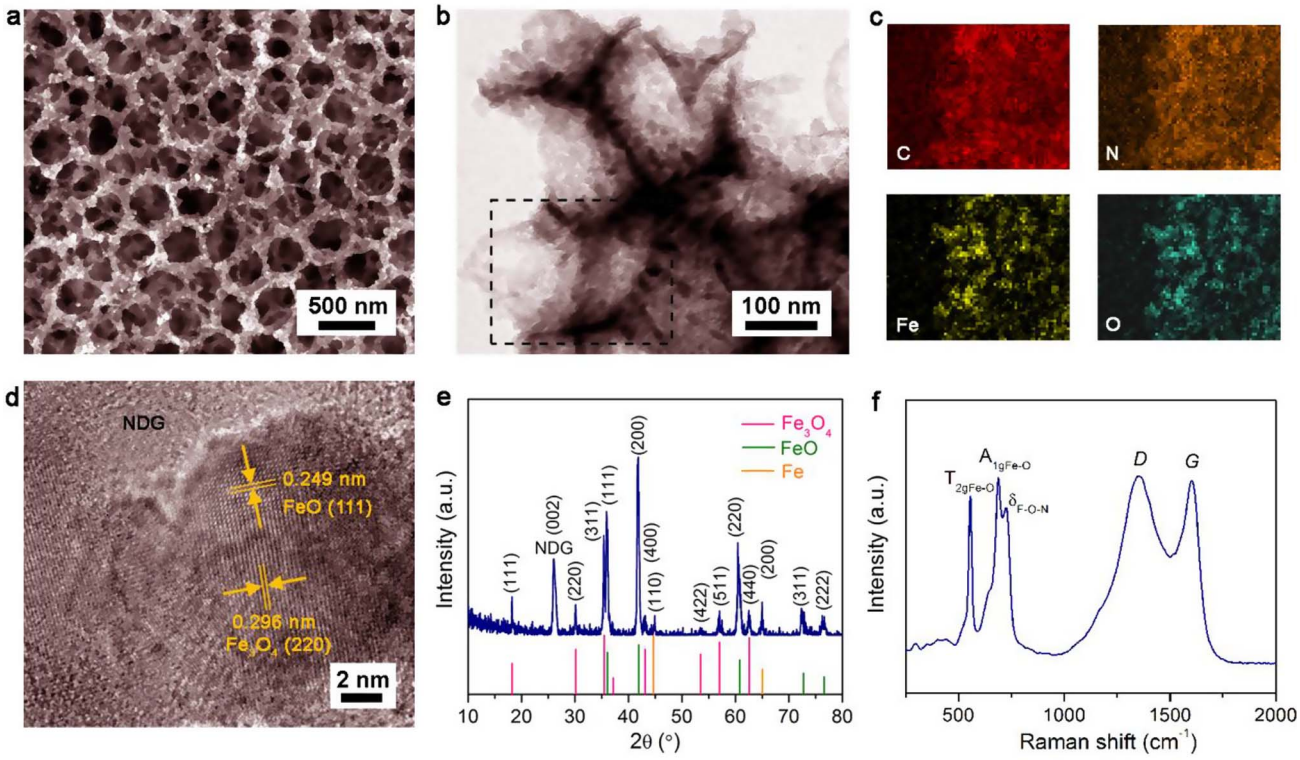

Fig. 2. Structural characterization. (a) SEM and (b) low-magnification TEM images of 3D NP NDG/FeO_x hybrid materials. (c) STEM-EDS mapping images of C, N, Fe and O elements in a marked square region in (b). (d) HRTEM image of iron oxides embedded in NP N-doped graphene. (e) XRD pattern of NP NDG/FeO_x hybrid electrode. The line patterns correspond to reference cards 11–0614, 06–0696, 06–0615 for Fe_3O_4, FeO and Fe, respectively, according to JCPDS. (f) Raman spectrum of NP NDG/FeO_x hybrid electrode.

remarkably depresses the device capacitance (C_{device}) in light of the equation $1/C_{device} = 1/C_{anode} + 1/C_{cathode}$, limiting the further increase of energy storage in ASCs [21–24]. In this regard, it is highly desirable to develop novel anode materials with matchable specific capacitance for the realization of energy storage in ASC devices with SC-like rate performance and battery-like capacity.

Distinguished from traditional carbonaceous nanomaterials, on which only EDLC is available, negative pseudocapacitive materials, such as metal oxides and nitrides with working voltage below 0 V (Fig. 1a), may replace these carbonaceous anodes to match with cathode TMOs in next-generation ASC devices (as schematically illustrated in Fig. 1b) because of their faradaic mechanisms offering higher level energy storage [9–26]. Amongst, iron oxides are of considerable interest because of their natural abundance, low cost and environmental friendliness, as well as low hydrogen evolution potential in aqueous electrolytes. In the perspective that nanostructures provide extremely large specific surface area of electrode/electrolyte interface to facilitate the fully use of high pseudocapcitance, initial strides have been made to reduce their dimensions down to the nanometer scale. Nevertheless, their assembled electrode systems usually encounter exceptionally high internal resistance, which arises from the high contact resistances at the supplementary interfaces of nanostructured blocks of anode materials and their intrinsically poor conductance. As a consequence, they usually exhibit unsatisfactory capacitive performance, for instance, the high-theoretical-capacity iron oxides (FeO_x) only show low capacitance ($< 300\ F\ g^{-1}$) even at slow scan rates, unfulfilling the high-energy and -power energy storage in ASCs [21,22,25,26].

Here we demonstrate a novel and monolithic hybrid electrode, which is composed of iron oxides embedded in 3D bicontinuous nanoporous N-doped graphene (NP NDG/FeO_x), as a promising anode