



Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec1 Synthesis of mesoporous reduced graphene oxide by Zn particles for
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ARTICLE INFO

Article history:

Received 24 November 2015

Received in revised form 5 August 2016

Accepted 3 September 2016

Available online xxx

Keywords:

Supercapacitors

Mesopores

Reduced graphene

Zinc particles

Ionic liquid electrolytes

ABSTRACT

Mesoporous reduced graphene oxide (*m*-rGO) was synthesized by mixing Zn and graphene oxide in acidic conditions followed by ultrasonication and was investigated as a supercapacitor electrode in a 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI) electrolyte. *m*-rGO shows a specific capacitance of 104.3 F g⁻¹ at 1 A g⁻¹ and a decrease in capacitance of 3% after 5000 cycles. The high performance is attributed to the significant mesopores, facilitating mass transport of the electrolyte. Thus, we report the facile synthesis of *m*-rGO with enhanced capacitance and durability in an ionic liquid electrolyte that has great potential for electrochemical energy storage applications.

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7 Introduction

8 Supercapacitors have attracted considerable attention recently
9 due to their high power density and long cycle life. They have
10 higher energy densities than conventional capacitors and higher
11 power densities than batteries and fuel cells, which enables their
12 application as the main or subsidiary power sources in electric
13 vehicles, heavy machines, and even portable devices [1–5].
14 Supercapacitors are categorized into electric double-layer capaci-
15 tors (EDLCs) and pseudocapacitors based on their charge storage
16 mechanism. An EDLC stores electric energy through a charge
17 separation maintained by electrostatic forces in the interfacial
18 double layer of an electrode material [1]. The electrodes of EDLCs
19 are usually made of carbon-based materials such as activated
20 carbons, carbon nanotubes, and graphenes, which are generally
21 selected because of their high surface area and electrical
22 conductivity. Pseudocapacitors store energy using redox reactions
23 at the electrode surfaces of conducting metal oxides (such as RuO₂,
24 IrO₂, Co₃O₄, and V₂O₅) or conductive polymers [4–6]. The
25 performance of a supercapacitor is determined largely by the
26 materials that constitute its electrode. Pseudocapacitors show
27 higher capacitance than EDLCs, but high material cost and low
28 electric conductivity limit their applications. The low energy

density of EDLCs can be overcome by increasing voltage limits,
which are determined by the stability of the electrolytes. Hence,
organic solvents or ionic liquids are widely used as electrolytes for
high energy density supercapacitors. Ionic liquids have wide
electrochemical windows, high thermal and electrochemical
stability, and moderate ionic conductivity [7–10], and are therefore
regarded as ideal electrolytes for supercapacitors. However,
supercapacitors in ionic liquid electrolytes are hindered by the
slow diffusion of large ions into the narrow pores of the carbon-
based materials [11,12]. For this reason, it is necessary to develop
mesoporous (2–50 nm) and macroporous (>50 nm) materials to
realize high performance supercapacitors.

Graphene-based EDLC electrode materials have been widely
studied because of their high surface area and conductivity. These
are the most important properties for achieving high capacity and
high power in supercapacitors. Chemical exfoliation is the most
widely used technique to prepare graphene because of its low cost
[13]. The final product of chemical exfoliation is graphene oxide
(GO), which needs to be reduced before it can be used as a
supercapacitor electrode. Reduction methods that have been
studied include thermal reduction [14,15], microwave and photo
reduction [16–19], chemical reagent reduction [20–22], photo-
catalyst reduction [23–25], electrochemical reduction [26–29], and
solvothermal reduction [30–32]. Chemical reduction using reduc-
ing agents such as hydrazine (N₂H₄) [20,22], sodium borohydride
(NaBH₄) [33–35], and hydroiodic acid (HI) [36,37] can be
accomplished in several hours at relatively low temperatures

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($>100^{\circ}\text{C}$). However, these reducing agents are toxic and dangerous. A facile and green approach to the synthesis of reduced graphene oxide (rGO) was recently developed, which involved mixing GO with particles of metals that have lower electrochemical potentials than GO (such as Zn, Fe, Al, Cu, and Ni) [38–50]. The reduction rate of Zn, in particular, is significantly promoted in acidic, alkaline, or ammonia solutions, or by ultrasonic treatment [39,40,44]. In spite of these advantages, few studies have explored the application of this reduction method in energy-related systems. Liu et al. evaluated rGO reduced by Zn particles for supercapacitor electrodes in aqueous electrolyte, in which rGO exhibited 116 F g^{-1} in KOH electrolyte [40]. However, the surface morphology and porosity, which are important factors in the performance of supercapacitors, of rGO reduced by Zn particles were not analyzed in detail.

In this study, we prepared mesoporous rGO (*m*-rGO) by the Zn particle reduction method which produced significant corrugation of the rGO sheet. *m*-rGO was tested as an electrode in a supercapacitor in a 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI) ionic liquid electrolyte to take advantage of its mesoporosity. Comparative studies of *m*-rGO and flat graphene (*f*-graphene) were carried out and the physico-

chemical properties of *m*-rGO were studied in relation to the supercapacitor performance.

Experimental

Preparation of *m*-rGO

Graphene oxide solution was purchased at Angstrom Materials (N002-ps, 0.5 wt% of GO in water). The GO solution was diluted to 0.1 wt% and acidified with hydrochloric acid (HCl) to a final HCl concentration of 10 mM. Commercial Zn powder (Kanto) was then added to the GO solution in varying amounts. We also tested Al, Ti, and Fe metal particles for comparison test with the same method to Zn particles, but no significant change was observed in short time. The Zn/GO solution was homogenized in an ultrasonic bath for 1 min at room temperature. During ultrasonic treatment, the color of the solution changed from dark brown to black. Residual Zn particles were removed with excess acid in 1 M HCl solution with gentle stirring for 1 day. Finally, the solution was filtered and washed with DI water until the pH of the rinse was neutral. The filtered *m*-rGO sample was dried at 60°C overnight.

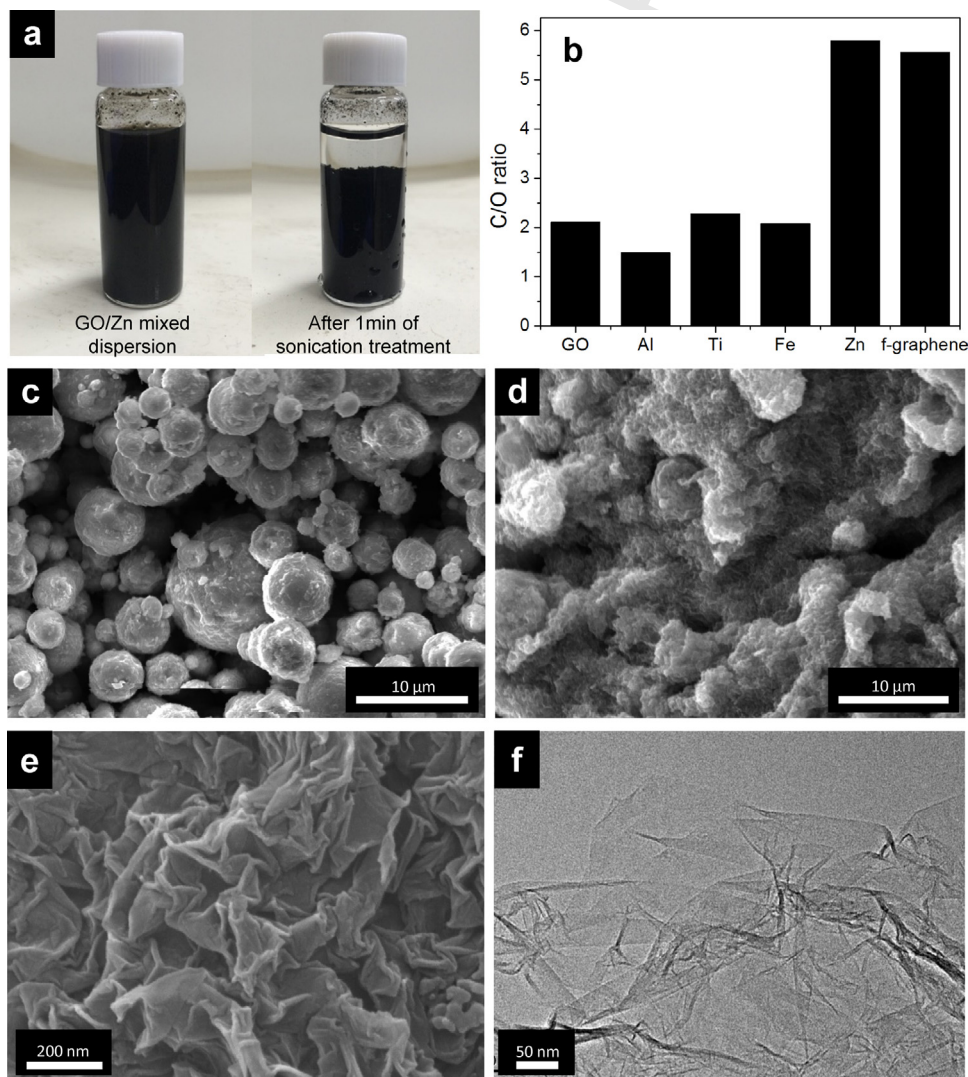


Fig. 1. (a) Digital photograph of GO/Zn dispersion before and after ultrasonic treatment, (b) carbon to oxygen atomic ratio of graphene reacted with Al, Ti, Fe, and Zn metal particles. Reaction time is 1 min in ultrasonic bath and elemental analysis is conducted by XPS survey spectrum. SEM images of (c) commercial Zn particles and (d) Zn/rGO after reduction, (e) high resolution SEM image of *m*-rGO after Zn etching, and (f) TEM image of *m*-rGO. White scale bars in the each figure indicate 10 μm (c), 10 μm (d), 200 nm (e), and 50 nm (f).

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