



# High-performance supercapacitors based on the reduced graphene oxide hydrogels modified by trace amounts of benzenediols



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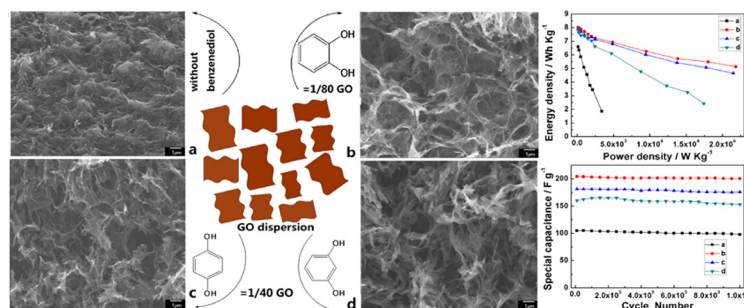
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## HIGHLIGHTS

- Reduced graphene hydrogels were prepared in presence of tiny amount of benzenediols.
- The prepared rGOHGs with various benzenediols have different 3D porous structures.
- Capacitive property of rGOHGs has been obviously improved by modifying benzenediols.
- Cells assembled by them show high capacitance, rate capability and cyclic stability.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Reduced graphene oxide hydrogels (rGOHGs) with three-dimensional (3D) porous structure are considered as promising electrode materials for supercapacitors. Here, the 3D rGOHGs have been prepared in presence of trace amount of benzenediols and their capacitive performances have been significantly improved. The optimized samples prepared by controlling mass ratios of graphene oxide (GO) to benzenediols to be about 80, 40 and 40 for *o*-, *p*-, and *m*-benzenediols have specific capacitance of about 253, 240 and 238 F g<sup>-1</sup> at 1 mV s<sup>-1</sup>, respectively. Furthermore, rGOHGs prepared in presence of different benzenediols exhibit different microstructures, and that modified with *o*-benzenediol possesses the largest specific surface area and total pore volume. Particularly, the rGOHGs modified with *o*-, *p*-, and *m*-benzenediols have fairly good rate-capability, and retain 98.1%, 96.9% and 95.5% of their initial capacitance respectively after 10,000 charging/discharging cycles, revealing their excellent stability. This provides a strategy to improve the capacitive properties of rGOHGs significantly by tiny amount of modifiers.

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## 1. Introduction

Graphene is one of the most promising carbon materials for supercapacitors because of its large specific surface area (2630 m<sup>2</sup> g<sup>-1</sup>), high electrical conductivity and excellent chemical stability [1–5]. However, the realistic specific capacitance of graphene materials are mostly in the range of 100–200 F g<sup>-1</sup> in previ-

ously reported literatures although the theoretical value has been predicted to be as high as 550 F g<sup>-1</sup>. The obviously decreased capacitance is mainly ascribed to the irreversible aggregation of graphene sheets caused by strong  $\pi$ - $\pi$  stacking, which makes effective specific surface area (SSA) decreased and unsatisfactory porous structure [6–9]. In order to resolve the re-stacking of graphene and achieve high electric double-layer capacitance (EDLC), many efforts have been devoted to construct macrostructure materials with 3D network by using graphene oxide (GO) as precursor [10–12].

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Reduced graphene oxide hydrogels (rGOHG) emerge as a new class of 3D network which consist of single or few entangled layers of graphene. This unique configuration partially retains the excellent intrinsic properties of graphene sheets, holds large surface area, high electrical conductivity and excellent mechanical strength. Moreover, the realistic capacitance can be improved by facilitating charge transfer through the abundant porous framework [6,13–15]. Now the solution-gel synthesis process is proved to be an effective route to prepare rGOHG [16,17]. Commonly, the gelation of GO dispersion occurs through strong hydrophobic interaction among the rGO sheets and lead to the phase separation, during which a large amount of the oxygenated functional groups are reduced, and the rGO sheets self-assemble into 3D porous network [18,19]. Recently, hydrothermal method in the presence of mild chemical reducing agents has been developed to produce rGOHG [15,20], in which the GO sheets can be more completely reduced by the reducing agent at an elevated temperature, and the entrapped water within the rGOHG will effectively prevent the re-stacking of rGO sheets [21]. This simple route provides a facile way to prepare rGOHG with high ratio of carbon to oxygen. A variety of reducing agents such as formic acid [22], L-ascorbic acid [16,23], hydrazine hydrate [24], sodium borohydride [25] and thiourea [26] have been used to prepare rGOHG under hydrothermal condition. Unfortunately, these systems have such disadvantages as using large amounts of reducing reagents, time-consuming and expensive. Furthermore, the resulting materials still have unsatisfactory electrochemical performance.

The electrochemical performance of rGOHG strongly depends on the properties of chemical reducing agents. Reducing agents can not only affect the reduction degree of GO but also adjust the morphology and structure of rGOHG. Hence, it is crucial to develop an effective chemical reducing agent to prepare 3D network rGOHG. For example, hydrazine and hydroiodic acid have been used to post-treat rGOHG, and the resulting graphene materials exhibit a specific capacitance ( $C_s$ ) as high as  $220 \text{ F g}^{-1}$  and a good rate capability [27]. Later, oxalic acid and sodium iodide are combined to replace the toxic HI to assemble rGOHG, but a large amount chemical reagent (0.5 g) have to be required to reduce 2–90 mg GO sheets [18]. Sodium hypophosphite ( $\text{NaH}_2\text{PO}_2$ ) has also been used as reducer and regulator to control the microstructure and the capacitive properties of rGOHG. The corresponding hydrogels prepared at low concentration of reducer ( $\text{GO}/\text{NaH}_2\text{PO}_2 = 1:1$ ) deliver a relatively low  $C_s$  of  $176.6 \text{ F g}^{-1}$ , while the samples obtained at high concentration of reducer ( $\text{GO}/\text{NaH}_2\text{PO}_2 = 1:9$ ) exhibit better rate capability [28].

Here, we propose a facile and efficient hydrothermal approach to prepare rGOHG by using GO as precursor and benzenediol isomers (*o*-benzenediol, *p*-benzenediol and *m*-benzenediol) as reducing agent and structural adjusting agent. It is worth noting that very small amount of benzenediols (mass ratios of GO/benzenediol = 40 and 80) can provide the resulting 3D rGOHG with fairly good capacitive performances. Therefore this strategy is convenient, cheap and eco friendly.

## 2. Experimental section

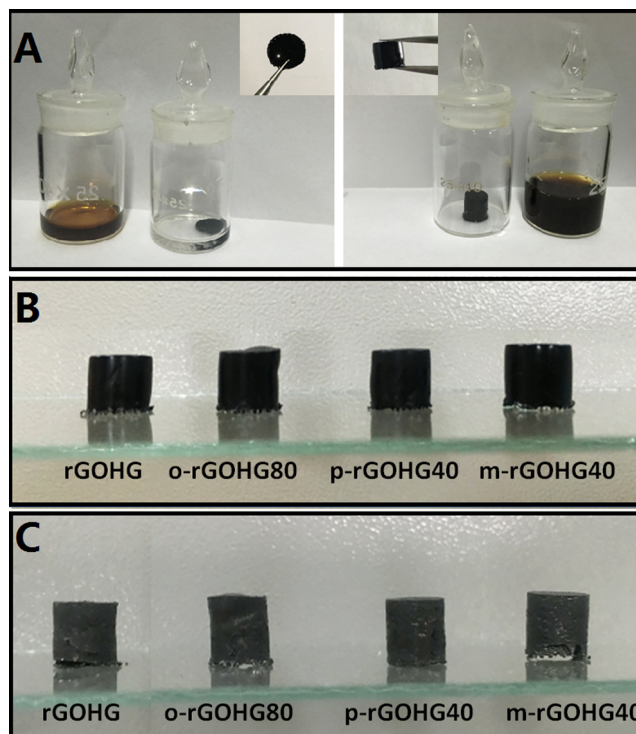
### 2.1. Synthesis of rGOHG

GO was prepared from natural graphite flake by a modified Hummers method according to literature [29]. Subsequently, benzenediol isomers were added into GO aqueous dispersion under stirring to form a homogeneous mixture. The final concentration of GO was  $2.0 \text{ mg mL}^{-1}$ , and with  $R_m$  (the GO/benzenediol isomers in mass ratio) = 120:1, 80:1, 40:1, 20:1 and 10:1. The total mixture was then transferred into a stainless steel autoclave and heated at

$160 \text{ }^\circ\text{C}$  for 12 h (the selection of the optimized hydrothermal temperatures was shown in Fig. S1). Meanwhile, the thickness of the gels can be regulated by adjusting the volume of GO dispersion as shown in Fig. 1A. The obtained rGOHG were then soaked in ethanol and distilled water for several times to remove the unreacted reagents and impurities. The rGOHG prepared in presence of *o*-benzenediol, *p*-benzenediol and *m*-benzenediol with different  $R_m$  were denoted as *o*-rGOHGx, *p*-rGOHGx and *m*-rGOHGx respectively, in which x referred to the mass ratios of GO to benzenediol isomers. In order to make comparisons, rGOHG was also prepared under the same condition without the addition of benzenediols. For structural characterization, a large amount of the rGOHG were prepared (Fig. 1B) by using the same procedure, and then freeze-dried (Fig. 1C) after being washed.

### 2.2. Structural characterization

The surface morphologies of the samples were observed by a JEOL-JSM-6701 scanning electron microscope (SEM) after freeze-drying. X-ray powder diffraction (XRD) patterns of the samples were conducted on a Bruker D8 advance X-ray diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ). X-ray photoelectron spectrometer (XPS) was performed on an ESCAL-ab 220i-XL spectrometer with a monochromatized Al  $K\alpha$  source at 1486.6 eV. Fourier transform infrared (FT-IR) spectra were recorded on an Infrared Spectrometric Analyzer (BRUKER TENSOR 27) with wave number range of  $400\text{--}4000 \text{ cm}^{-1}$ . The Raman spectra of the samples were recorded on a LabRAM HR Evolution (Horiba Jobin Yvon) by using a 532-nm laser as incident light. Nitrogen adsorption-desorption experiments were carried out on a Micromeritics ASAP-2460 surface analyzer system. Before the tests of  $\text{N}_2$  adsorption/desorption, a large amount of freeze-dried rGOHG were dried under vacuum to remove moisture, then transferred into the sample tubes and



**Fig. 1.** Photograph of GO suspension and graphene hydrogels prepared from 1.0 and 5.0 mL GO suspensions with a concentration of  $2 \text{ mg mL}^{-1}$  (A). The photographs for the hydrogels of rGOHG, *o*-rGOHG, *p*-rGOHG and *m*-rGOHG prepared from 8.0 mL GO suspension (B) and the corresponding freeze-dried aerogels (C).

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