Electronic Supplementary Information (ESI)

For

Ultra-high pseudocapacitance of mesoporous ZnCo$_2$O$_4$ nanosheets on reduced graphene oxide utilizing neutral aqueous electrolyte

In Kyu Moon$^a$ and Kyoung-Yong Chun$^b$

$^a$ R&D Center, Byucksan Paint & Coatings Co., Ltd., Incheon 404-201, Rep. of Korea. E-mail: inkmoon@naver.com
$^b$ Development Group for Creative Research Engineers of Convergence Mechanical System, College of Engineering, Korea University, Anam-dong, Seongbuk-gu, Seoul 136-791, Rep. of Korea. E-mail: kychun@gmail.com

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Experimental Section

Fabrication of rGO/NF.

The NF were provided by Alantum Co. The number of pores per inch (PPI) is 110-80, corresponding to an average aperture size of 580-800 μm with the thickness of 2.0 mm. GO was prepared from natural graphite powder (Bay Carbon, SP-1 graphite) using the modified Hummers and Offenman’s method with H$_2$SO$_4$, NaNO$_3$ and KMnO$_4$. The NF were immersed in a 3 M HCl solution for 10 min to get rid of the possible surface oxide layer before they were used, and washed thoroughly with deionized (DI) water with the assistance of ultrasound. And then, a piece of NFs was immersed in GO aqueous dispersion (1 mg·mL$^{-1}$) by stirring for 24 h. After drying in a vacuum oven at 60 °C for 24 h, the obtained GO/NFs were thermally reduced using quartz tube furnace at 400 °C in 5% H$_2$/Ar for 30 min (see Fig. 1(a) rGO/NF).

Self-assembly of ZnCo$_2$O$_4$ nanosheets on the rGO/NF.

0.5 mmol of Zn(NO$_3$)$_2$·6H$_2$O and 1 mmol of Co(NO$_3$)$_2$·6H$_2$O were dissolved into a mixed solution of 40 mL of deionized (DI) water and 20 mL of absolute ethanol at room temperature to form a clear pink solution, followed by the addition of 6 mmol of hexamethylene-tetramine for 30 min at room temperature. A piece of rGO/NFs were fixed in a Teflon sample holder. These were then vertically dipped in the precursor solution and then capped. The growth solution was kept in a preheated oven for 12 h at 90 °C. After the completion of growth ZnCo$_2$O$_4$ on rGO/NF, the sample was a carefully cleaned in the aqueous solution in order to remove the solid ZnCo$_2$O$_4$ powder from surface of the nanostructures by ultrasonication, and then rinsed with DI water repeatedly and dried in the air. Finally, the rGO/NF with Zn-Co
precursor was annealed at 320 °C for 2 h with a heating rate 2 °C·min⁻¹ to obtain crystallized ZnCo₂O₄ mesoporous nanosheets (see Fig. 1a ZnCo₂O₄/rGO/NF (yellow dotted line part)).

*Characterization of ZnCo₂O₄/rGO/NF.*

The micro-structure was observed by using a scanning electron microscope (SEM) (Hitachi S-4300) at an acceleration voltage of 10 keV. The TEM images, selected area electron diffraction (SAED) pattern, and chemical composition were obtained from a TEM (Tecnai, G²F30) installed with an energy dispersive X-ray (EDX) operated. ZnCo₂O₄/rGO/NF cross-sections for TEM analysis were prepared by focused-ion-beam (FIB) milling using a FEI Quanta 200 3D DualBeam FIB/SEM (FEI Corp., OR). Transmission electron microscope (TEM) specimen of ZnCo₂O₄/rGO/NF was fabricated in a focused ion beam (FIB) (Quanta 3D 200).

*Electrochemical performance measurement.*

Electrochemical performance measurements were conducted with a three-electrode system (CHI 627b, CH Instrument) using Ag/AgCl as a reference electrode and platinum mesh (1 x 1 cm²) as a counter electrode. An aqueous solution of 0.1 M Na₂SO₄, purged by argon gas for 1 h to evacuate the dissolved oxygen component as much as possible, was used as an electrolyte solution. Cyclic voltammetry (CV) and galvanostatic curves were evaluated in 0.1 M Na₂SO₄ liquid electrolyte at 25 °C. The potential is scanned between −0.2 and 0.8 V with different scan rates. The working area of the electrode is set at 1 × 1 cm². The mass loading of the ZnCo₂O₄ mesoporous nanosheets on rGO/NF was around 0.38 mg/cm².
Calculation of electrochemical capacitance, energy density and power density.

The specific capacitances are calculated by two different methods. First, specific capacitance is computed by using cyclic voltammetry (CV) method with following formula,

\[
C_{sp} = \frac{Q(ZnCo_2O_4 - RGO - Ni Foam) - Q(Ni foam)}{\Delta V \times \text{mass}(ZnCo_2O_4 - RGO)}
\]

where \( Q \) is the charge and \( \Delta V \) is the width of the voltage window.

Second, the specific gravimetric capacitance is obtained by constant current charging/discharging (CD) method, with the following definition formula,

\[
C_{sp} = \frac{(I\Delta t)(m\Delta V)^{-1}}{1}
\]

where \( I \) is the discharging current, \( m \) is the mass of the active material, \( \Delta t \) is the discharging time, and \( \Delta V \) is the resulting potential window size. Here, ZnCo_2O_4 is taken as the sole active material.
The rGO/NF was drop-coated with a poly(methyl methacrylate) (PMMA) solution (3 wt% in tetrahydrofuran), and then dried at 100 °C for 1 h, resulting in the formation of the a thin PMMA film on the rGO/NF surface to prevent possible structural failure of the resultant r GO/NF when the NF was etched away. Then, nickel was removed by immersing the sample in a HCl (3 M) solution at 70 °C for 5 h to obtain PMMA/rGO foam. Finally, the free-standing rGO foam was obtained by dissolving the PMMA protective layer in hot acetone.

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Table S1. Elemental composition of ZnCo$_2$O$_4$/rGO/NF

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass%</th>
<th>Atom%</th>
</tr>
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<tr>
<td>C-K</td>
<td>21.11</td>
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<td>O-K</td>
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<td>Co-K</td>
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<td>Zn-K</td>
<td>15.69</td>
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</table>

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