

Supplementary information

Highly Interconnected Hollow Graphene Nanospheres as an Advanced High Energy – High power Cathode for Sodium Metal Batteries

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Experimental

Silica spheres were synthesized using a two-step method. In the first step, tetraethyl orthosilicate (TEOS) was hydrolyzed in an ethanol/water solution mixture in the presence of ammonium hydroxide catalyst. In the second step, hydrolyzed TEOS was allowed to condense for 2 h at ambient conditions with continuous stirring. This was followed by repeated washing with DI water and ethanol to remove any impurities and then dried in a vacuum oven at 110 °C for 12 h. To surface modify the prepared silica spheres, silica particles were dispersed in methanol using ultrasonication for 30 min followed by the addition of 3-aminopropyltrimethoxysilane. The functionalization reaction was allowed to proceed for 2 h with continuous stirring at room temperature. The resulting product was washed several times with methanol and then vacuum dried at 110 °C for 12 h.

Aminofunctionalized silica spheres were dispersed in water using ultrasonication for 30 min and then graphene oxide (GO) was added to the solution. The ratio of aminofunctionalized silica to GO was 4:1. Then the solution was ultrasonicated for 2 h followed by stirring overnight to wrap the functionalized silica using electrostatic attraction between the positively charged aminofunctional groups and the negatively charged GO. Then the solution was centrifuged to remove any free GO in the solution followed by drying at 110 °C for 12 h. In the next step, the sample was thermally treated in a tube furnace at 700 °C for 1 h in argon atmosphere to obtain rGO-covered templates. Finally, the template was removed using 10 % hydrofluoric acid and then the product was washed thoroughly with DI water until the pH became neutral.

Characterization

Physical Characterization

The morphologies of all samples were examined using a field-emission scanning electron microscope (FE-SEM, S4700, Hitachi, Japan) and transmission electron microscope (TEM, TECNAI, Philips, Netherlands 200 k eV). The surface composition of GO, rGO and HGS was evaluated by X-ray photoelectron spectroscopy (XPS) analysis utilizing a Multilab instrument (monochromatic Al K α radiation $h\nu = 1486.6$ eV). The Raman spectrum was obtained using a Raman dispersive spectrometer (Lab Ram HR 800, Horiba, Japan). The specific surface area and pore size distribution were measured using a BET analyzer (Micromeritics ASAP 2010) at 77 K.

Electrochemical Characterization

The electrochemical measurements of HGS electrodes were carried out using a 2032 coin cell with pure metallic sodium foil as the counter electrode and reference electrode at 25 °C. The working electrodes were prepared by thoroughly mixing the hollow graphene nanospheres, Ketjenblack, and Teflonized acetylene black in the weight ratio of 7.5:1:1.5. The slurry was pressured over a stainless steel mesh and dried at 160 °C for 4 h in vacuum, and the mass loading of the electrode is about 1.5 – 1.8 mg cm⁻² and the electrode density is ~0.21 g cc⁻¹. The coin cells were assembled inside an argon filled glove box with negligible moisture content and the electrolyte used was 1 M NaClO₄ in propylene carbonate. For sodium metal full-cell, sodium metal deposited carbon coated aluminum foil (CAF) were used as anode. The sodium metal was deposited electrochemically over CAFs in a 2032 coin cell using sodium metal as reference and counter electrode at 0.25 mA cm⁻² for 5 h. The current density and discharge capacity in full-cell studies is based on mass of HGS. Cyclic voltammetry (CV) was analyzed with a Bio-Logic electrochemical work station (SP-150), France and Won-A-Tech Battery cyler (WBCS 3000,

Korea) was used for galvanostatic cycling studies between 1.5 to 4.2 V at different current densities under ambient conditions. The specific discharge capacity (mAh g^{-1}) is calculated as $q = I * t / m$, where I is the applied current (mA), t is the time (h), and m is the mass in electrode (g). With voltage V , the specific energy density (E) is calculated as, $E = \int Vdq \text{ Wh kg}^{-1}$, and the specific power density (P) is calculated as $P = E / t \text{ kW kg}^{-1}$, where t is the discharge time (h).

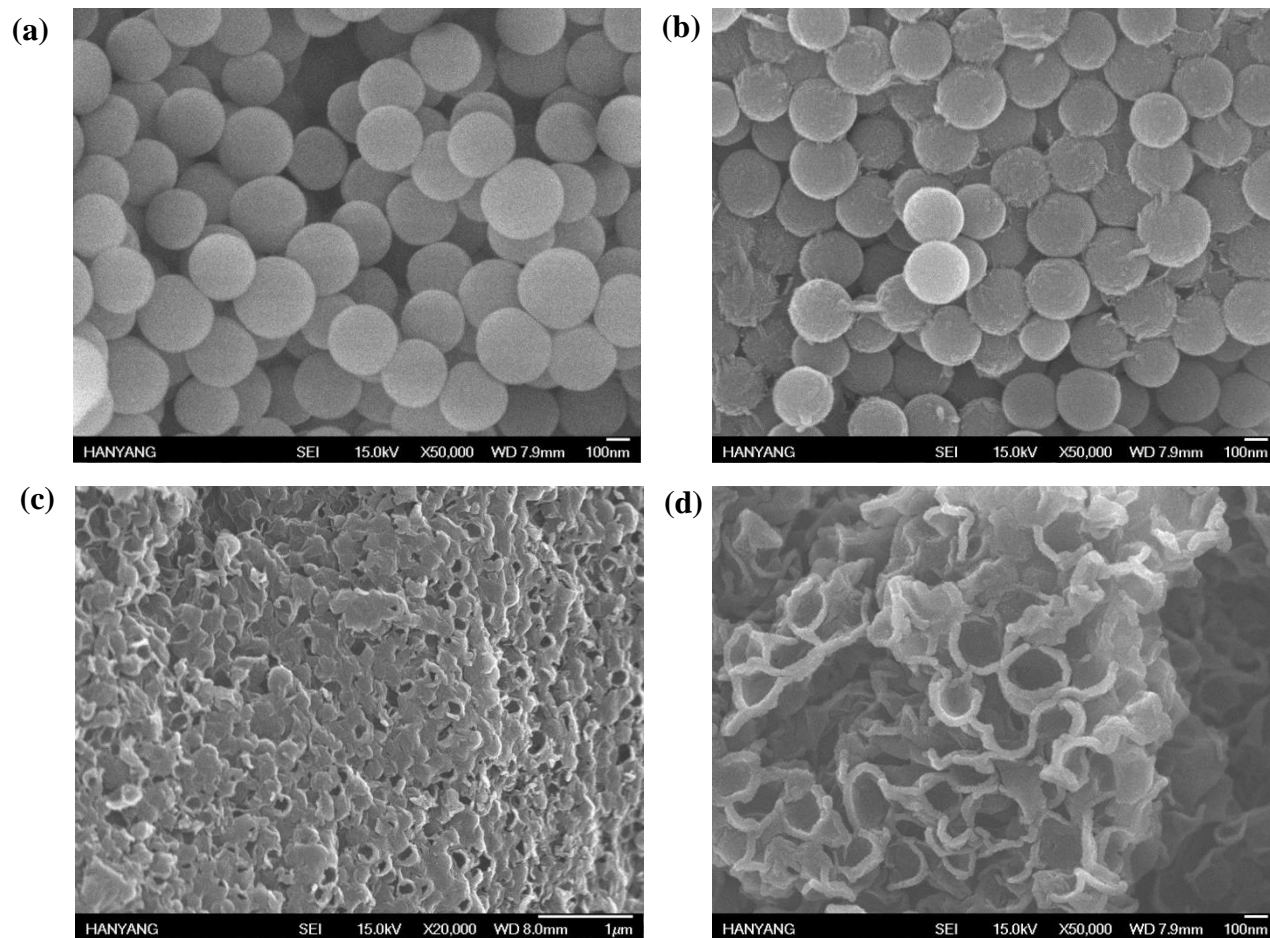


Fig. S1 (a) SEM image of SiO₂ template, (b) SEM image of rGO cover SiO₂ template, (c), and (d) SEM images of HGS.

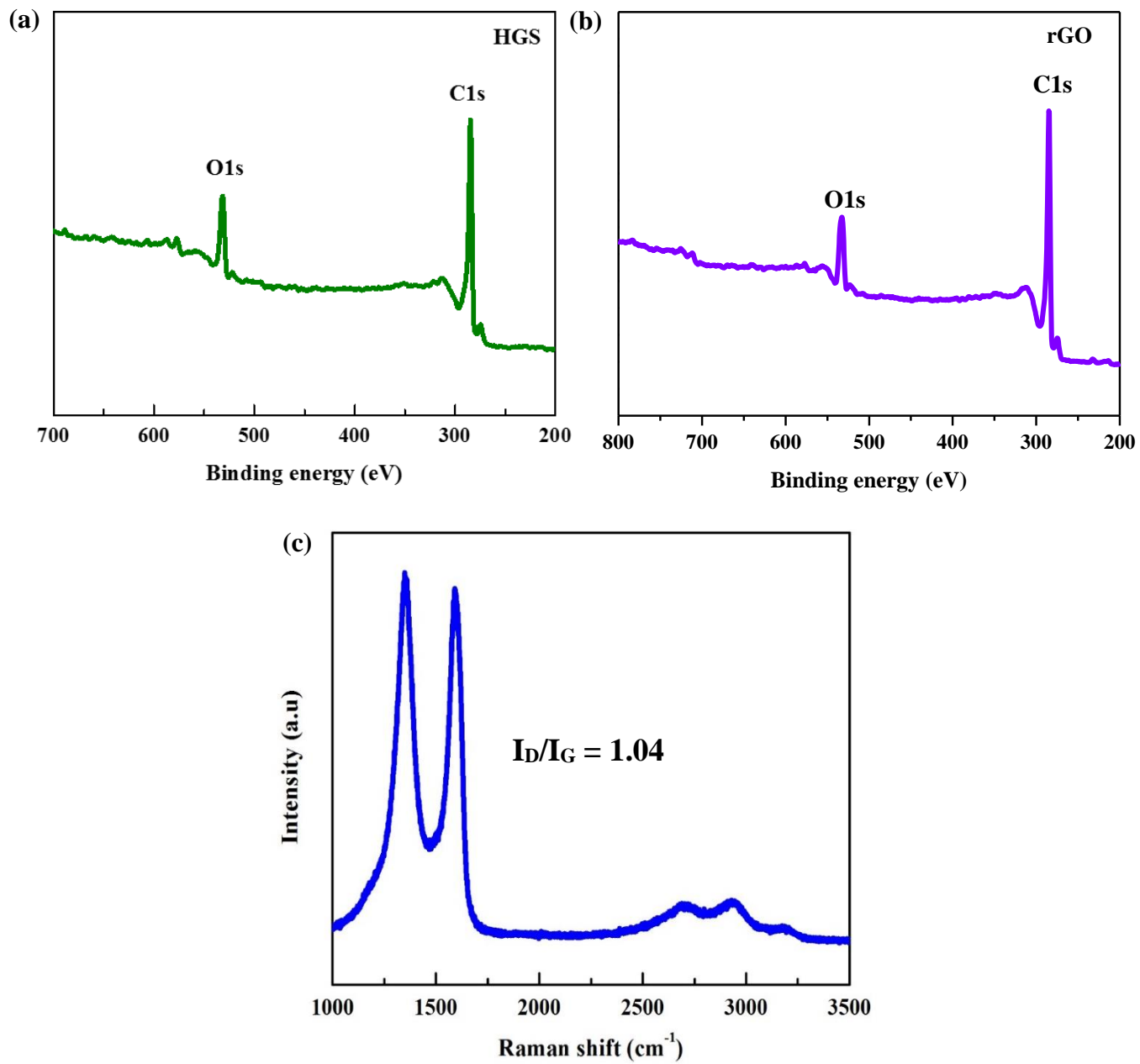


Fig. S2 (a) XPS survey spectrum of HGS, (b) XPS survey spectrum of rGO, and (c) Raman spectrum of HGS,

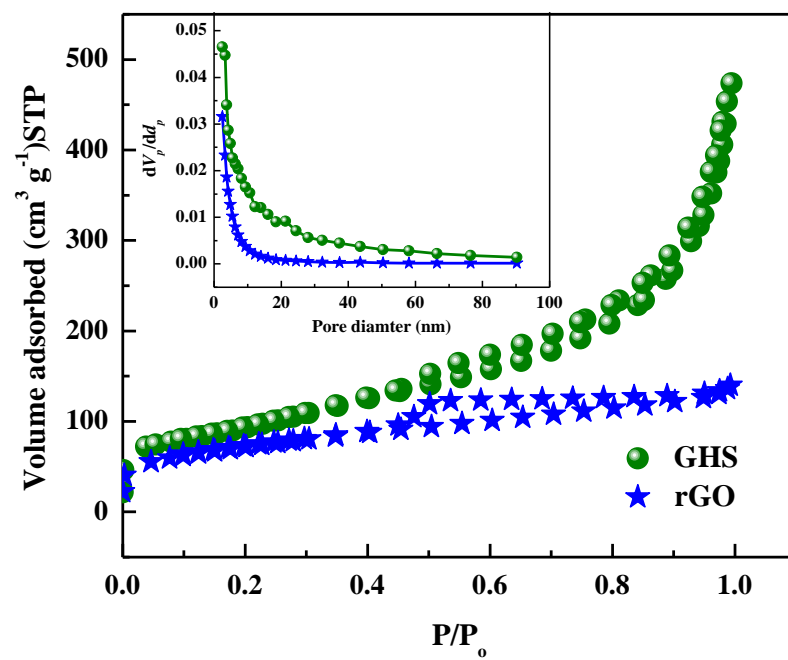


Fig. S3 N₂ adsorption/desorption isotherm of GHS and rGO, Inset: BJH pore size distribution

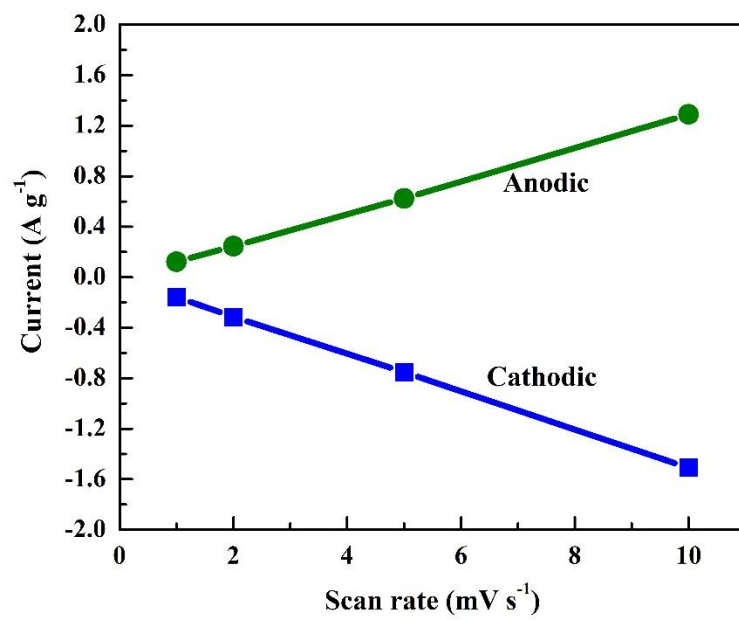


Fig. S4 Current vs. scan rate relationship from CV curves of HGS

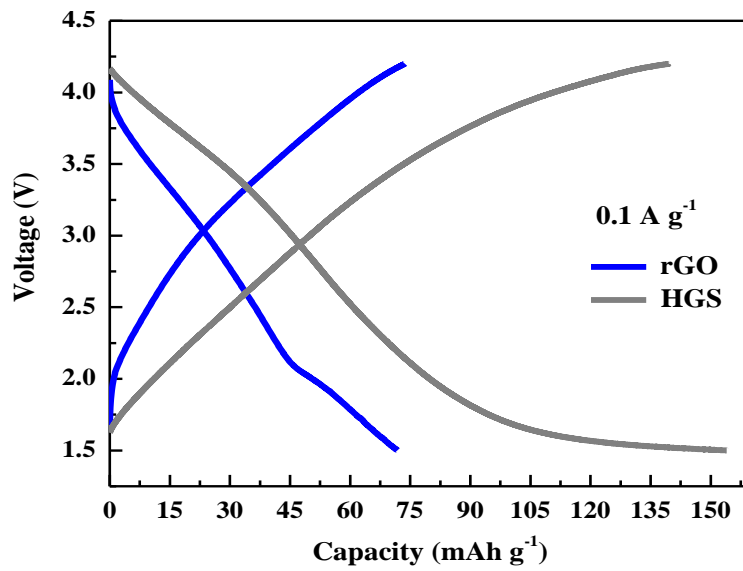


Fig. S5 Comparison of CD curves of rGO and HGS at 0.1 A g⁻¹.

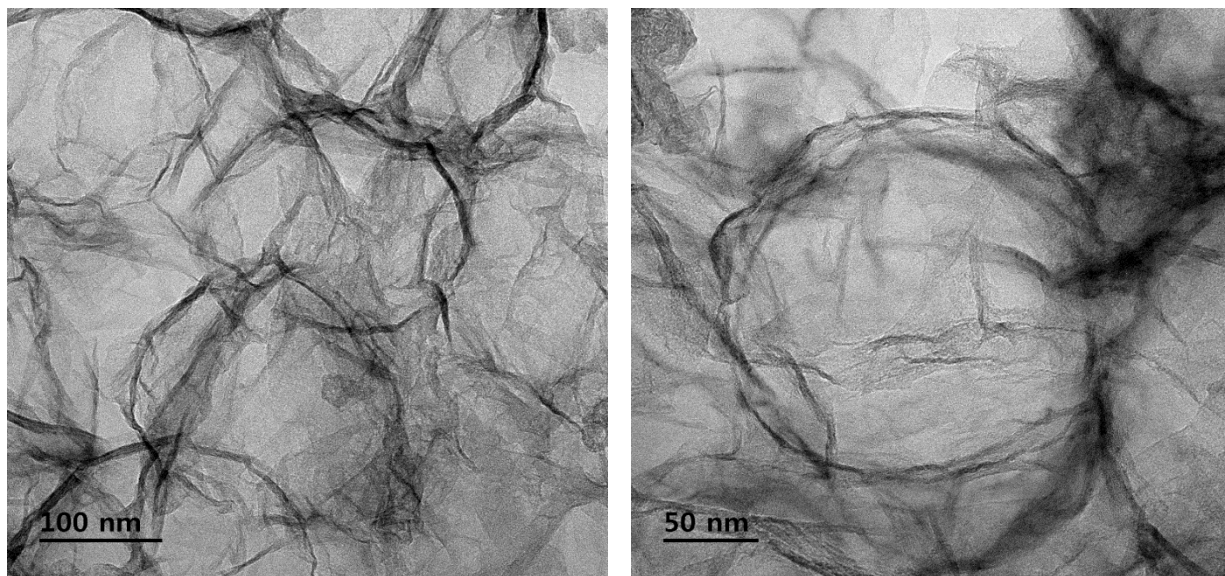


Fig. S6 TEM images of HGS after cycling.

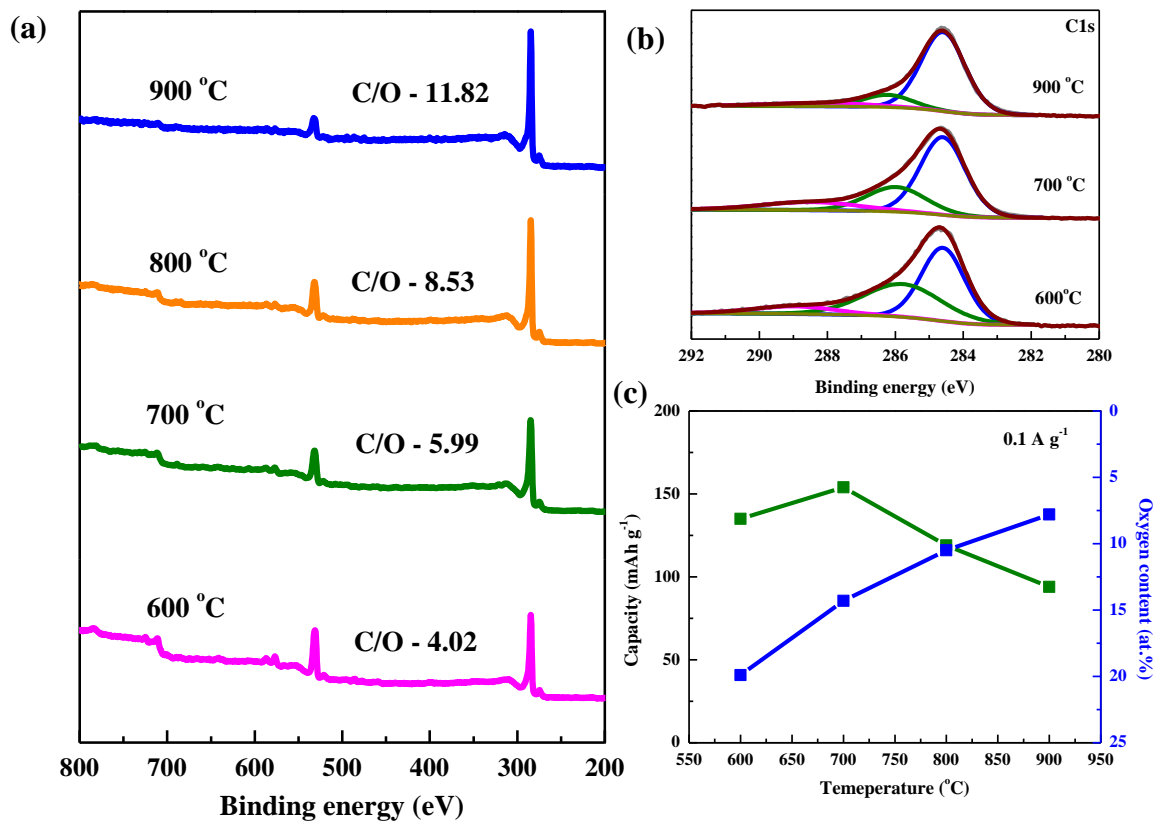


Fig. S7 (a) XPS survey spectrum of GHS reduced at different temperatures, (b) C1s spectrum of HGS and (c) discharge capacity and oxygen contents as a function of the temperature.

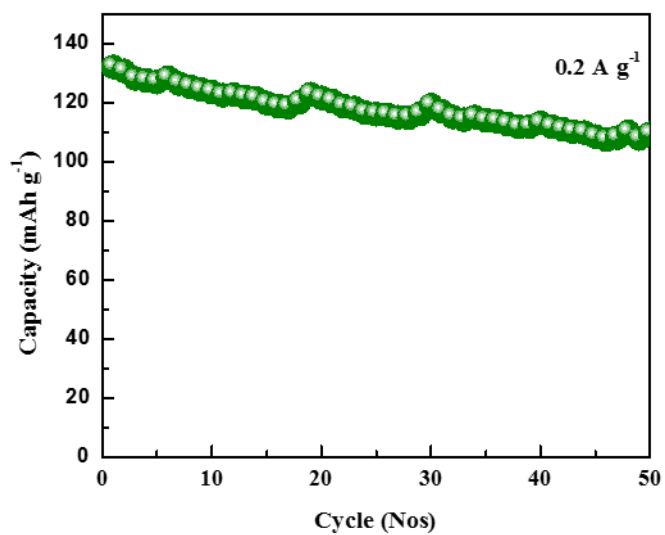


Fig. S8 (a) Cyclic stability of full-cell at 0.2 A g⁻¹.