

## Electronic Supplementary Information for:

# Synthesis of a highly conductive and large surface area graphene oxide hydrogel and its use in a supercapacitor

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## 1. Chemicals

Natural graphite, ethylene diamines (EDA), concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), potassium permanganate (KMnO<sub>4</sub>), hydrochloric acid (HCl), nitric acid (HNO<sub>3</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) were purchased from Aldrich. All chemicals were used as received without further purification.

## 2. Experimental

### 2.1. Synthesis of Graphene oxide (GO)

The expandable graphite (Grade 1721, Ashbury Carbon) was mixed with HNO<sub>3</sub> and KMnO<sub>4</sub> following expansion by microwave heating for 1 min. Graphene oxide (GO) was prepared from expanded graphite using the modified Hummer's method described in our previous work.<sup>S1</sup> Typically, 500 mL of concentrated H<sub>2</sub>SO<sub>4</sub> was charged into a 3 L beaker equipped with a teflon impeller. Next, 5 grams of expanded graphite was gradually added under stirring at 0 °C. The 30 g of KMnO<sub>4</sub> was slowly added while keeping the temperature below 20°C followed by stirring the suspension for 2 hr at 35°C. Subsequently, 1 L of deionized water was slowly added while maintaining the temperature below 70 °C. The mixture was stirred for 1 h and subsequently diluted with 5 L of deionized water. Fifty milliliters of H<sub>2</sub>O<sub>2</sub> (30 wt%) was slowly added and vigorous bubbles appeared as the color of the suspension changed from dark brown to yellow. The suspension was centrifuged and washed with 10% HCl solution four times followed by centrifugation at 10,000 rpm and washed with deionized water to completely remove the acid until the pH of the GO dispersion reached 7. The as-synthesized GO dispersion was a paste. The concentration of GO was determined as 1.0 wt% after drying the GO dispersion at 80 °C under vacuum for 24 h.

### 2.2. Synthesis of GOH and rGH

One milliliter of an aqueous solution EDA was dispersed into 10 mL GOs (with concentrations 5, 7.5, 10, 12.5, 15 mg mL<sup>-1</sup>) and ultrasonicated at 10 °C for 2 h. The crosslinking reaction was performed at 80°C for 8 h. The obtained graphene oxide hydrogel (GOH) was submerged into 2 L deionized water for 1 h in order to wash the unreacted EDA. This process was repeated 5 times. A reduced graphene oxide hydrogel (rGH) was also fabricated to improve the conductivity of GOH by submerging it into the hydrazine at 90 °C for 2 days followed by filtering and washing with deionized water for 5 times. Finally, the GOH and rGH was freeze-dried at -37 °C for 2 days in order to remove water without destroying their structure.

## 3. Characterization

### 3.1. Instrumental analysis

The chemical and physical structures of GO, GOH and rGH were characterized by scanning electron microscopy (SEM, JOEL JSM-6500FE), X-ray photoelectron spectra recording using a K-alpha (Thermo Fisher), X-ray diffraction (XRD) pattern characterized using a high power X-Ray diffractometer (Rigaku, D/MAZX 2500V/PC) with Cu-K $\alpha$  radiation (35 kV, 20 mA,  $\lambda = 1.5418 \text{ \AA}$ ) at a scan rate of  $2^\circ (2\theta)$  per minute and a Raman spectra using a WITec confocal raman microscopy (WITec, Alpha300S) at 532 nm wavelength incident lasers light. Thermal gravimetric analysis was performed under a nitrogen atmosphere with a  $10^\circ \text{C}$  per minute heating rate (TA Instrumrnts, Q50).

### 3.2. Electrical and mechanical property

The GOH and rGH were compressed with 2.5 kPa to 350  $\mu\text{m}$  film at  $200^\circ \text{C}$  to determine the electrical conductivity and break strength. The electrical conductivity of hydrogels were calculated via the sheet resistance which was determined by four probes stationed using the Keithley 4200 semiconductor character system (MS Tech). The mechanical properties of GH were measured by a texture analyzer (TA plus - LLOYD instruments, AMETEK Company) controlling the strain ramp rate at 2 mm/min.

### 3.3. Electrochemical performance

The electrochemical properties and the capacitor of a supercapacitor were determined by cyclic voltammetry (CV) curves, galvanostatic charge-discharge (CD) curves and electrochemical impedance spectroscopy (EIS) using the battery analyzer BST8-3 (6-3000mA, up to 5V). The rGH was cut for plates with thickness 1 mm followed by submergence in 2M KOH solution for 1day before using them as supercapacitor electrodes. The glass microfiber filter was used as a separator between the two electrodes and 2M KOH was used as the electrolyte. The CV curves were scanned at a scan rate from  $50 \text{ mV s}^{-1}$  to  $200 \text{ mV s}^{-1}$  and CD curves were measured at  $1 \text{ A g}^{-1}$  constant current. Impedance spectroscopy was measured at a dc bias of 0.7 V and the frequency range from 0.01 Hz to 100 kHz.

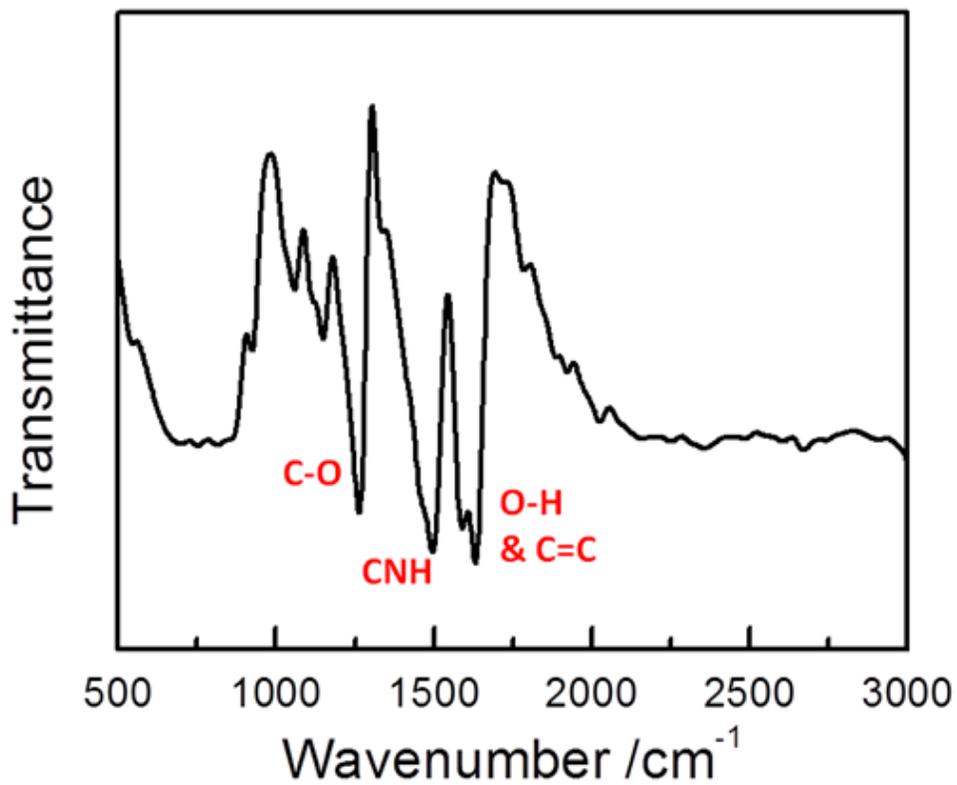


Fig. S1. FT-IR spectrum of GOH.

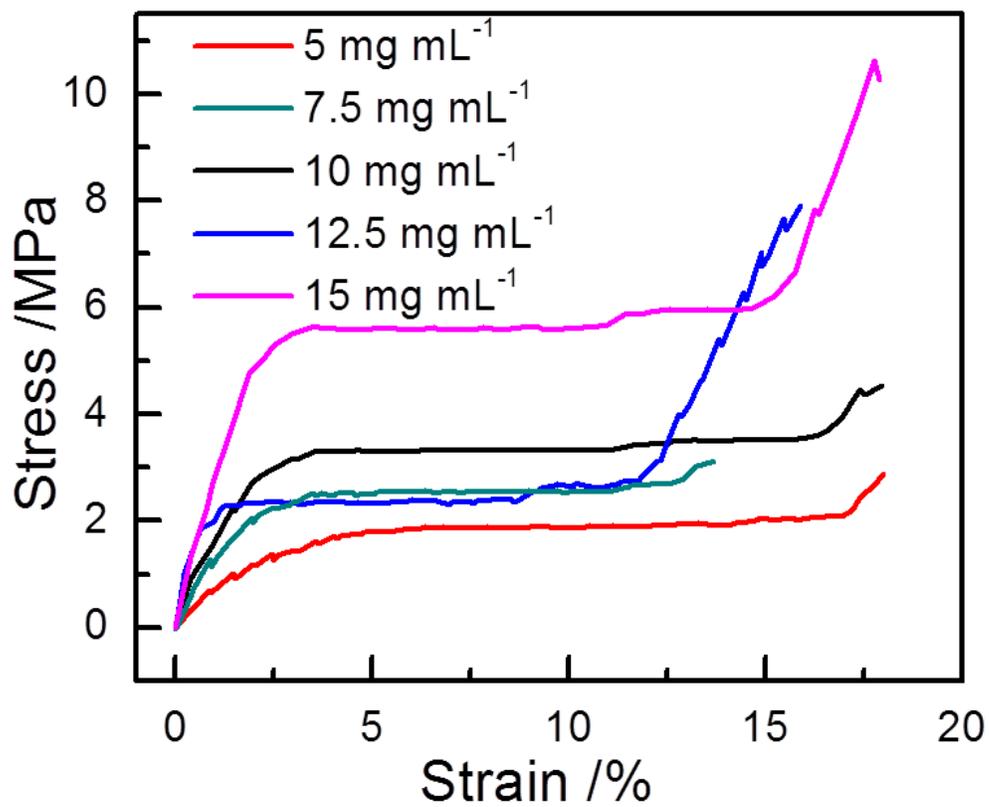


Fig. S2. Stress-strain curves GOHs fabricated at various GO concentrations.

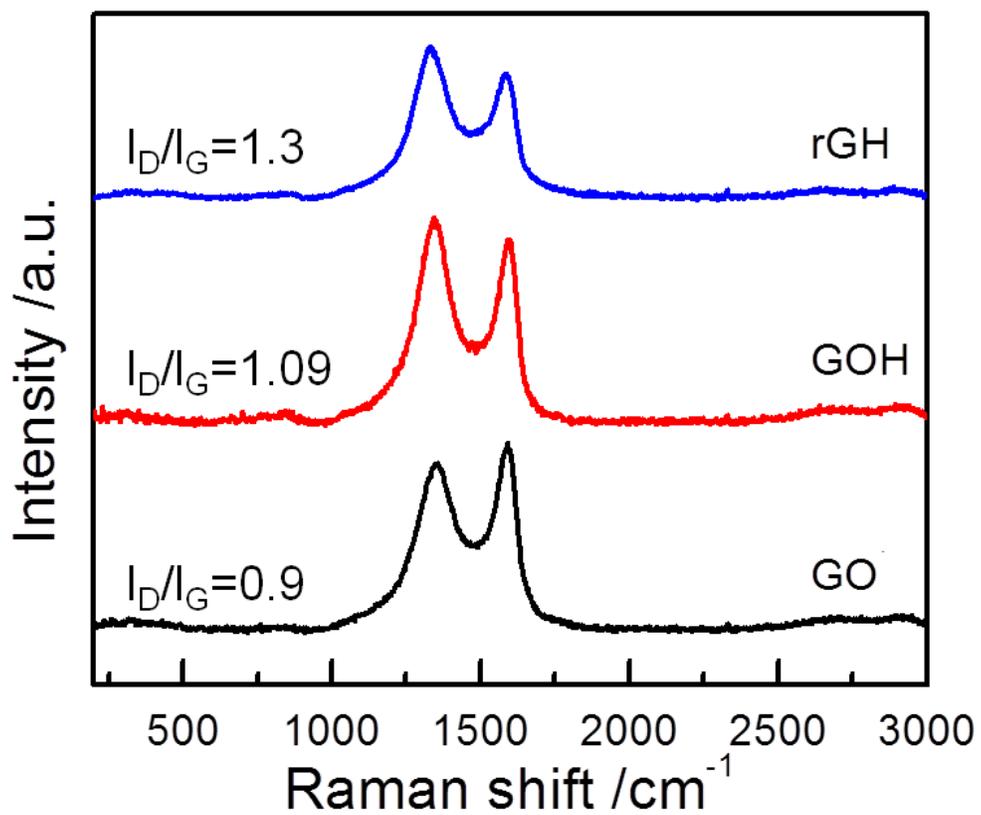


Fig. S3. Raman spectra of GO, GOH and rGH.

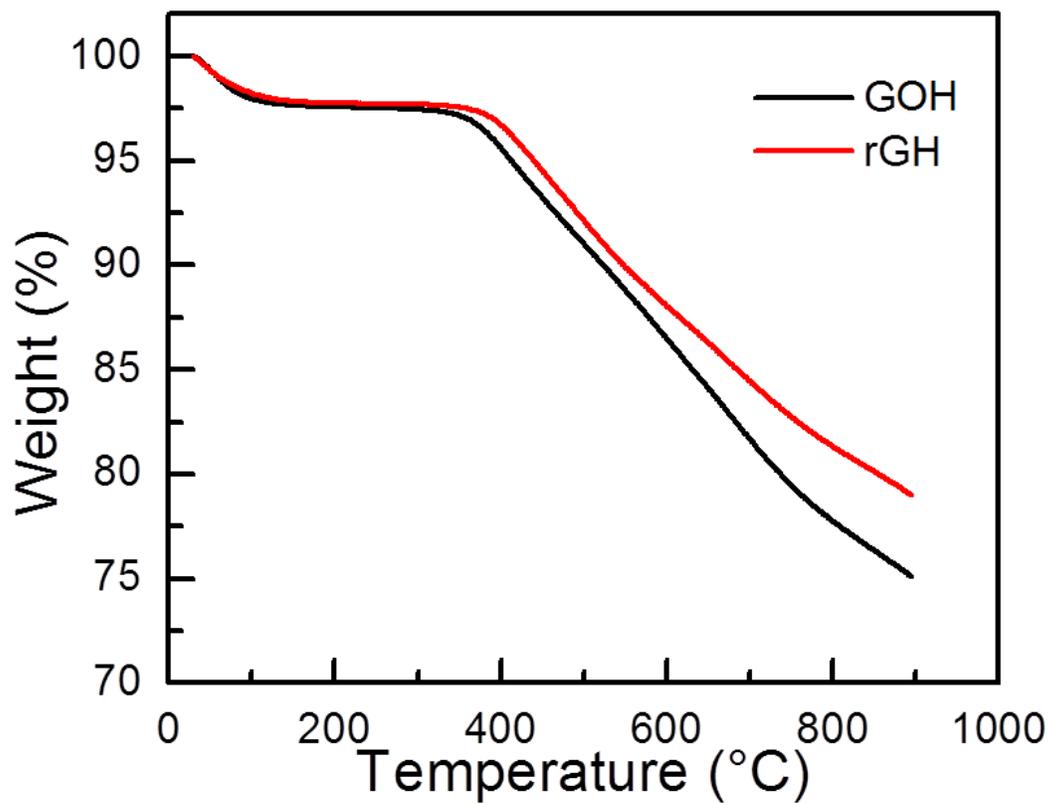
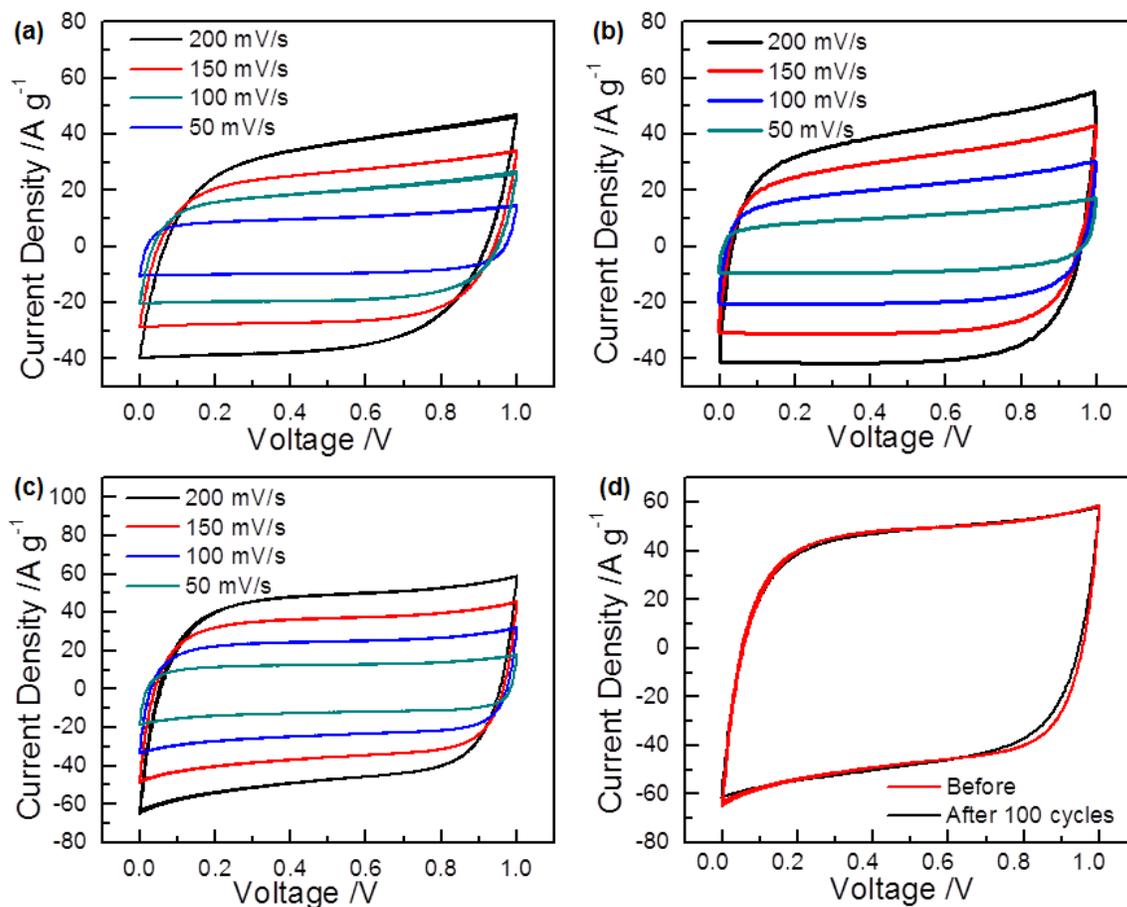


Fig. S4. TGA curves of GOH and rGH.



**Fig. S5.** The CV curves at a scan rate 50, 100, 150 and 200 mV s<sup>-1</sup> with rGH fabricated at (a) 5, (b) 10 and (c) 15 mg mL<sup>-1</sup> GO concentration, (d) the CV curves before and after 100 cycles (rGH fabricated from 15 mg mL<sup>-1</sup> GO concentration).

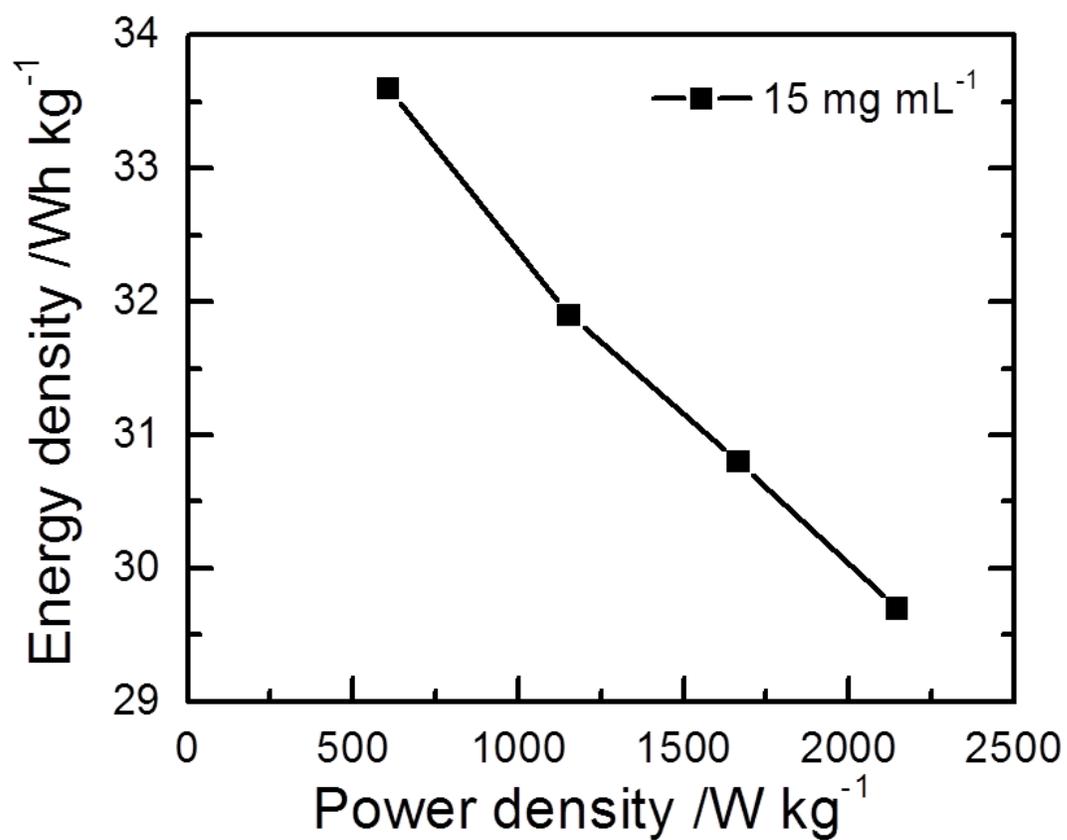
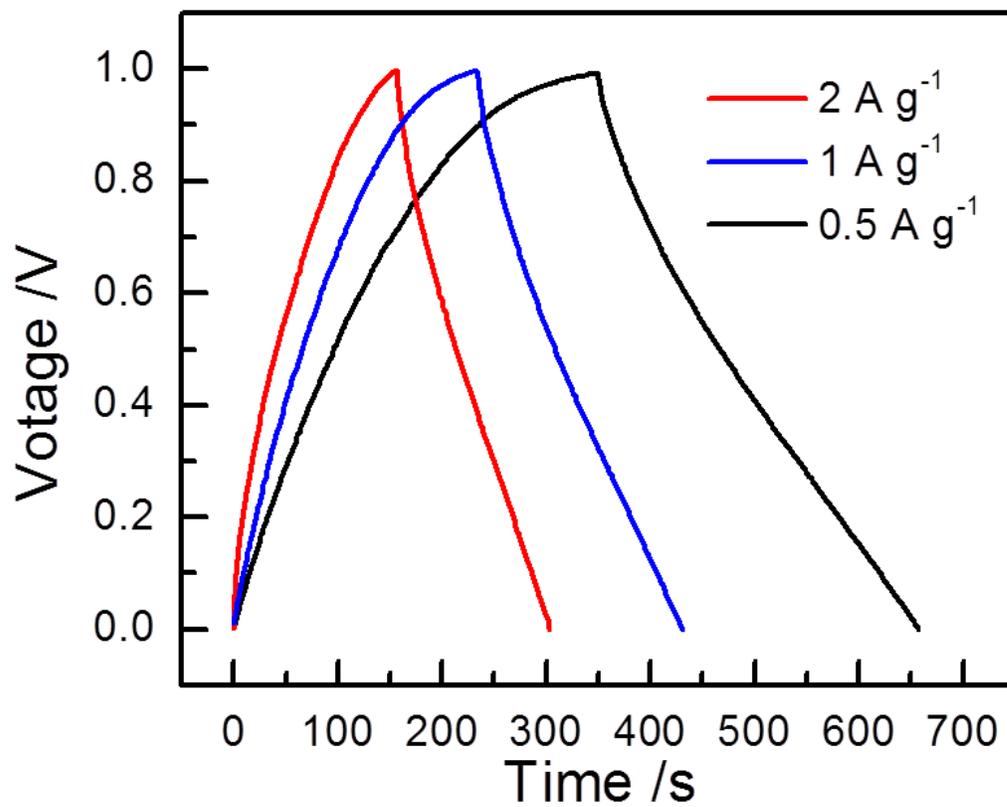


Fig. S6. The Ragone plot of energy density vs. power density.



**Fig. S7.** The CD curves at a various current density for the sample 3 (10 mg mL<sup>-1</sup>).

#### References

S1 V. H. Luan, H. N. Tien, T. V. Cuong, B. S. Kong, J. S. Chung, E. J. Kim and S. H. Hur, *J. Mater. Chem.*, 2012, **22**, 8649-8653.