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Electronic Supplementary Information

FeO_X and Si Nano-dots as Dual Li-storage Centers Bonded with Graphene for High Performance Lithium Ion Batteries

Jinlong Yang[a,b+], Jiaxin Zheng[a+], Lin Hu[b], Rui Tan[a], Kai Wang[a], Shichun Mu[b] and Feng Pan[a*]*

[a]School of Advanced Materials, Peking University Shenzhen Graduate School, Shenzhen 518055, China

[b]State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

EXPERIMENTAL SECTION

Sample Preparation. The free LFSNR was synthesized via a hydrothermal method. First of all, 0.02 mol of $Fe(NO_3)_3 \cdot 9H_2O$ and 0.02 mol of ascorbic acid were thoroughly dissolved in 20 mL ethylene glycol until the crimson fade; then, 0.08mol of $LiOH \cdot 2H_2O$ and 0.02 mol of tetraethyl orthosilicate (TEOS) were added into 100 mL of deionized water vigorous stirring for 1h; third, two solution was rapidly mixed to obtain dark green colloid solution, which was then transferred into a 200 mL Teon-lined stainless steel autoclave maintained at 200 ℃ for 6 days. The grayish precipitate was collected, washed by water and ethanol several times, and dried at 100 ℃ in vacuum for 8 h. A simple PVP anchoring technology was used to prepare the

LFSNR@GNS hybrid sheets. 300 mg of LFSNR powder was firstly added to 30 ml of homogeneous aqueous solution with 30 mg of PVP and 30 mg of graphene oxide nanosheets prepared by a modified Hummers' method[14]. The mixture was vigorously stirred for 30 minutes, subsequently freeze-dried and mildly heated at 600 ℃ for 6 h under Ar atmosphere.

Characterization techniques. Microstructures were observed by Field-emission scanning electron microscopy (FESEM) (Hitachi S-4800, 10 kV), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM), (JEM-2100F). X-ray diffraction (XRD) data of samples were collected with a D_8 Advance X-ray diffractometer, using Cu Kα radiation (λ = 1.5418 Å) in a 2θ range from 10° to 80° at room temperature. Valence state of the key elements in samples was studied by X-ray photoelectron spectroscopy (XPS, PHI Quantera, U-P). Raman spectra were obtained using an RM-1000 Renishaw confocal Raman microspectroscope with 514.5 nm laser radiation at a laser power of 0.04 mW in the range of 600-2000 cm^{-1}.

Electrochemical measurements. Electrochemical properties of samples were tested with 2032-type coin cells assembled in a glove box filled with pure argon. Lithium pellet was used as the anode, Celgard 2400 as the separator and a 1.0 M solution of $LiPF_6$ in EC/DMC/EMC (1/1/1 by volume) (bought from Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd. China) as the electrolyte, and the anode electrodes were produced with 75% active material, 15% conducting agent (acetylene black), and 10% poly (vinylidene fluoride) (PVDF) binder. The thickness of

electrodes in this work was 85±5 μm, and loading density was 8.0±0.5 mg cm^{-2}. Galvanostatic charge/discharge measurements were performed between 0.001V and 3 V at a multichannel battery testing system (LAND CT2001A). All the measurements were carried out at room temperature.

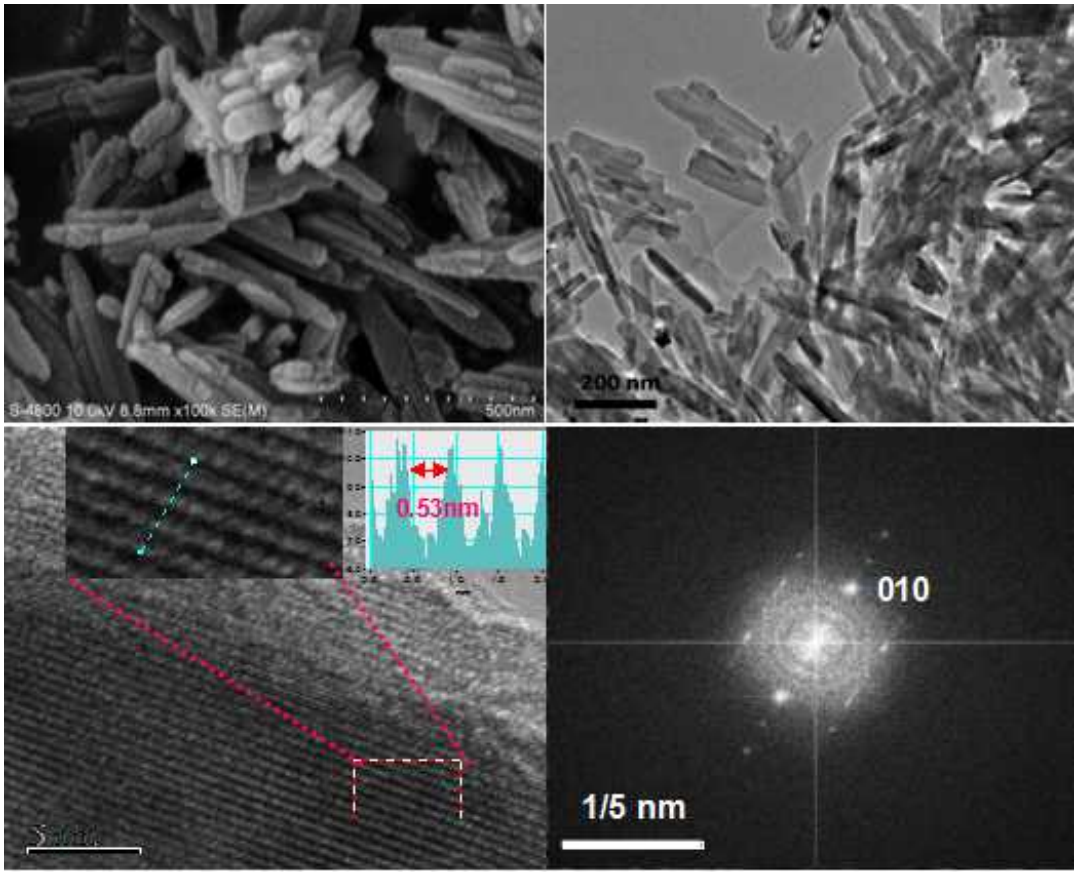

Figure S1 SEM and TEM images of pristine LFSNR obtained at hydrothermal process.

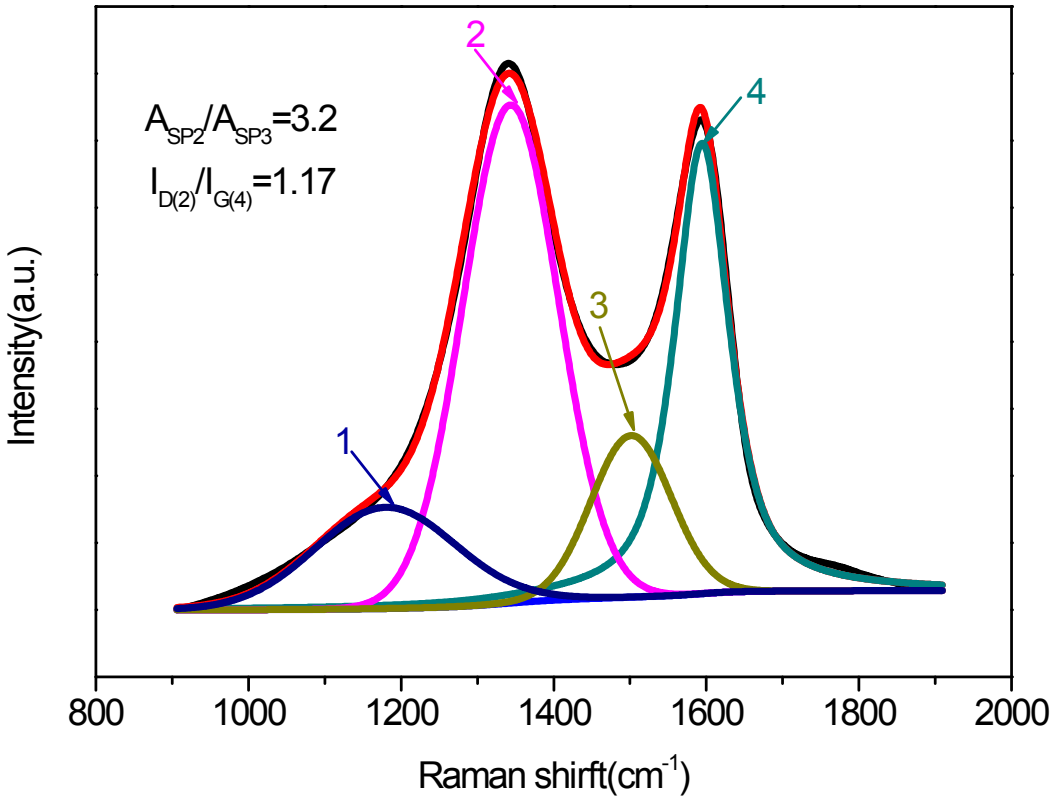

Figure S2 Raman spectra of the pristine GNS.

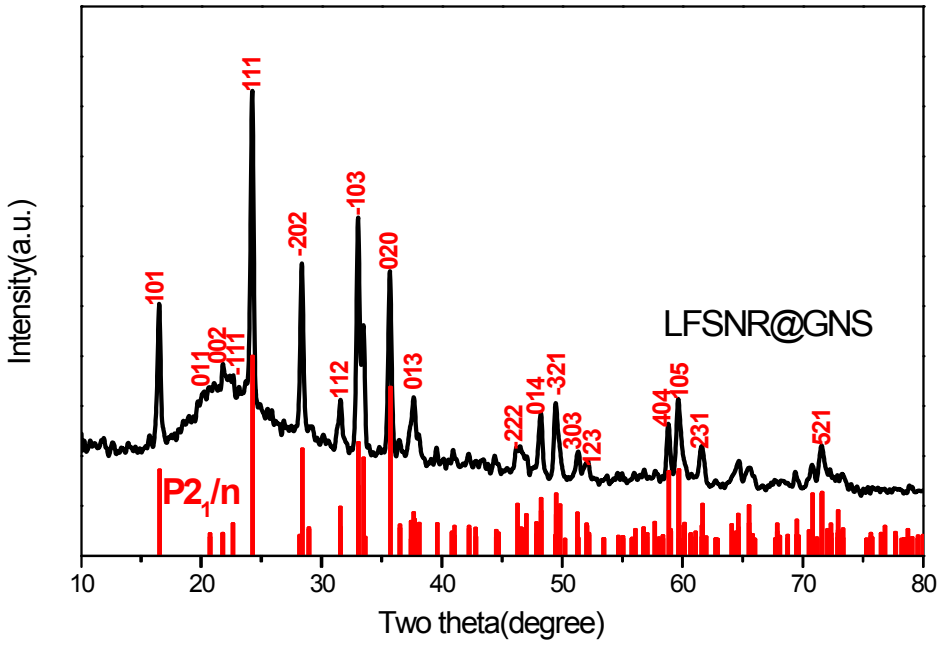

Figure S3 XRD of the LFSNR@GNS hybrid.

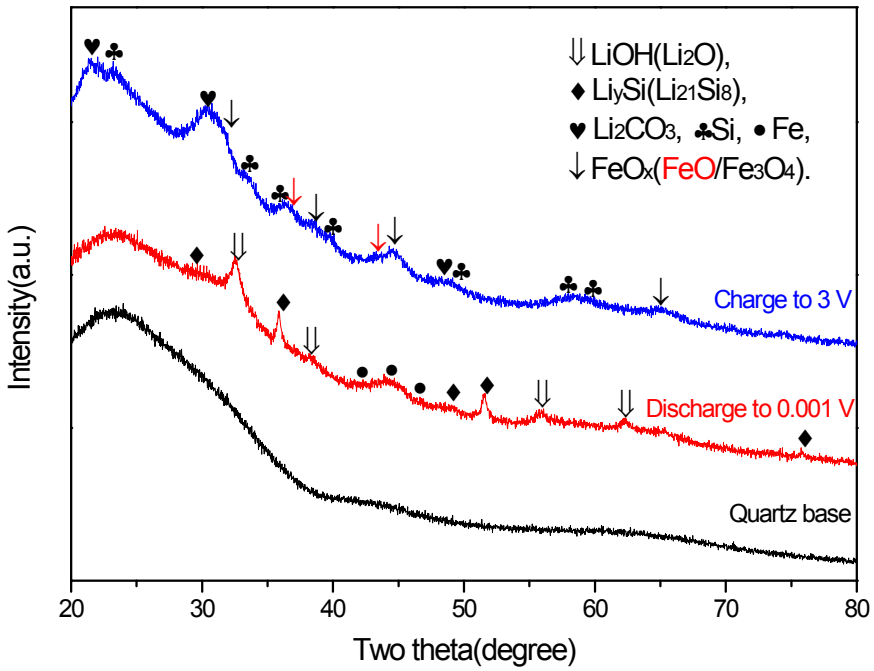

Figure S4 XRD of the hybrid anodes after 2nd cycles. The anodes were composed of 75% hybrids, 15% acetylene black, and 10% PVDF. After 2nd charged to 3V or discharged to 0.001V, the anodes were removed from batteries and dried in the Ar gas glove box, fina1ly placed on quartz glass for XRD testing.

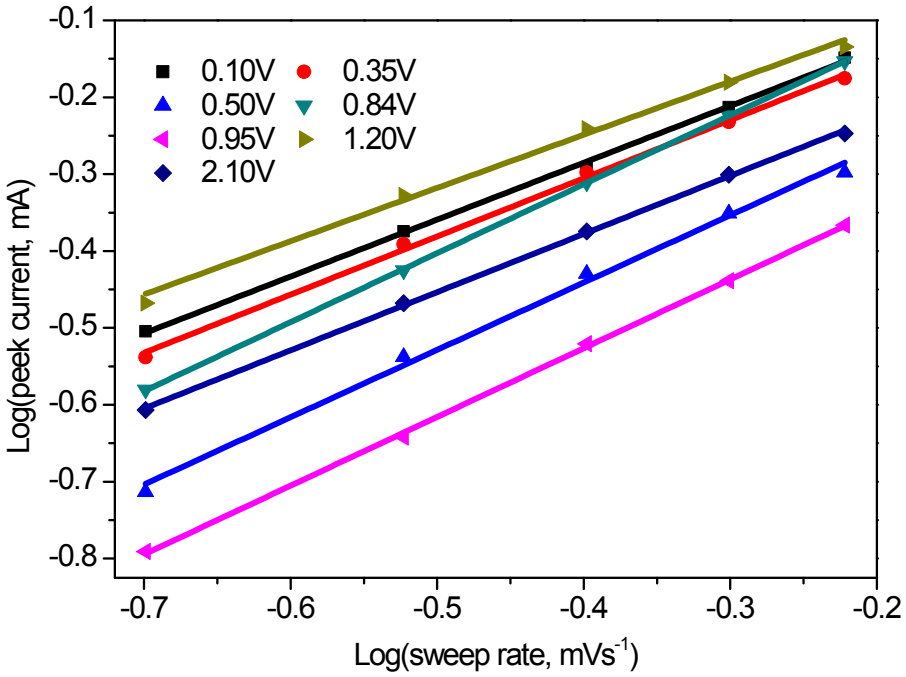

Figure S5 Slope of the peak current versus the potential scan rate in a logarithm scale at different anodic and cathodic peaks position.

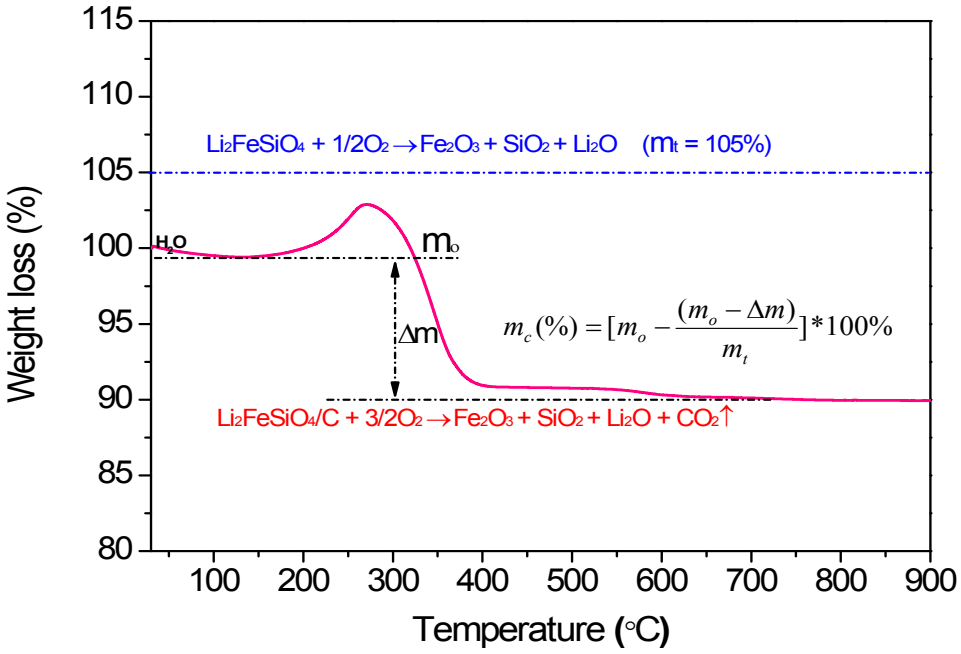

Figure S6 TG curve of the LFSNR@GNS. The amount of carbon released from the sample was measured using TG method (Fig. S5) within a temperature range of room temperature to 900 ℃ under O_2 flow. The oxidation of samples under O_2 can be carried out on the basis of the reactions (S1) and (S1):

$$Li_2FeSiO_4 + \frac{1}{2}O_2 \rightarrow Li_2O + \frac{1}{2}Fe_2O_3 + SiO_2 \quad \text{(S1)}$$

$$Li_2FeSiO_4/C + \frac{3}{2}O_2 \rightarrow Li_2O + \frac{1}{2}Fe_2O_3 + SiO_2 + CO_2\uparrow \quad \text{(S2)}$$

According to the theoretical calculation from reaction (S1), the pure Li_2FeSiO_4 suffered from a weight increase to 105wt%. According to reaction (S2), the lose of weight are from combustion of carbon, the amount of carbon can be calculated by the following formula (S3):

$$m_c(\%) = [m_o - \frac{(m_o - \Delta m)}{m_t}] * 100\% \quad \text{(S3)}$$

Therefore, the content of carbon in the LFSNR@graphene hybrid is 12.3%, which include that of the PVP($(C_6H_9NO)_n$)-Pyrolysis carbon and graphene. According to the experiment, the content of PVP is 8.3%, deducing the content ($m_{c\text{-}pvp}$ = [8.3% * 72/114.14] * 100%) of PVP-Pyrolysis carbon is 5.4%, the other, the content ($m_{c\text{-}G}$ = m_c - $m_{c\text{-}pvp}$) of graphene is 6.9%.

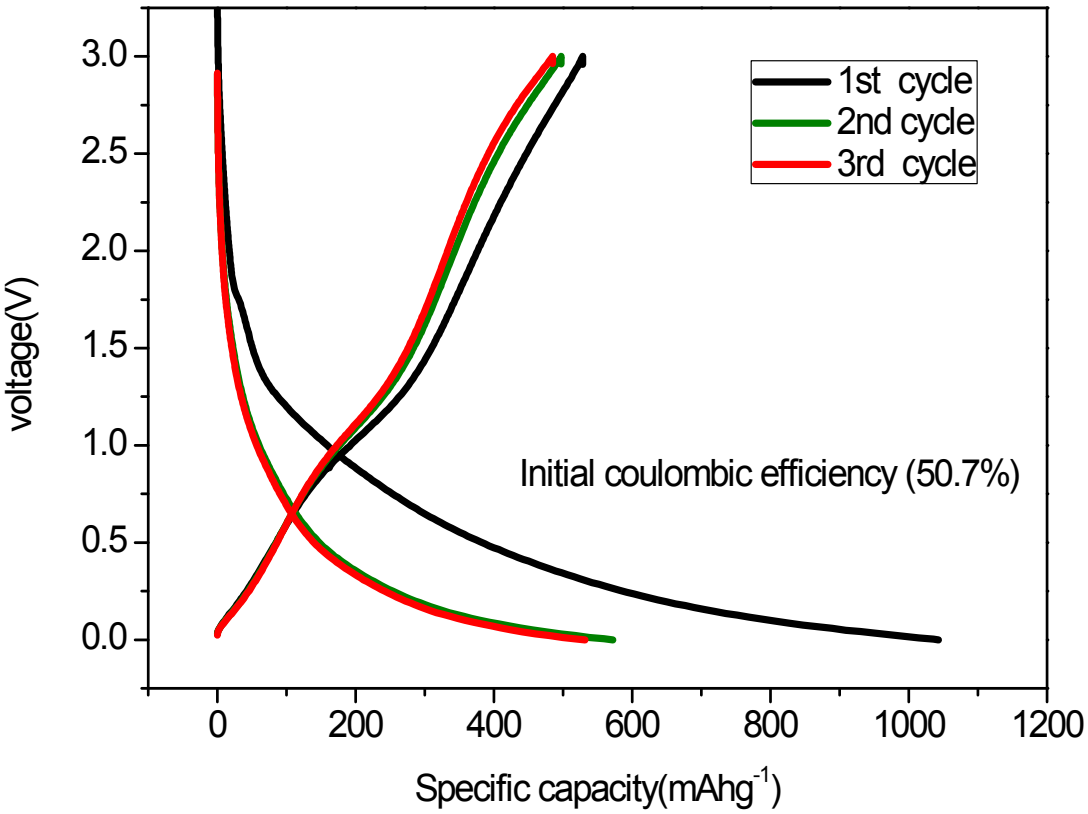

Figure S7 Charge-discharge curves of pristine GNS.

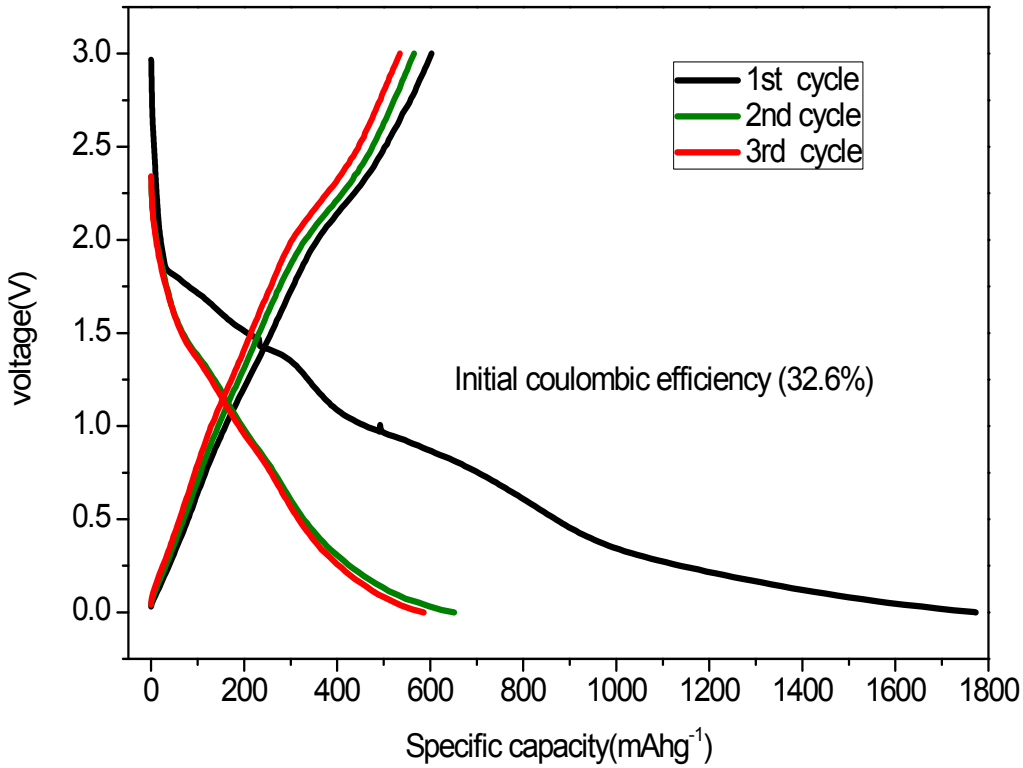

Figure S8 Charge-discharge curves of pristine LFSNR.

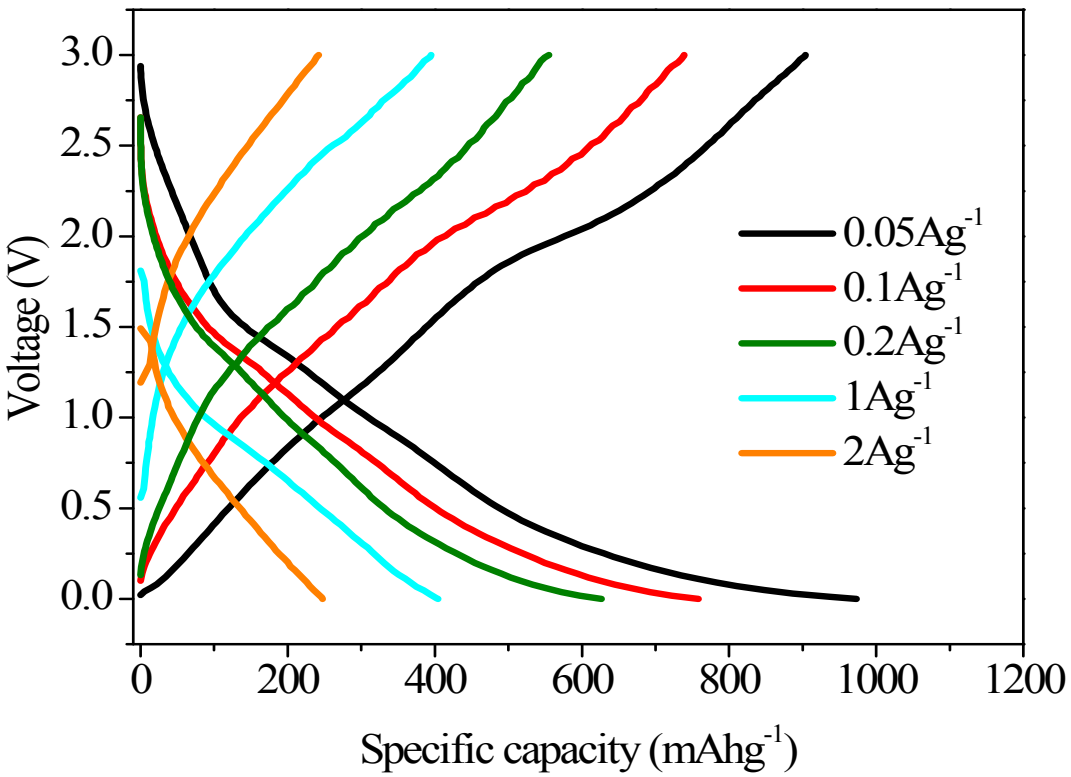

Figure S9 Typical charge-discharge curves at various current densities between 0.001-3 V for the hybrid.

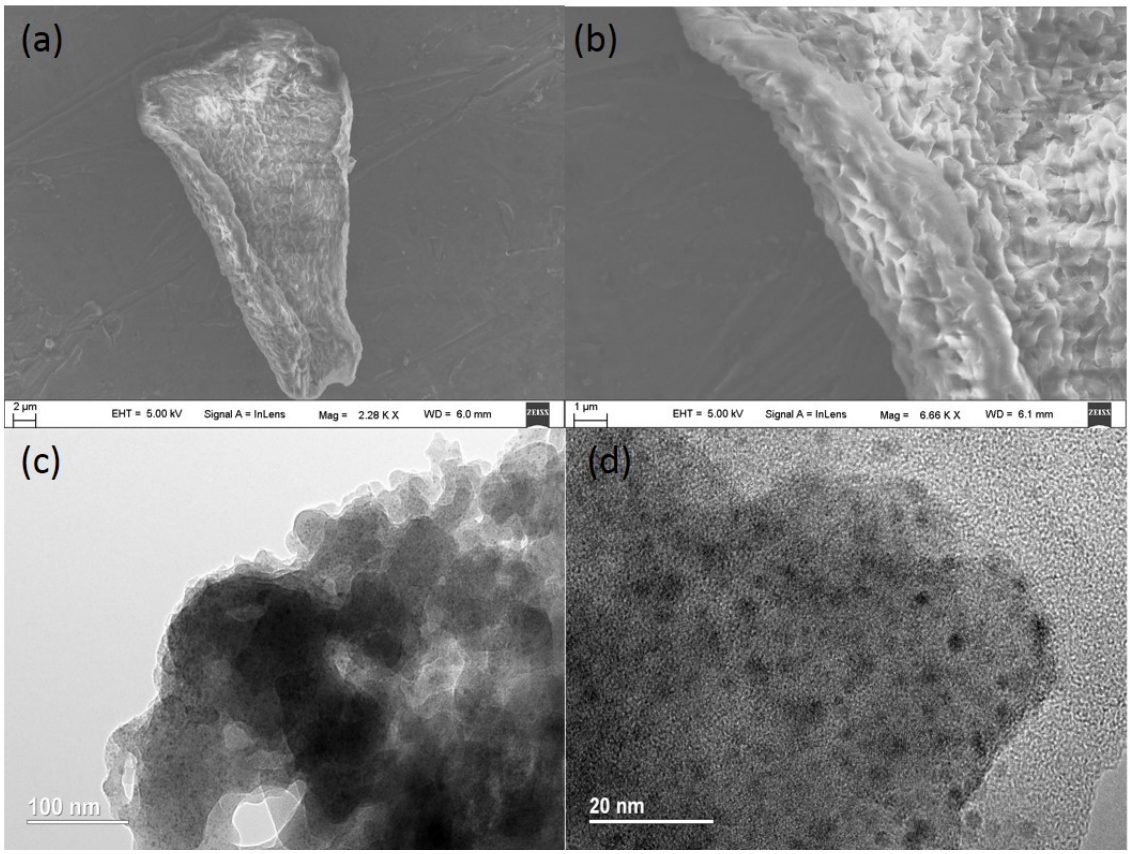

Figure S10 (a, b) SEM and (c, d) HRTEM images of the nanocomposites after 100 cycles.