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Supporting information for:

Fabrication of double-shell hollow NiO@N-C nanotubes for high-performance supercapacitor

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Experiment section

Materials

All chemicals applied were analytical-grade and directly used without further purification. Ammonium molybdate tetrahydrate (AR), ammonium persulfate (APS, 99%), potassium peroxodisulfate (97%), sodium hydroxide (97%), and the p-toluene sulfonic acid ($C_6H_4CH_3SO_3H{\cdot}H_2O$, p-TSA) were bought from aladdin. Pyrrole (Py) was obtained from Sinopharm Chemical Reagent Co., Ltd. Nickel sulfate hexahydrate (AR) was purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd. $NH_3{\cdot}H_2O$, distilled deionized water, and ethanol absolute were used in all experiments. Ni foam was used as received.

Preparation of MoO_3 rod templates

The MoO_3 templates with rod-like morphology were facile synthesized by a previously reported solvothermal method [1]. 2.8 g of ammonium molybdate tetrahydrate ($H_{32}Mo_7N_6O_{28}$) was dissolved into 80 mL of mixed solution containing nitric acid and deionized water (HNO_3:H_2O = 1:5) with intense agitation for 30 min to acquire a transparent and homogeneous liquid. Subsequently, the mixture was transferred to 100 mL Teflon-lined stainless-steel autoclave and kept at 200 °C for 20 h. The precipitate was taken out autoclave and collected by centrifugation and through washing with distilled water three times, finally, dried at 60 °C for 48 h.

Preparation of PPy@MoO_3

The PPy@MoO_3 was prepared by anionic polymerization. Typically, 0.5 g MoO_3 nanotubes and 0.416 g p-TSA were directly put into 30 mL ethanol absolute for sonication. The mixture was put into ice-water bath and uniformly stirred for 5 min. Afterwards, 0.2 mL Py, 0.24 g APS and 20 mL distilled deionized water were added sequentially for 30s with vigorous stirring. After that, the resultant was loaded into the dark for 4 h and was centrifuged with distilled deionized water and ethanol absolute. Finally, the PPy@MoO_3 was dried for 12 h in vacuum at 60 °C.

Preparation of PPy hollow nanotube

The as-prepared PPy@MoO_3 was dispersed in 2 M NaOH at 85 °C for 12 h. After centrifugalization, the precipitate was washed with deionized water until the filtrate became neutral and colorless. Subsequently, the products were dried at room temperature.

Preparation of $Ni(OH)_2$@PPy double-shell nanotube

The $Ni(OH)_2$@PPy double-shell nanotube was synthesized by chemical bath deposition (CBD) [2]. In a typical preparation, 10 mL of $NiSO_4 \cdot 6H_2O$ aqueous solution was added into 6 mL of aqueous solution containing 0.5 g PPy hollow nanotube and 0.33 g $K_2S_2O_8$. Afterwards, 2 mL of $NH_3 \cdot H_2O$ was added dropwise the mixed solution and magnetically stirred for 10 min. The product was washed by centrifugation and dried for overnight at 60 °C.

Preparation of NiO@N-C hollow double-shell nanotube

The NiO@N-C was prepared by a controllable heat treatment. The as-prepared $Ni(OH)_2$@PPy materials were annealed 1h in N_2 at 700 °C with an increasing rate of 5 °C/min. The reaction process of NiO@N-C can be summarized as:

$$MoO_3+OH^-=MoO_4^{2-}+H_2O \qquad (1)$$

$$NiSO_4+2NH_3 \cdot H_2O=Ni(OH)_2\downarrow+(NH_4)_2SO_4 \qquad (2)$$

$$Ni(OH)_2=NiO+H_2O \qquad (3)$$

Structure characterizations

The surface structures and morphology of the samples were characterized by a field-emission scanning electron microscopy (FE-SEM) (Hitachi, SU8000) and transmission electron microscopy (TEM) (JEOL, JEM-2010, 200 kV). An X-ray powder diffractometer (XRD, Rigaku, TTR-III) was used to characterize the structures of the obtained samples. The FT-IR spectra measurements were performed by a Bruker TENSER II FT-IR spectrophotometer (Germany) within the 4000-400 cm^{-1} region.

Electrochemical measurements

First of all, the as-prepared NiO@N-C, acetylene black and polytetrafluoroethylene (PTFE) were mixed sufficiently with a mass ratio of 80:15:5 in 6 mL ethanol, then the hybrid materials were dried at 60 °C for 12 h. 10 mg of the as-prepared hybrid materials were loaded on cleaned Ni foam in 1 cm^2 by applying suitable compressive force, which was obtained as the working electrode of supercapacitor. A saturated calomel electrode (SCE) and Pt plate (10 mm *10 mm) were used as the reference and counter electrode, respectively. Eventually, all of the electrochemical measurements were tested in a three-electrode system using an CHI760E electrochemical workstation (shanghai) with 6 M KOH solution as the electrolyte. The cyclic voltammetry (CV) measurements were performed the electrochemical properties of the samples in a voltage cutoff window of 0-0.6 V, which were carried out in a range of scan rate from 5 mV/s to 50 mV/s. Galvanostatic charge/discharge (GCD) measurements were employed to calculate the specific capacitance of the prepared materials in a voltage cutoff window of 0-0.4 V. Electrochemical impedance spectroscopy (EIS) was used to prove the conductivity properties in 6 M KOH solution within the frequency range from 0.05 Hz to 100 kHz. The cycling stability of the working electrode was performed by the galvanostatic charge/discharge measurement during 2000 cycles at a current density of 3 A/g. The specific capacity of the electrode was calculated on the basis of the galvanostatic charge/discharge curve by using the following equation:

$$C_s = \frac{I \times t}{m \times \Delta V} \qquad (4)$$

Where C_s (F/g) is the specific capacity of the working electrode, *I* represents the discharging current density (A), t is the discharging time (s), m (g) is the mass of the products used for the preparation of the electrode and ΔV (V) expresses the change of potential during the course of discharge.

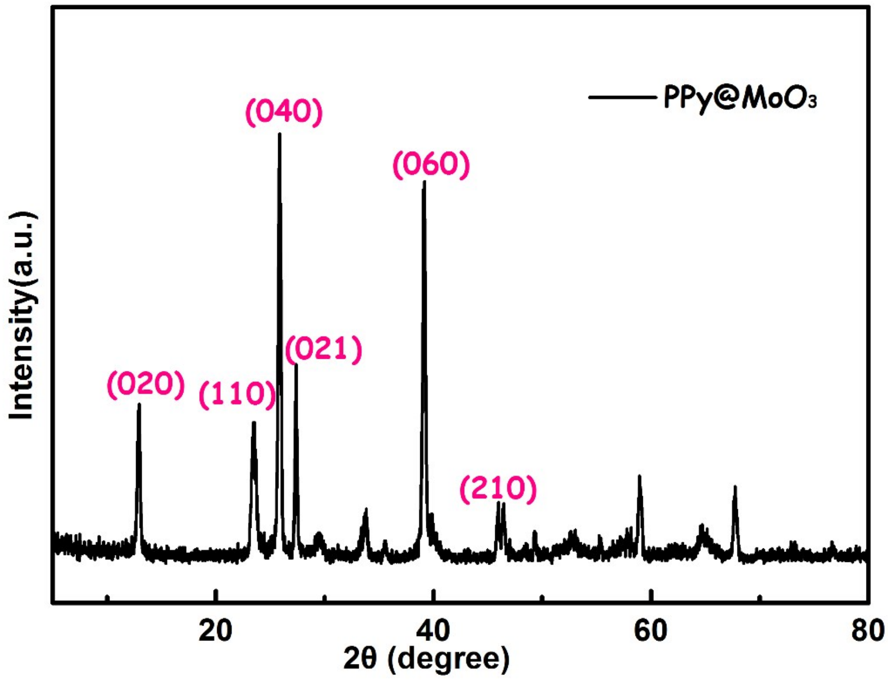

Fig.S1 The XRD pattern of PPy@MoO$_3$.

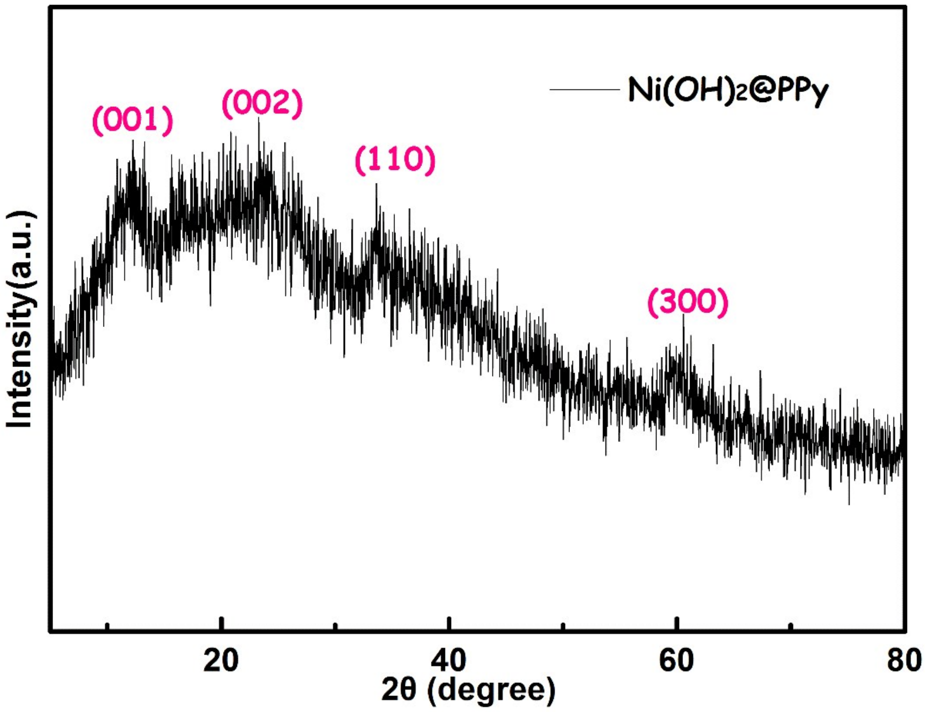

Fig.S2 The XRD pattern of Ni(OH)$_2$@PPy.

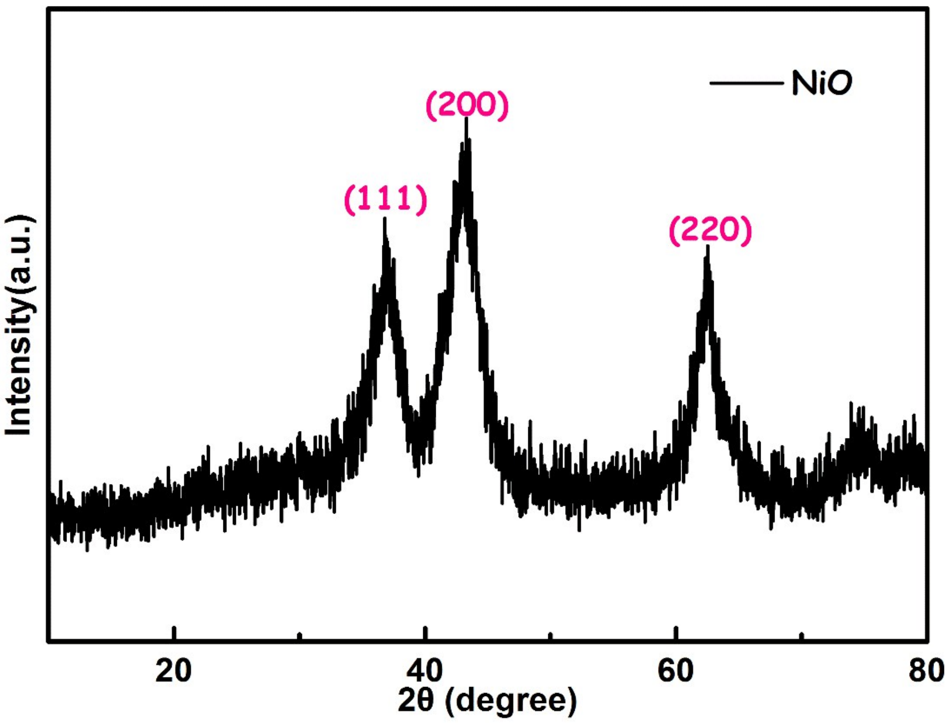

Fig.S3 The XRD pattern of NiO.

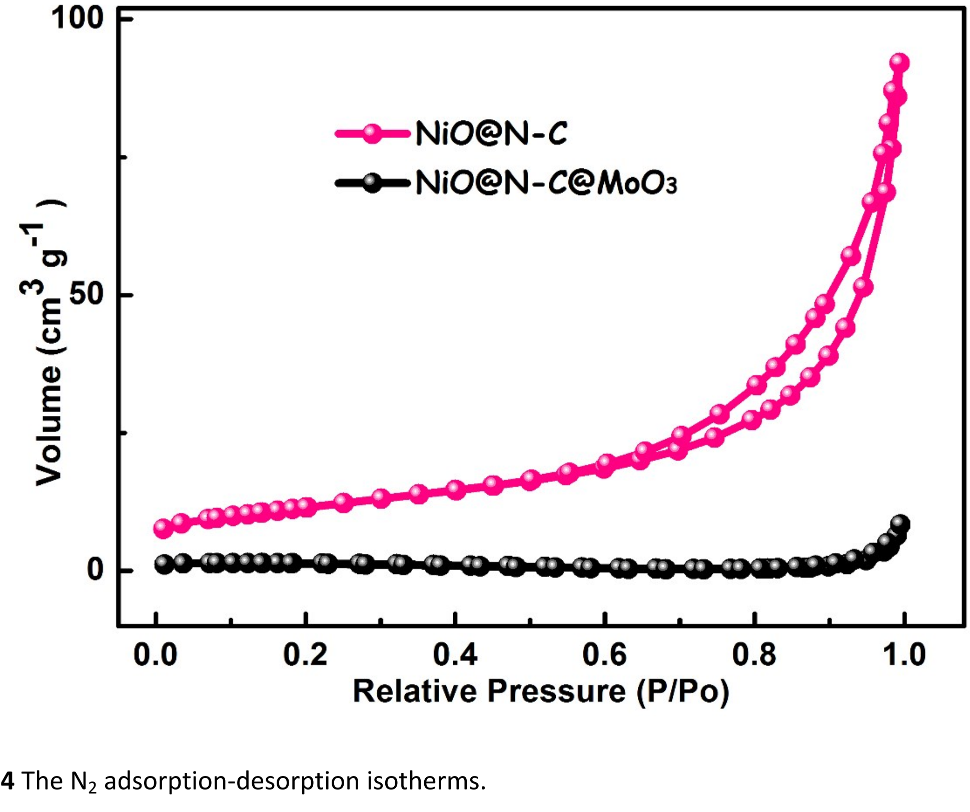

Fig.S4 The N_2 adsorption-desorption isotherms.

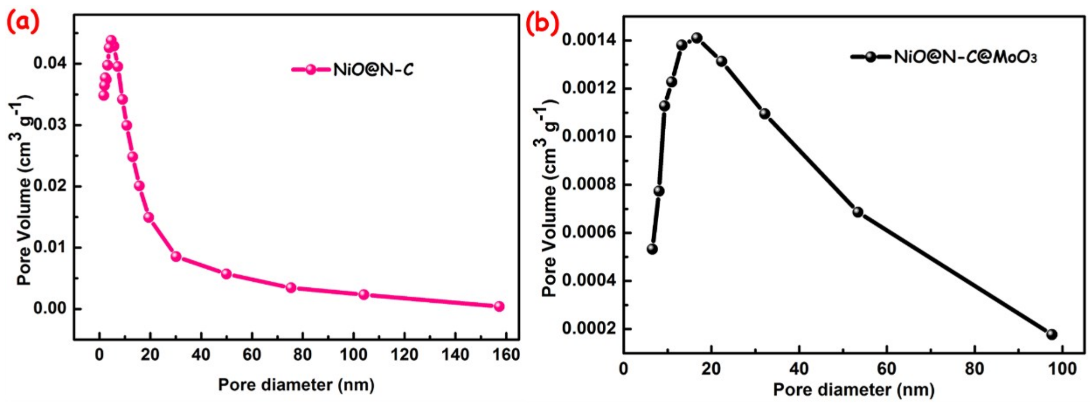

Fig.S5 (a) The pore distribution of NiO@N-C composite. (b) The pore distribution of NiO@N-C@MoO$_3$ sample.

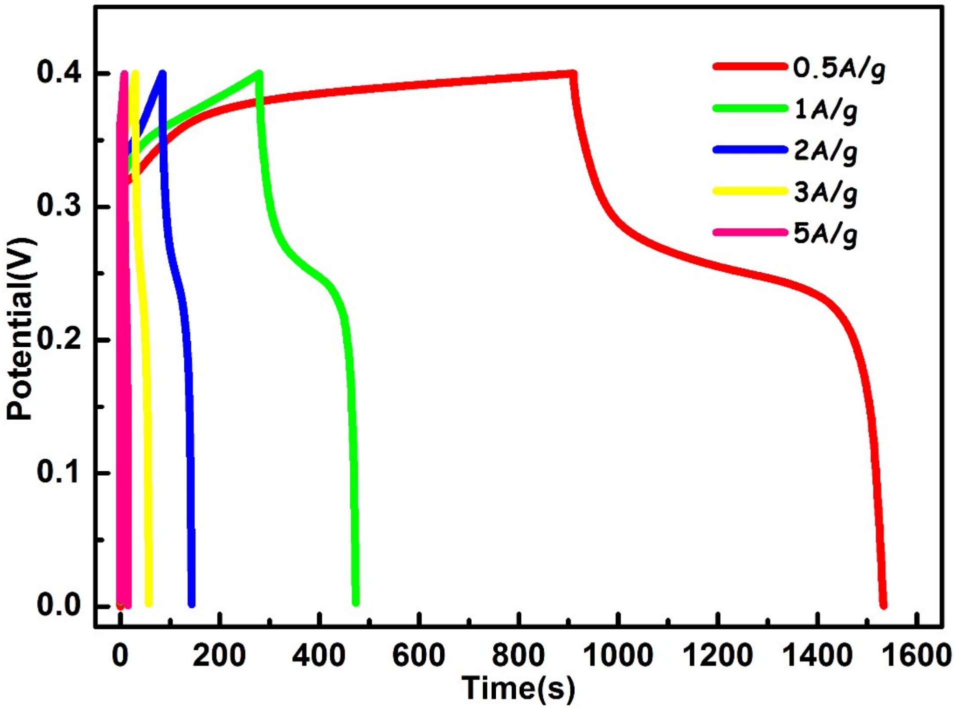

Fig.S6 The GCD curves of the as-prepared NiO@N-C composite electrodes at different current density.

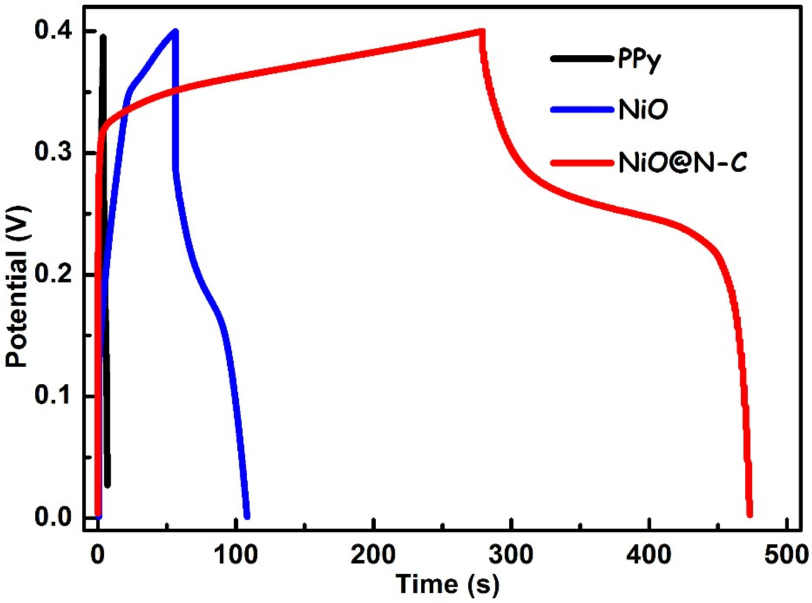

Fig.S7 Comparison between the GCD curves of the pure PPy, NiO and NiO@N-C composite electrodes at a current density of 1 A/g.

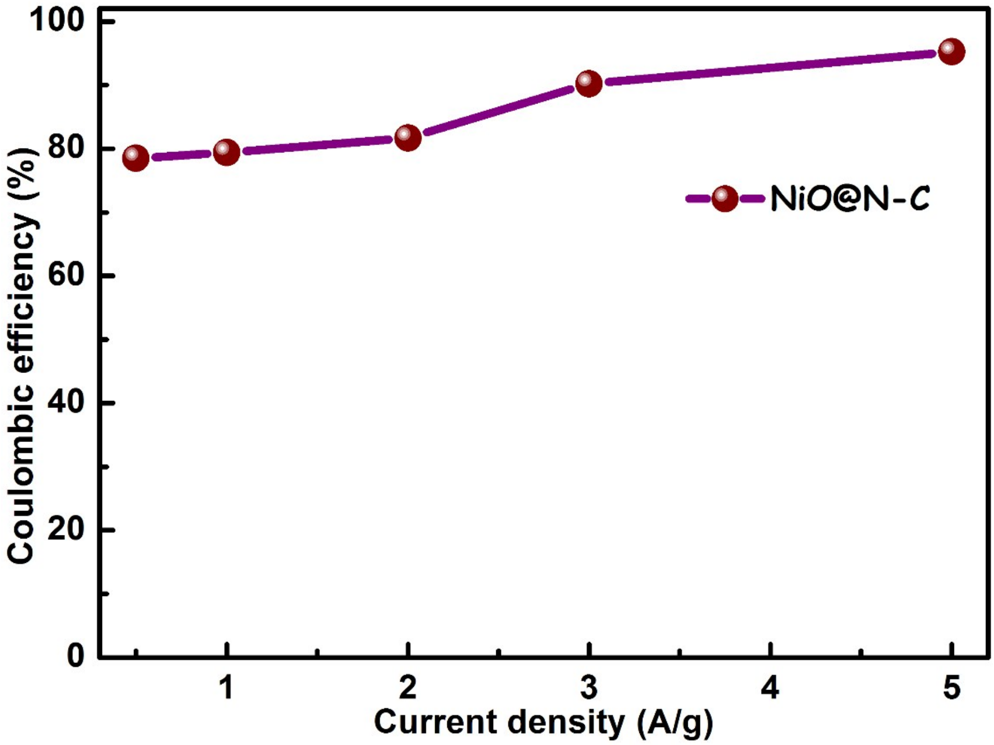

Fig.S8 Coulombic efficiency of NiO@N-C electrode.

Table S1. Comparison of NiO-based and carbon materials for supercapacitors.

samples	electrolyte	Voltage (V)	current density	capacitance (F/g)	capacitance retention	Ref.
NiO/C-HS	2M KOH	0.45	1 A/g	686	83%	[3]
NiO hollow nanospheres	2M KOH	0.7	0.5 A/g	612	90%	[4]
NiO/PCNF	6M KOH	0.4	1 A/g	850	96.7%	[5]
NiO@C/graphene	2M KOH	0.5	1 A/g	408	68%	[6]
RGO/NiO	6M KOH	0.5	0.8 A/g	689	86.3%	[7]
NiO@N-C	6M KOH	0.4	0.5 A/g	782	89.8%	**This work**

Notes and references

1. F. X. Ma, H. B. Wu, B. Y. Xia, C. Y. Xu and X. W. Lou, *Angew. Chem. Int. Edit.*, 2015, **54**, 15395-15399.
2. N. A. Alhebshi, R. B. Rakhi and H. N. Alshareef, *J. Mater. Chem. A.*, 2013, **1**, 14897.
3. T. Liu, L. Zhang, B. Cheng, W. You and J. Yu, *Chem. commun.*, 2018, **54**, 3731-3734.
4. Z. Yang, F. Xu, W. Zhang, Z. Mei, B. Pei and X. Zhu, *J. Power. Sources.*, 2014, **246**, 24-31.
5. Q. Li, J. Guo, D. Xu, J. Guo, X. Ou, Y. Hu, H. Qi and F. Yan, *Small.*, 2018, **14**, e1704203.
6. L. Yu, G. Wang, X. Peng, Z. Dou, X. Li, K. Wang, S. Lin and G. Wang, , *RSC. Adv.*, 2016, **6**, 14199-14204.
7. C. Lamiel, V. H. Nguyen, D. Tuma and J.-J. Shim, *Mater. Res. Bull.*, 2016, **83**, 275-283.