Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Electronic Supplementary Information

Highly dispersed carbon nanotube/ polypyrrole core/shell composite with improved electrochemical capacitive performance

Experimental section

Materials

CNT (outside diameter: 20-30 nm, length: 10-30 μm) was purchased from XFNano Materials Tech Co. (China). Pyrrole (AR) and hydrogen peroxide (H_2O_2, 30%, AR) were purchased from Sinopharm Chemical Reagent Co. (China). $FeCl_2$ and hydrazine hydrate (80%, AR) were purchased from Shanghai Chemical Reagent Co. (China). Deionized water was applied for all polymerization and reaction processes.

Synthesis of CNT/PPy hybrids

The CNT powder was dispersed in water by stirring and ultrasonication (1 mg mL^{-1}). CNT/PPy composites were prepared by using in situ polymerization of pyrrole with CNT. The weight feed ratio of CNT to PPy was varied as 4:1, 2:1, 1:1, 1:2 and 1:4. In a typical synthetic procedure for 1:1 hybrids, 100 mg CNT was dispersed in 100 mL H_2O by ultrasonication, the obtained CNT dispersion was mixed with 0.1mL pyrrole monomer and 0.01g $FeCl_2$. In situ polymerization was initiated with the addition of 0.5 mL H_2O_2 to the mixture and lasted for 6 h during a vigorous stirring. The products were concentrated by centrifugation and sequentially washed with water several times to remove unused reactants and reaction byproducts, then dispersed in distilled water at a concentration of 0.1% wt.

Characterization

Transmission electron microscopy (TEM) images were obtained with a JEM 2100 high-resolution TEM. High-resolution Transmission electron microscopy (HRTEM) images were obtained with a FEI Tecnai F30 operated at 200 kV. Scanning electron microscopy (SEM) imaging was performed on a JEOL-JSM-7600F SEM. Raman analysis was performed with a Jobin Yvon HR800. Zeta

potential was recorded on a Malvern Nano-Z Instrument. X-ray photoelectron spectroscopy (XPS) measurements are performed on a PHI 5000 VersaProbe. All electrochemical characteristics were evaluated by cyclic voltammetry (CV) and galvanostatic charge/discharge measurements on a CHI660d (Shanghai CH Instrument Company, China). The electrochemical cell used was a conventional three-electrode cell with a bare or modified glassy carbon electrode (GCE; diameter=3mm) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as the counter electrode in 1 M KCl solution. The electrochemical performance was also evaluated by two-electrode cell. The electrode was prepared by pressing the mixture of CNT/PPy, carbon black, polytetrafluoroethylene (PTFE) with a mass ratio of 85:10:5 onto Ni foam at a pressure of 30 MPa. A polypropylene film in a 1 mol/L aqueous KCl electrolyte solution was used as a separator. The symmetrical button cell was assembled according to the order of electrode-separator-electrode. Galvanostatic charge/discharge measurements were run on from -0.2 V to 0.6 V at different current densities.

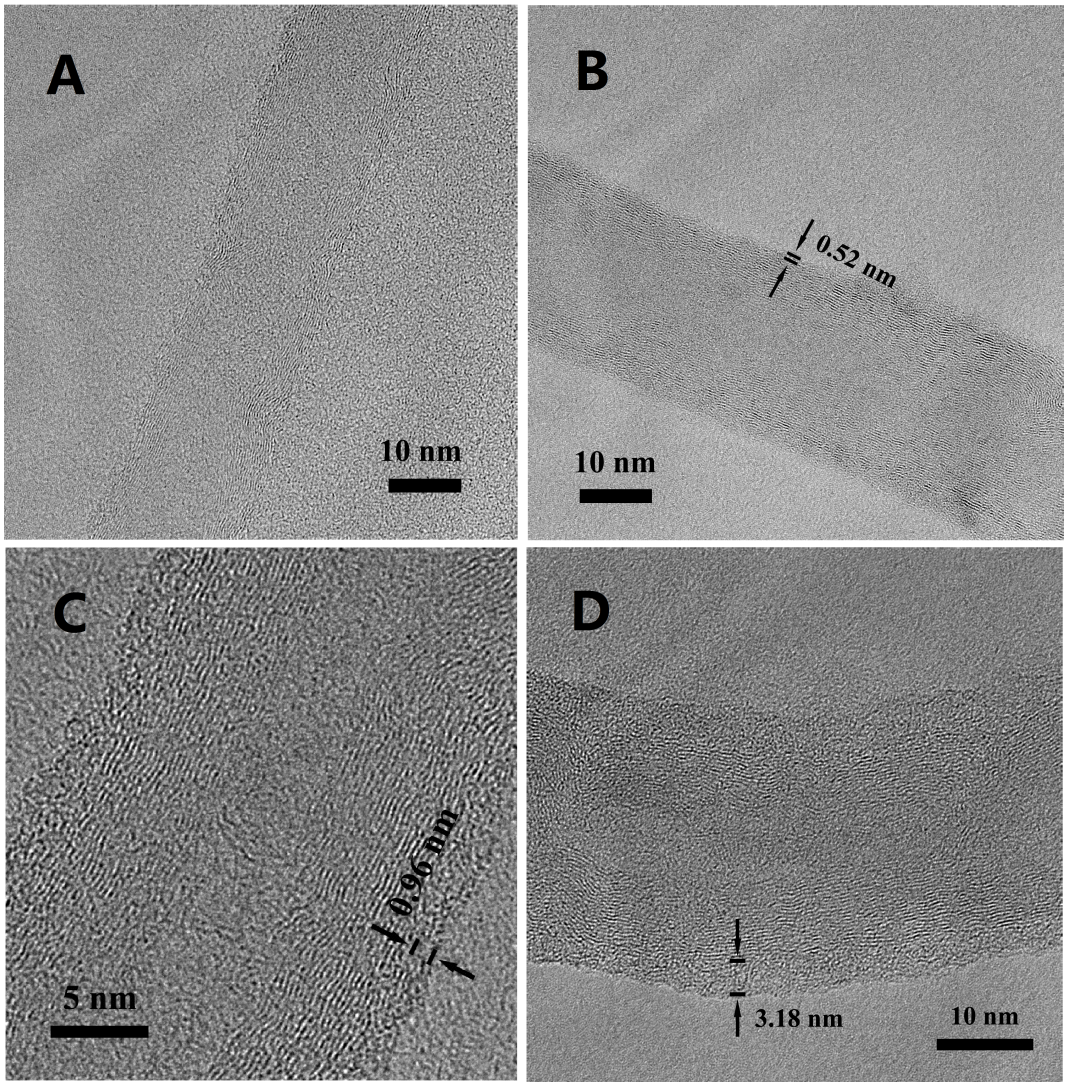

Fig. S1 HRTEM images of (A) pure CNT and CNT/PPy core/shell composite with weight ratio of (B) 4:1, (C) 2:1, and (D) 1:2 respectively.

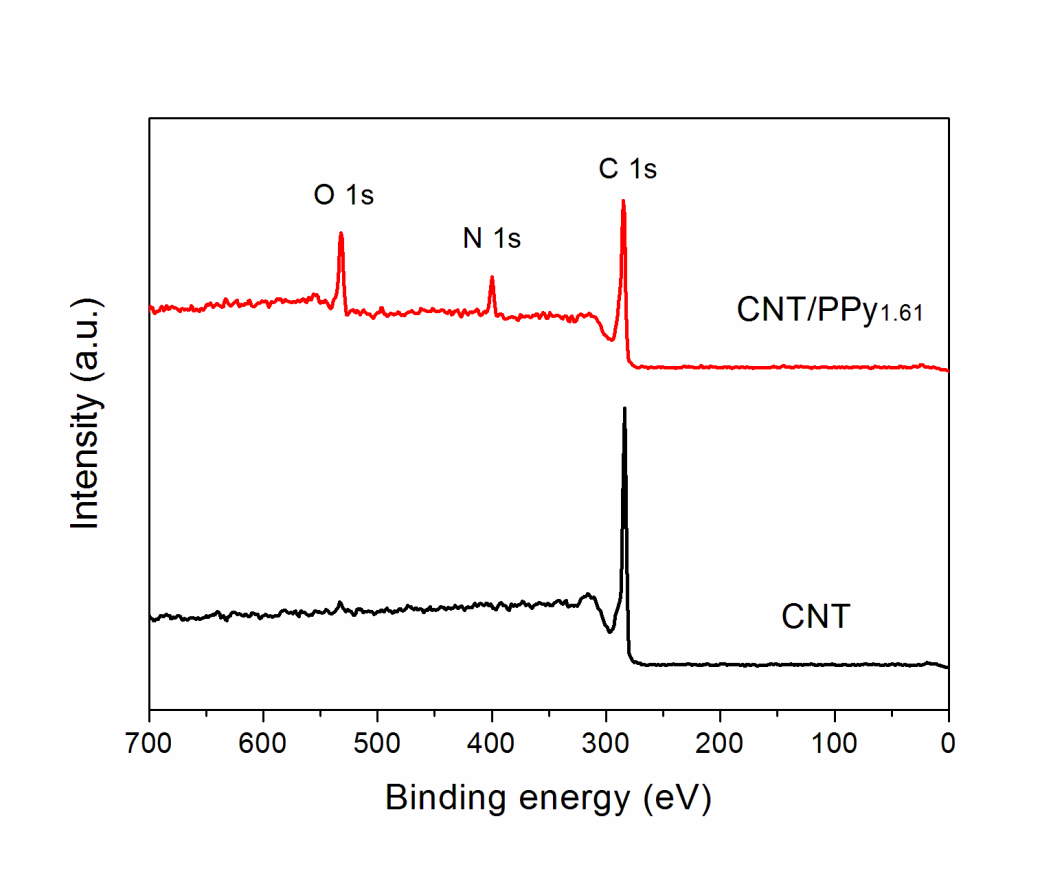

Fig. S2 XPS spectra of the pristine CNT and prepared CNT/$PPy_{1.61}$ composite.

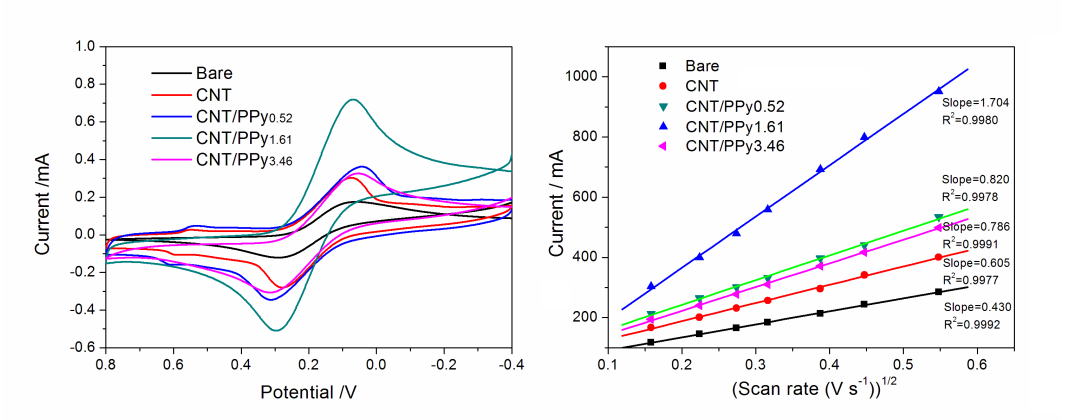

Fig. S3 (A) Cyclic voltammograms of bare GCE, CNT, CNT/$PPy_{0.52}$, CNT/$PPy_{1.61}$ and CNT/$PPy_{3.46}$ modified GCE in a 10 mM $[Fe(CN)6]^{3-/4-}$ and 0.1 M KCl solution at a scan rate of 100 mV s^{-1}, (B) Peak currents as a function of scan rate for the determination of the effective working surface area.

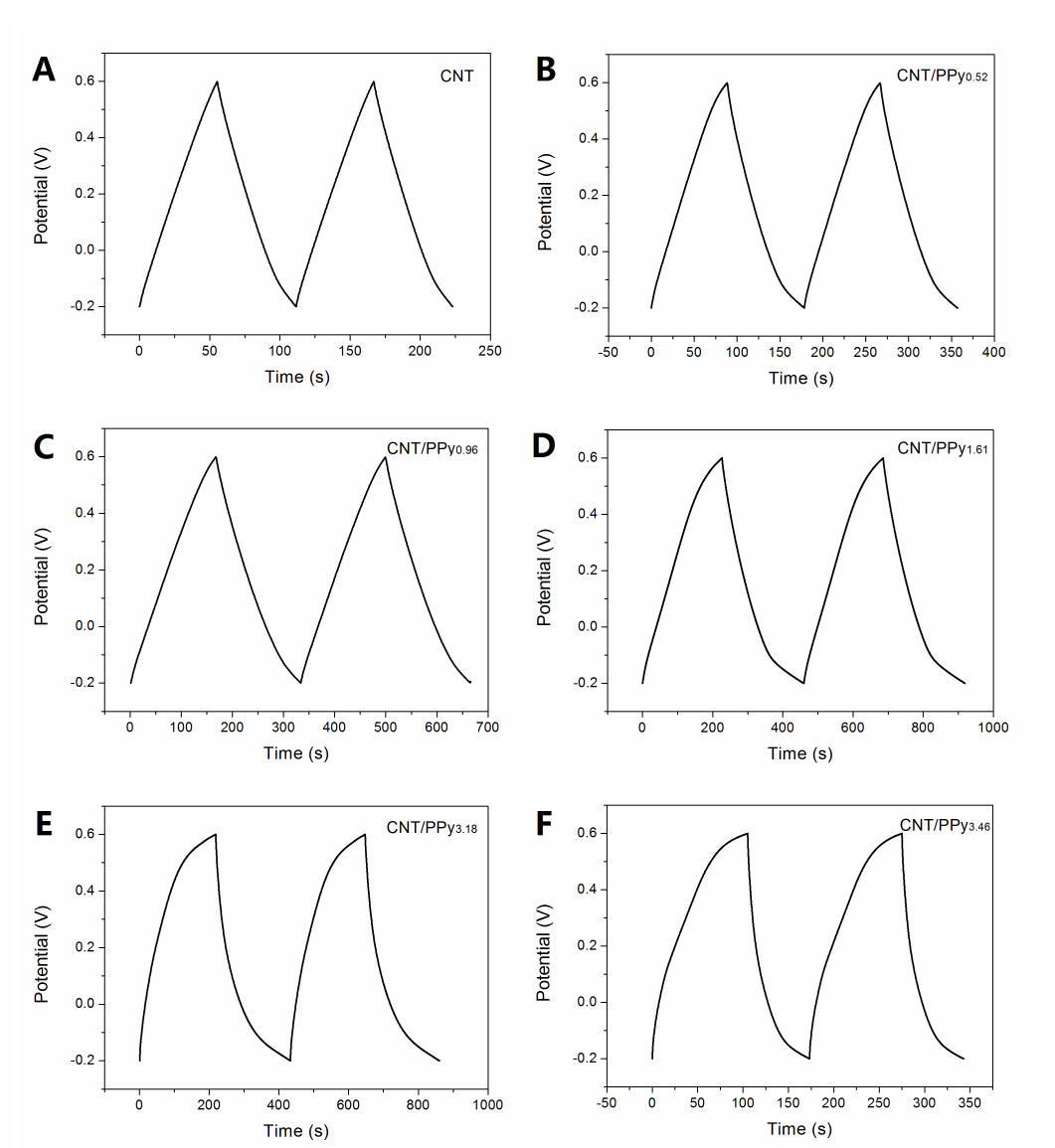

Fig. S4 Galvanostatic charge/discharge curves of (A) pure CNT and (B, C, D) CNT/PPy core/shell composites modified electrodes at a current density of 1 A g^{-1} in 1.0 M KCl solution.

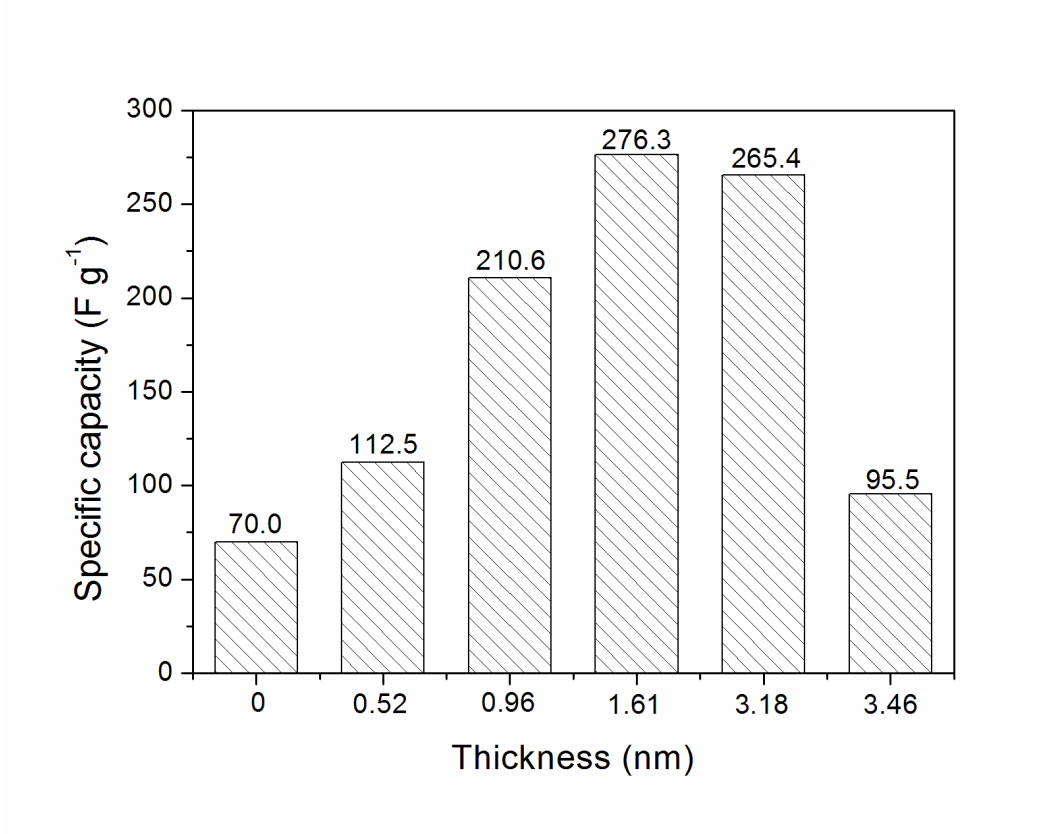

Fig. S5 The specific capacitance of CNT/PPy composites with different thickness of PPy shell.

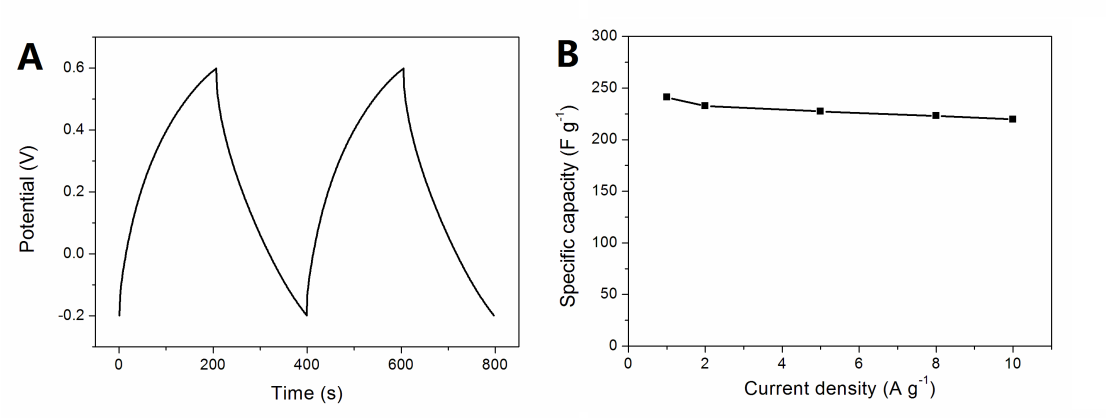

Fig. S6 (A) Galvanostatic charge/discharge curves of CNT/$PPy_{1.61}$ core/shell composite evaluated by two-electrode cell. (B) The specific capacitances of CNT/ $PPy_{1.61}$ composite at different current densities.

Table S1 Sample names of CNT/PPy composites with different thickness of decorated PPy shell.

Weight feed ratio of CNT to PPy	4:1	2:1	1:1	1:2	1:4
Thickness of PPy shell (nm)	0.52	0.96	1.61	3.18	3.46
Sample name	CNT/PPy$_{0.52}$	CNT/PPy$_{0.96}$	CNT/PPy$_{1.61}$	CNT/PPy$_{3.18}$	CNT/PPy$_{3.46}$

Table S2 Zeta potential data of pristine CNT and CNT/PPy core/shell composites.

	CNT	CNT/PPy$_{0.52}$	CNT/PPy$_{1.61}$	CNT/PPy$_{3.46}$
Zeta potential (mV), pH=7.0	−8.9	−33.8	−34.2	−34.2

Table S3 Comparison of the proposed CNT/PPy composite with other capacitor materials.

capacitor materials	specific capacitance		References
	Three-electrode	Two-electrode	
PPy/MWNTs [a]	250	190	1
PPy/MWCNT [b]	--	165	2
NC-CNTs@PPy [c]	205	--	3
GN-PPy/CNT [d]	211	--	4
CNT/PPy	276	241	This work

[a] polypyrrole/multiwalled carbon nanotubes. (Electroconducting PPy was deposited on MWNTs by chemical polymerization of pyrrole with $FeCl_3$ in HCl aqueous solution.)

[b] polypyrrole/multi-walled carbon nanotube. (PPy/MWCNT composites were synthesized in water, dichloromethane and *n*-hexane solvents.)

[c] nitrogen-doped carbon layer coated carbon nanotubes coated with a polypyrrole layer. (NC-CNTs were prepared by using a simple two step procedure of in situ polymerization of pyrroles onto CNTs and subsequent carbonization, without using template removal and activation treatment.)

[d] graphene-polypyrrole/carbon nanotube nanocomposite. (Unique flexible films with PPy/CNT composite homogeneously distributed between graphene GN sheets are successfully prepared by flow-assembly of the mixture dispersion of GN and PPy/CNT.)

Reference

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