Supporting information:

Connecting Carbon Nanotubes to Polyoxometalate Clusters for Engineering High-Performance Anode Materials**

Wei Chen, Lujiang Huang, Jun Hu, Feifei Jia and Yu-Fei Song*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, 100029 Beijing, China.

Experimental Section. All reagents were obtained from Alfa Asear Company and used as received unless otherwise noted. The CNTs were purchased form *Chengdu Organic Chemistry Co. LTD, Chinese Academy of Science.* The detailed information of the CNTs are as follows: Purity>99.9wt%, ID: 5-10 nm, OD: 20-30 nm, Length: 10-30 μm, SSA: >110 m^2/g, ASH: <1.5 wt%, Bulk density: 0.28 g/cm^3, True density: ~2.1 g/cm^3, EC:> 100s/cm, Making method: CVD, Color: Black.

Measurements. FT-IR spectroscopy was measured using KBr pellets and recorded on a NICOLET 6700 (Thermo) instrument. ^{1}H-NMR, ^{13}C-NMRspectra were recorded on a Bruker AV400 NMR spectrometer at room temperature (298K), and the chemical shifts were given relative to TMS as the internal reference. C, H, N elemental analysis was performed on a Vario EL cube from Elemental Analysis system GmbH. Electrospray ionization mass spectrometry (ESI-MS) was obtained on Xevo G2 Q-TOF. Scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) analytical data were obtained using a Zeiss Supra 55 SEM equipped with an EDX detector. High resolution TEM (HRTEM) was conducted on JEOL JEM-2100 under an accelerating voltage of 400 kV. Thermogravimetric (TG) and differential thermal analyses (DTA) were acquired using a TG/DSC 1/1100 SF from METTLER TOLEDO in flowing N_2 with a heating rate of 10 $^oC \cdot min^{-1}$. Raman spectra were measured on a Renishaw Raman spectrometer at a laser excitation wavelength of 633 nm. Fluorescence spectra were recorded on a Hitachi F-7000 luminescence spectrometer with a Xe lamp as the excitation source.

Battery analyses of CNTs-SiW_{11}. The as-prepared CNTs-SiW_{11} nanocomposite was used as an anode material for rechargeable lithium-ion batteries. Electrochemical measurements were carried out using coin-type cells. The lithium battery is a coin cell with 2 cm in diameter. For preparing working electrode, a mixture of CNTs-SiW_{11}, carbon black, and poly(vinylidene fluoride) (PVDF) at a weight ratio of 30:50:20 was pasted on a Cu foil. The electrode was dried in vacuum. The testing coin cells were assembled in an argon-filled glove box with the working electrode as-fabricated, metallic lithium foil as a counter electrode, and 1 M $LiPF_6$ in solution of 1:1 v/v ethylene carbonate (EC)/diethyl carbonate (DEC) as the electrolyte. Galvanostatic charging/discharging measurements were performed in a potential range of 0-3 V *vs.* Li/Li^+ using a LAND-CT2001A test system at room temperature. The cells were assembled in an argon-filled glove box. The specific charge/discharge capacities were calculated based on the whole composite material.

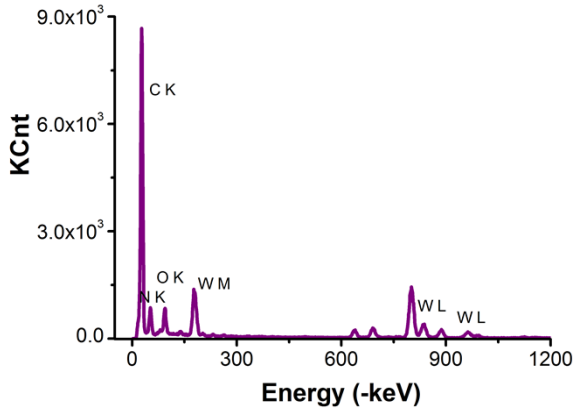

Figure S1. EDX spectrum of CNTs-SiW_{11} shows the presence of W, C, O etc.

Table S1. Electrochemical parameters of electrode materials consisting of POMs or POM-CNTs-based nanocomposites

Type	Electrode Type	Current Rate	Residual reversible capacity ($mAhg^{-1}$)	Ref.
Cathode	$K_3[PMo_{12}O_{40}]$	0.05 mA	160	S1
	$K_4[SiMo_{12}O_{40}]$	0.05 mA	163	S2
	$K_{5.72}H_{3.28}[PV_{14}O_{42}]$	0.05 mA	212	S3
	$TBA_3[PMo_{12}O_{40}]$-Graphene	1.0 mA	140	S4
	$TBA_3[PMo_{12}O_{40}]$-SWNT	1.0 mA	320	S5
Anode	$TBA_2[Mo_6O_{18}$-N-Ph-(*o*-CH3)2-*p*-SCN]	50 mA g^{-1}	876	24
	$TBA_4[Py\text{-}SiW_{11}]$-SWNTs	0.5 mA cm^{-2}	580	7a
	CNTs-SiW_{11}	0.5 mA cm^{-2}	650	This work

Note: PANI: polyaniline

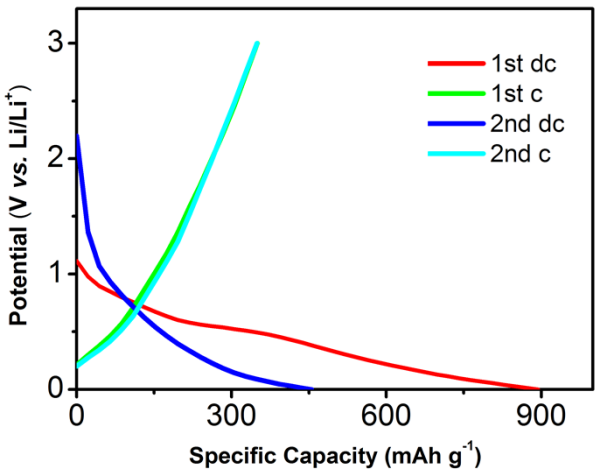

Figure S2. The 1st and 2nd charge and discharge curves of the physical mixture of CNTs and SiW_{11} ; current density is 0.5 mA cm^{-2}.

References:

[S1] N. Sonoyama, Y. Suganuma, T. Kume, Z. Quan, *J. Power Sources*., 2011, 196, 6822–6827.

[S2] E. Ni, T. Kume, S. Uematsu, Z. Quan, N. Sonoyama, *Electro. Soc. Jap*., 2014, 82, 14-18.

[S3] S. Uematsu, Z. Quan, Y. Suganuma, N. Sonoyama, *J. Power Sources*., 2012, 217, 13-20.

[S4] K. Kume, N. Kawasaki, H. Wang, T. Yamada, H. Yoshikawa, K. Awaga, *J. Mater. Chem. A*., 2014, 2, 3801-3807.

[S5] (a) N. Kawasaki, H. Wang, R. Nakanishi, S. Hamanaka, R. Kitaura1, H. Shinohara, T. Yokoyama, H. Yoshikawa, K. Awaga, *Angew. Chem. Int. Ed*., 2011, 50, 3471-3474; (b) H. Wang, N. Kawasaki, T. Yokoyama, H. Yoshikawa, K. Awaga, *Dalton Trans*., 2012, 41, 9863–9866.

[S6] R. Naumaan, N. Khan, N. Mahmood, C. Lv, G. Simaa, J. Zhanga, J. Haoa, Y. Hou, Y. Wei, *RSC Adv*., 2014, 4, 7374-7379.