Supporting Information

Selective Separation of Single-Walled Carbon Nanotubes in Aqueous Solution by Assembling Redox Nanoclusters

Anquan Zhu[#], Xusheng Yang[#], Lei Zhang, Kun Wang, Tianhui Liu, Xin Zhao, Luyao Zhang, Lei Wang, Feng Yang*

Experiment Section

***Preparation of Cluster-SWCNT Hybrids*.** Tuball-SWCNTs (purity>90%, d_t=0.9–2.2 nm) were provided from the OCSiAl company. CoMo-SWCNTs were purchased from Sigma Aldrich (CG100, purity>89%, d_t=0.7–1.3 nm). $H_3PW_{12}O_{40}\cdot xH_2O$ was purchased from Meryer (Shanghai) Chemical Technology Co., Ltd. $Na_2WO_4\cdot 2H_2O$ was bought from Shanghai Aladdin Biochemical Technology Co., Ltd. $H_6P_2W_{18}O_{62}\cdot xH_2O$ and $K_{12}H_2P_2W_{12}O_{48}\cdot xH_2O$ were synthesized according to the reported methods. For a typical process of synthesizing the $\{PW_{12}O_{40}\}$@Tuball-SWCNTs, the raw SWCNTs were annealed in air at 420 °C for 5 min to open ends of nanotubes. For the synthesis of $\{PW_{12}O_{40}\}$-CoMo-SWCNTs, annealing process is not necessary. Then, the SWCNTs (40 mg) were mixed with aqueous $\{PW_{12}O_{40}\}$ solution (800 mg $\{PW_{12}O_{40}\}$/12 mL deionized water). The mixture was stirred for 4 days at room temperature. Then the $\{PW_{12}O_{40}\}$@SWCNTs were isolated by centrifugation and washed with deionized water for 10 times to remove $\{PW_{12}O_{40}\}$ clusters outside nanotubes. After drying at room temperature, the $\{PW_{12}O_{40}\}$@SWCNT hybrids were collected. Other types of clusters and salts ($H_6P_2W_{18}O_{62}\cdot xH_2O$, $K_{12}H_2P_2W_{12}O_{48}\cdot xH_2O$, and $Na_2WO_4\cdot 2H_2O$) within SWCNTs were carried out by the same method.

Dispersion of SWCNTs in DOC Aqueous Solution. DOC ($C_{24}H_{39}O_4Na$, 98%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd, and used to

disperse SWCNTs. Typically, 2 mg {$PW_{12}O_{40}$}@SWCNT hybrids were added into 20 mL 1 wt% DOC solution, followed with a sonication treatment by using a tip ultrasonicator (500 W in pulse mode with 2 s on/3 s off interval) for 80 min. After that, the resulting suspension was centrifuged at 13000 *g* for 1 h to remove the precipitation of SWCNT bundles. Then the supernatant was collected for measurement. The pristine SWCNTs and other cluster@SWCNT hybrids were dispersed by 1 wt% DOC aqueous solution with the same method.

SEM and TEM Characterization. SEM images were recorded on a ZEISS Merlin SEM operating at 1.0 kV. HAADF-STEM images were collected from a FEI Titan I Titan Themis apparatus with an X-FEG electron gun and a DCOR aberration corrector operating at 300 kV. STEM-EDX mapping was performed on an FEI Talos F200X electron microscope with a HAADF detector and acceleration voltage of 200 kV. EDX was acquired from a Bruker super-X detection system.

Characterization of SWCNTs. UV-Vis-NIR absorption spectra were measured by using a Shimadzu UV-2600 spectrometer. The Raman spectra of the SWCNT and cluster@SWCNT aqueous dispersions were collected with a Jovin Yvon-Horiba LabRam HR evolution system (laser excitations: 532 and 785 nm). In addition, the SWCNT and {$PW_{12}O_{40}$}@SWCNT dispersion were deposited on Si/SiO_2 substrate to obtain individual nanotubes for Raman and AFM (Veeco diMutiMode V, operated at tapping mode) measurements.

RESULTS

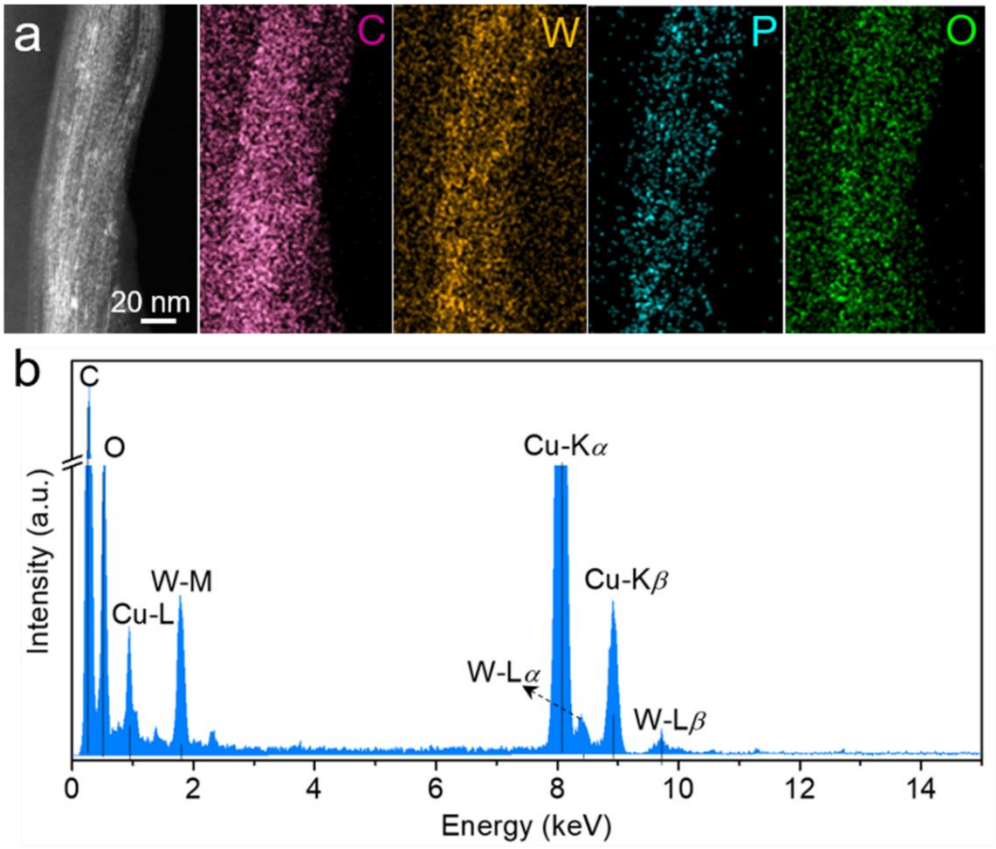

Figure S1. **a**, HAADF-STEM image of $\{PW_{12}O_{40}\}$@Tuball-SWCNTs and STEM-EDX elemental mapping. **b**, EDX spectrum.

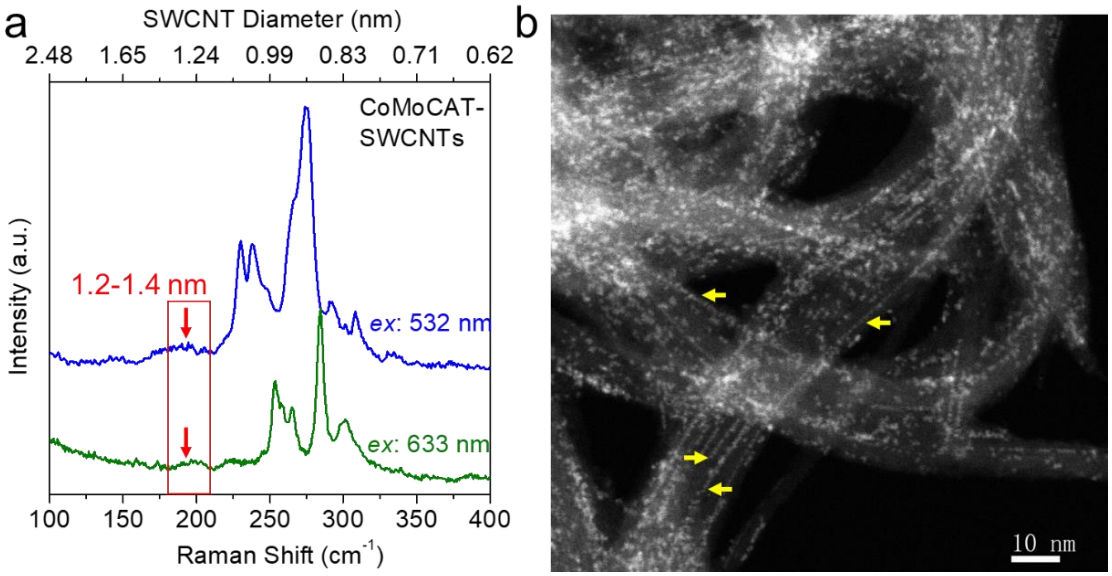

Figure S2. **a**, Raman spectra of pristine CoMo-SWCNTs (excitation wavelength: 532 nm and 633 nm). **b**, HAADF-STEM images of CoMo-SWCNTs with $\{PW_{12}O_{40}\}$. The cluster encapsulated within SWCNT as a linear structure was marked by arrows.

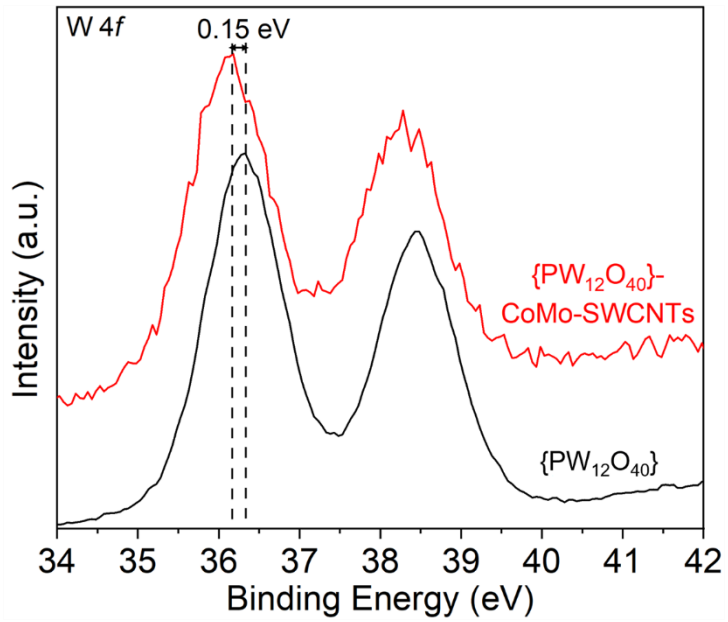

Figure S3. The XPS W *4f* spectra of $\{PW_{12}O_{40}\}$ and $\{PW_{12}O_{40}\}$-CoMo-SWCNT hybrid.

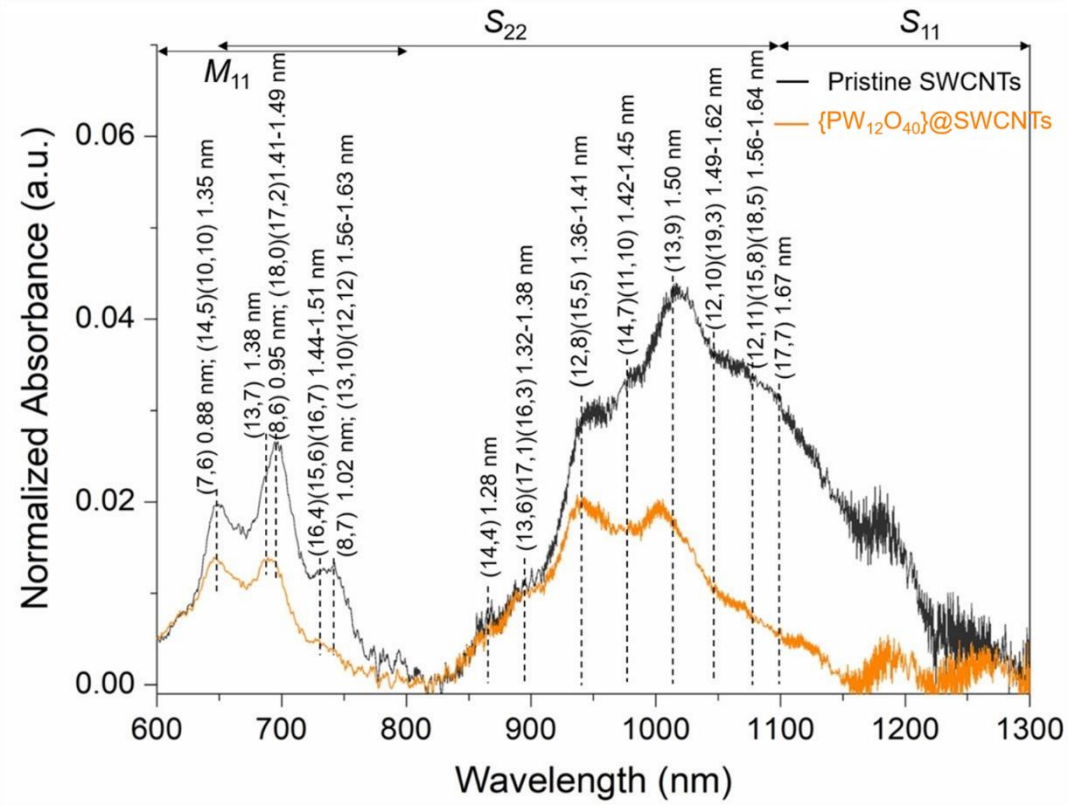

Figure S4. The possible chirality assignment of DOC-dispersed Tuball-SWCNTs.

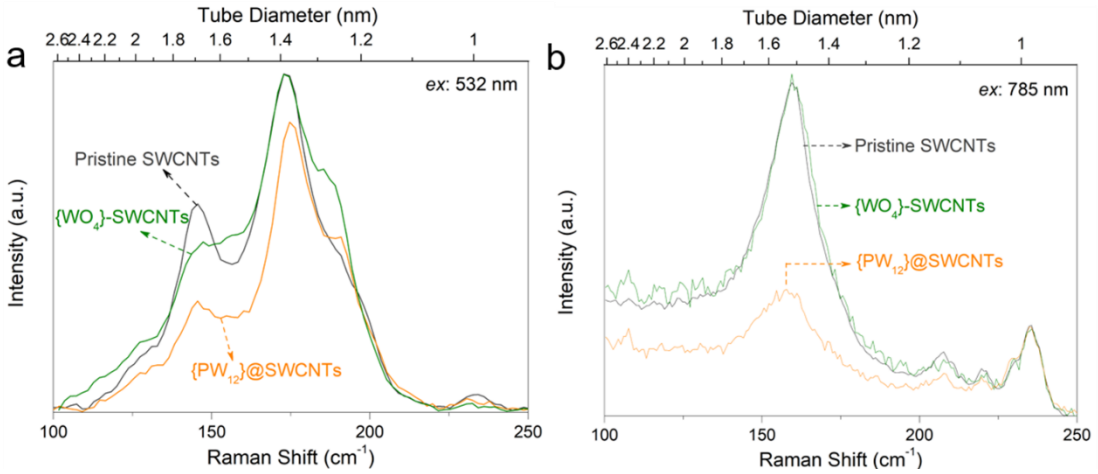

Figure S5. **a**, **b**, Raman spectra of the dispersed pristine Tuball-SWCNTs and cluster@Tuball-SWCNTs showing RBM region (ω_{RBM}=214.4/d_t+18.7). Laser excitations: 532 nm (**a**), 785 nm (**b**). The pristine Tuball-SWCNTs were used as a reference. RBM region was normalized relative to the intensity of the smallest tube diameter, with RBM frequency at 230 cm^{-1}.

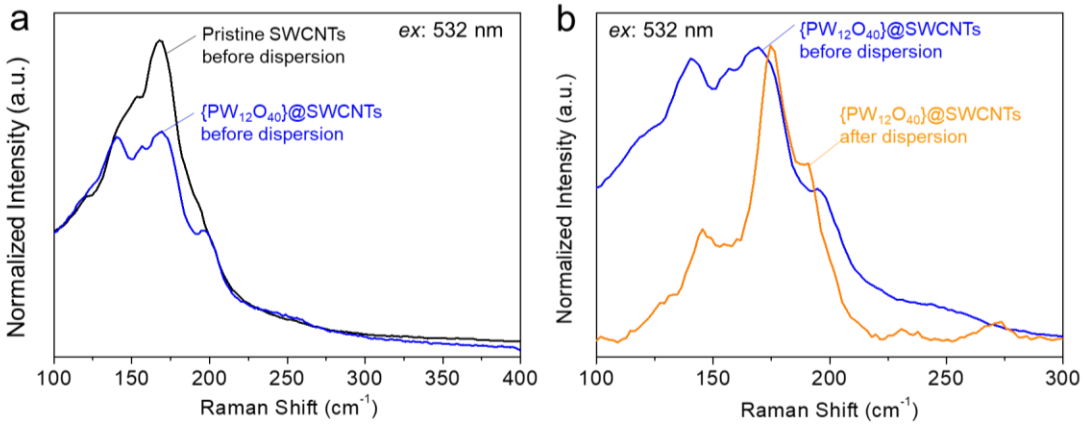

Figure S6. **a**, Raman RBM region of pristine and $\{PW_{12}O_{40}\}$ encapsulated Tuball-SWCNT powder samples before dispersion. **b**, Raman RBM region of $\{PW_{12}O_{40}\}$@SWCNTs before and after dispersion. The spectra were calibrated with respect to Si peak (302.5 cm^{-1}).

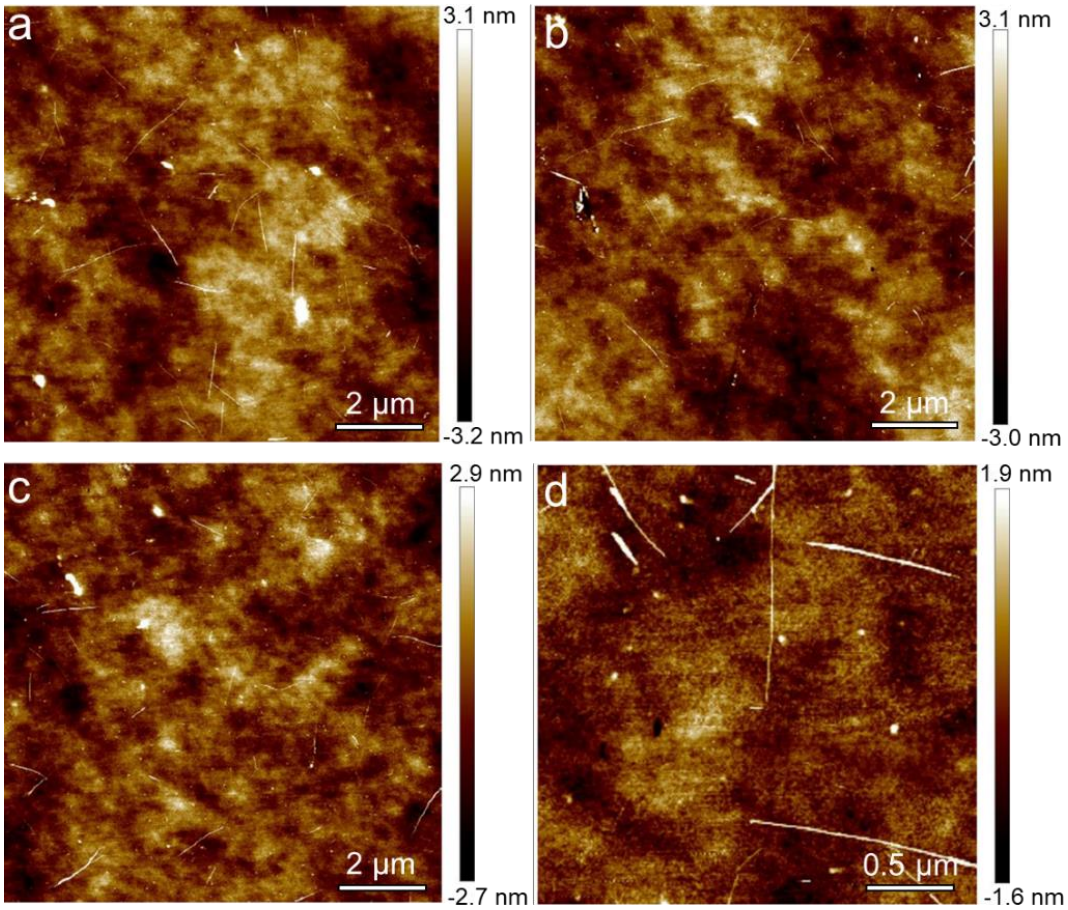

Figure S7. **a**–**d**, Atomic force microscopy images of dispersed $\{PW_{12}O_{40}\}$@Tuball-SWCNTs.

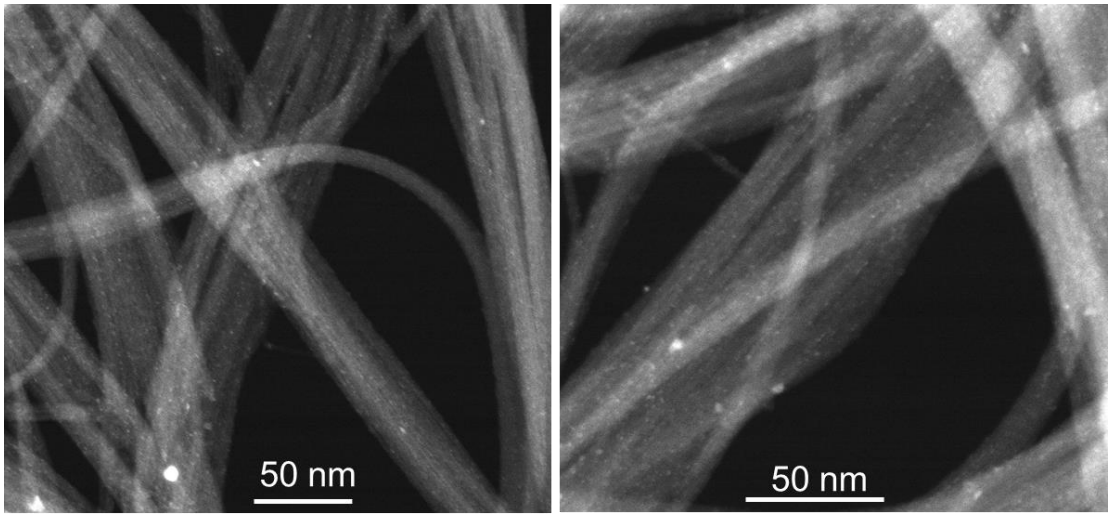

Figure S8. Typical HAADF-STEM images of WO_4^{2-}-Tuball-SWCNTs.

The smallest SWCNTs (d_{tube}) encapsulating a {PW_{12}} cluster can be estimimated by the following model (Fig. S9), where ionic bonding between O^{2-} of {PW_{12}} and C cation of graphene lattice is considered.

$$y \approx \text{ionic radius of } O^{2-} + \text{ionic radius of } C^{+} = 1.26\ \text{Å} + 0.95\ \text{Å} = 2.21\ \text{Å}$$

where ionic radius of C^+ (0.95 Å) is estimated based on the tropylium cation $(C_7H_7)^+$,

$$x = (y^2 - 1.42^2)^{1/2} = 1.69\ \text{Å}$$

$$d_{tube} = d_{cluster} + 2x = 10\ \text{Å} + 2 \cdot 1.69\ \text{Å} = 13.4\ \text{Å}$$

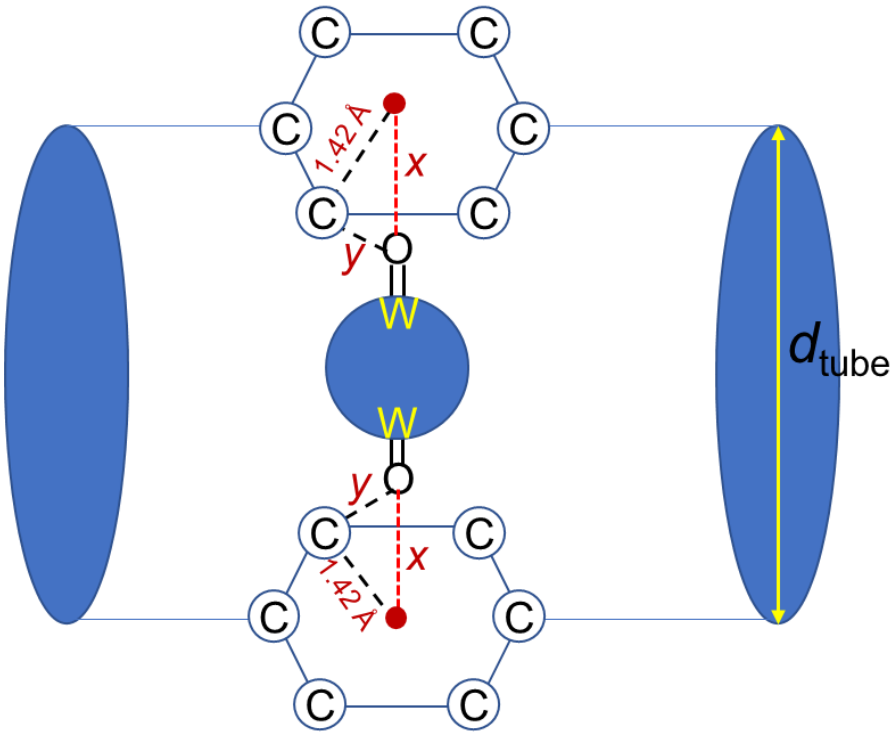

Figure S9. Model showing the eatimation of the smallest SWCNT encapsulating a $\{PW_{12}\}$ cluster.

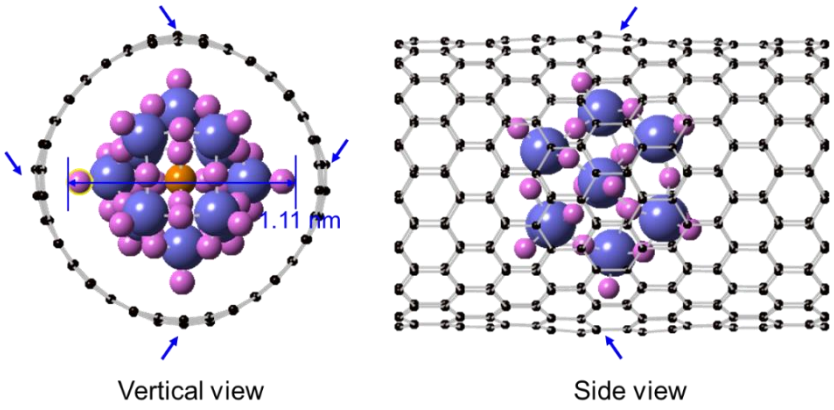

Figure S10. Vertical and side views of $\{PW_{12}O_{40}\}$@SWCNTs after DFT calculation. The distortion of SWCNT was marked by arrows.

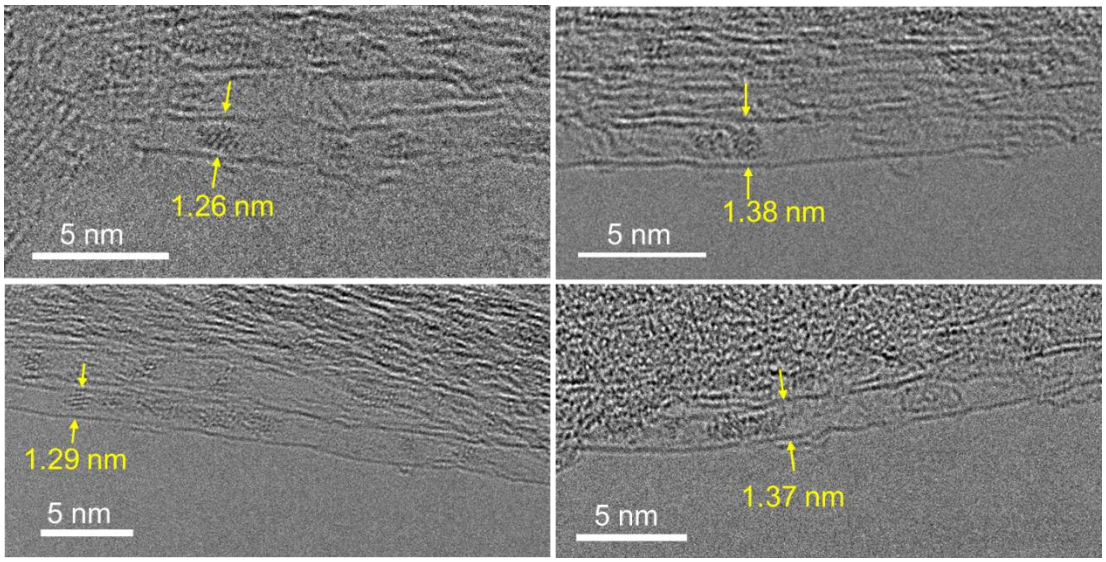

Figure S11. aberration-corrected TEM images of 1.26-1.38 nm SWCNTs encapsulating {PW_{12}} clusters.

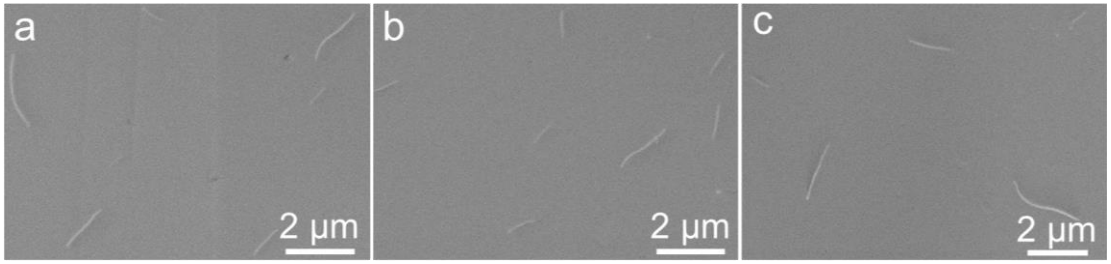

Figure S12. SEM images of individual dispersed {$PW_{12}O_{40}$}@Tuball-SWCNTs on Si/SiO_2 substrate. The sample was used to perform Raman at the single nanotube level.

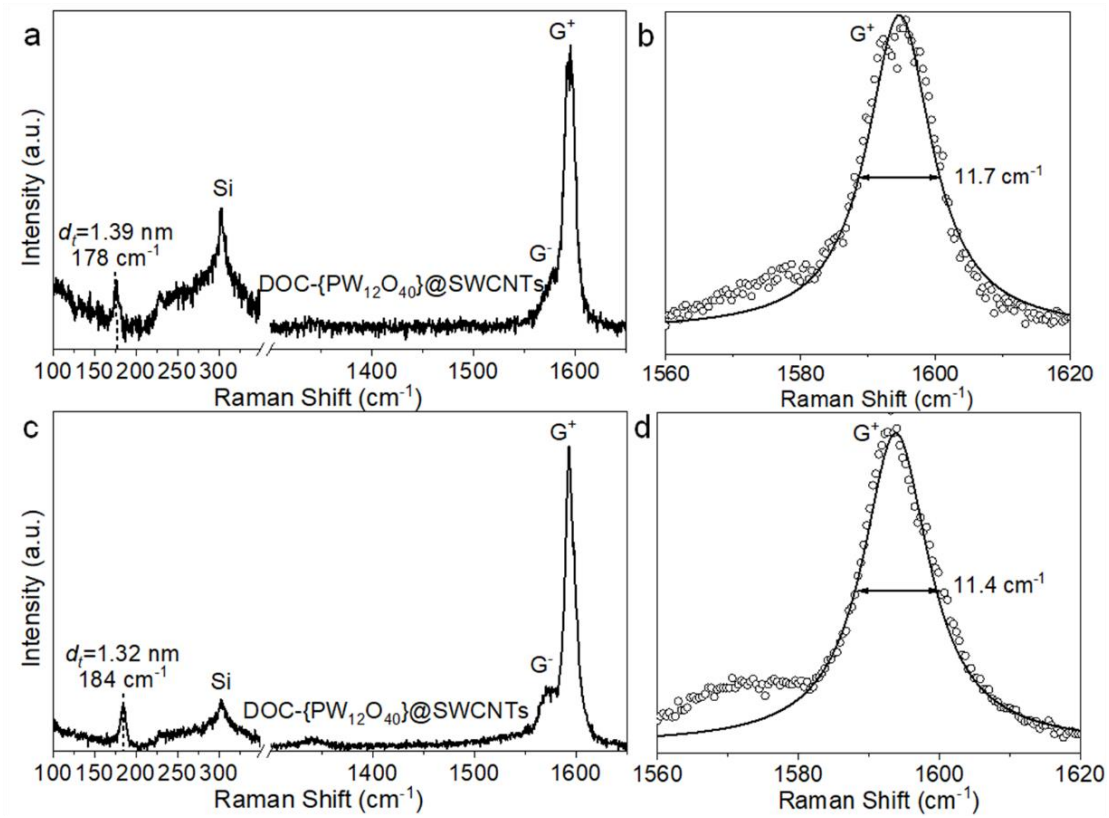

Figure S13. **a**–**d**, Raman spectra of individual $\{PW_{12}O_{40}\}$@Tuball-SWCNTs dispersed by DOC (**a**, **c**) and corresponding close-up view of *G* band region (**b**, **d**). Excitation: 532 nm.

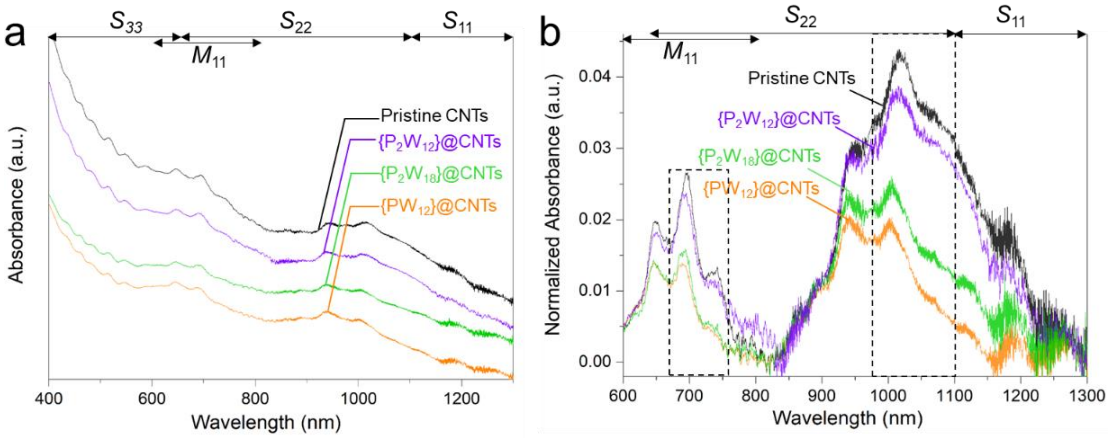

Figure S14. a, UV–Vis–NIR absorption spectra of DOC dispersed pristine SWCNTs and SWCNTs encapsulated with $\{P_2W_{12}O_{48}\}$, $\{P_2W_{18}O_{62}\}$, and $\{PW_{12}O_{40}\}$. **b**, The baseline-subtracted absorption spectra in the S_{11}, S_{22}, and M_{11} regions. The plot of $\{PW_{12}O_{40}\}$@CNTs and pristine CNTs in (**a**, **b**) were reproduced from Figure 3(a, b) in main text.

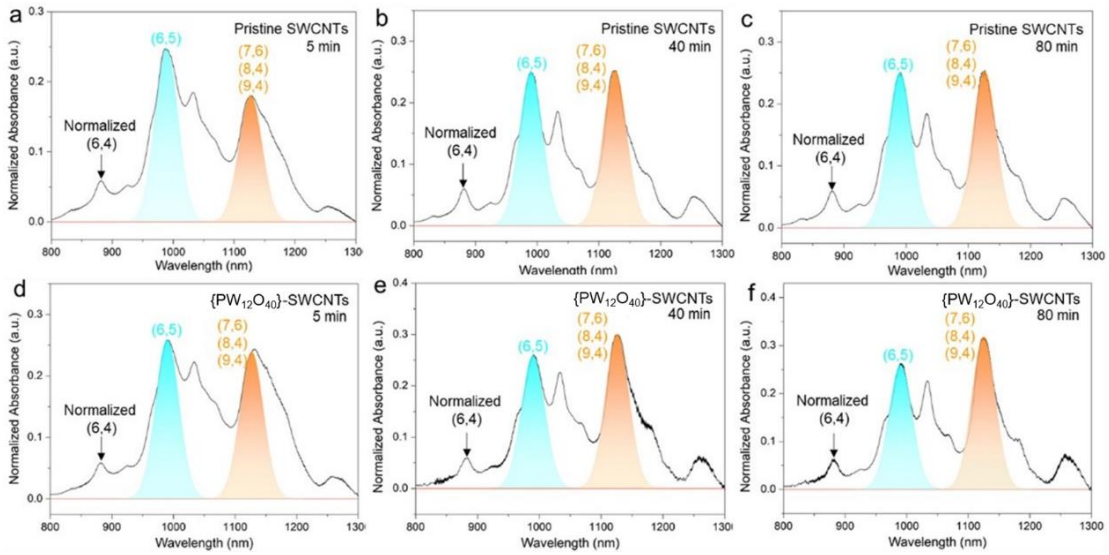

Figure S15. Absorption spectra (normalized at 880 nm) of sorted raw CoMo-SWCNTs and $\{PW_{12}O_{40}\}$-CoMo-SWCNTs with sonication time of 5, 40, and 80 min. The colored peaks were fitted with the same FWHM value of 45 cm^{-1}.

Table S1. The relative peak area of sorted raw CoMo-SWCNTs and $\{PW_{12}O_{40}\}$-CoMo-SWCNTs with the chirality of (8,4)(9,4)(7,6) and (6,5) with different sonication time (5, 40, and 80 min).

Sample	DOC dispersed raw CoMo-SWCNTs		DOC dispersed $\{PW_{12}O_{40}\}$-CoMo-SWCNTs	
Absorption band	989 nm	1126 nm	989 nm	1126 nm
(*n*,*m*)	(6,5)	(8,4)(9,4)(7,6)	(6,5)	(8,4)(9,4)(7,6)
Fitted peak area $A_{(n,m)}$ / Sonication time	$A_{(6,5)}$	$A_{(8,4)(9,4)(7,6)}$	$A_{(6,5)}$	$A_{(8,4)(9,4)(7,6)}$
5 min	11.88	8.66	12.43	11.46
40 min	12.00	12.11	12.43	14.41
80 min	12.01	12.12	12.44	15.22

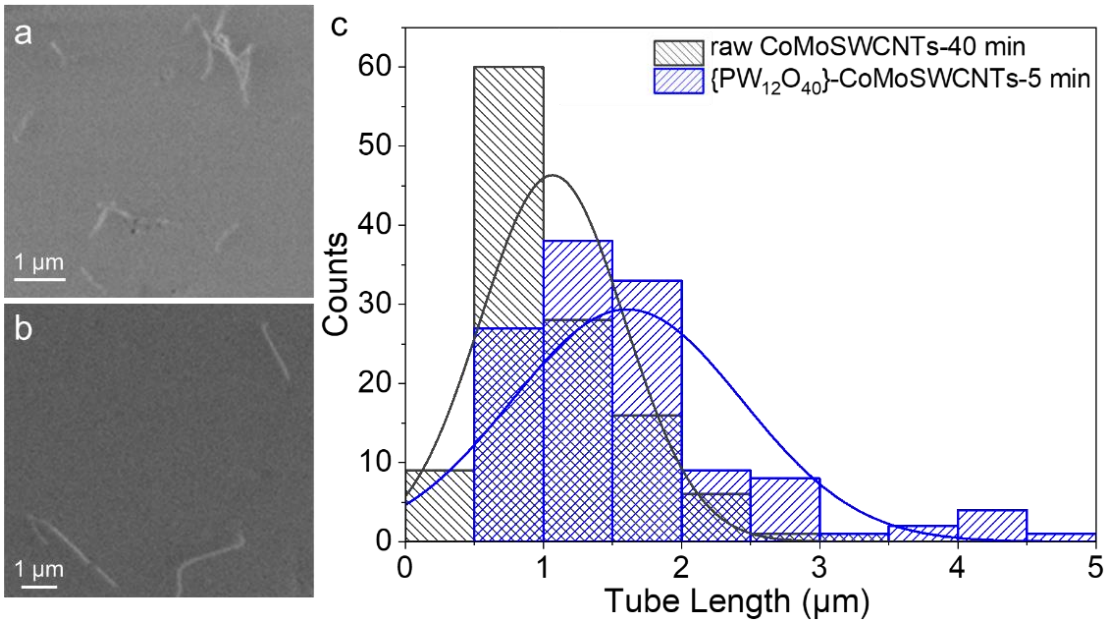

Figure S16. **a**, **b**, SEM images of $\{PW_{12}O_{40}\}$-CoMo-SWCNTs with 5 min sonication (**a**) and CoMo-SWCNTs with 40 min sonication (**b**) deposited on SiO_2/Si substrate. **c**, The corresponding tube length distributions.

Reference

1. X. Yang, T. Liu, R. Li, X. Yang, M. Lyu, L. Fang, L. Zhang, L. Zhang, A. Zhu, K. Wang, C. Qiu, Y. Z. Zhang, X. Wang, L.-M. Peng, F. Yang and Y. Li, *J. Am. Chem. Soc.*, 2021, **143**, 10120–10130.