Supporting Information

Polyoxometalate Steric Hindrance Driven Chirality-Selective Separation of Subnanometer Carbon Nanotubes

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Supporting Results

Figure S1. a–c, Typical HAADF-STEM images of {PW$_{12}$}-CoMo-SWCNTs.

Figure S2. Thermogravimetric curves of {PW$_{12}$}-SWCNTs and raw SWCNTs.
Figure S3. Raman spectra of polyoxometalate-SWCNTs and pristine SWCNTs. The spectra were normalized with respect to the intensity of $G$ bands. A laser filter (25%) was applied to the powder sample to avoid any laser heating effect induced Raman shift.

Figure S4. XPS spectra of $\{\text{PW}_{12}\}$ and $\{\text{PW}_{12}\}$-SWCNTs.
**Figure S5.** Absorption spectra of sodium deoxycholate dispersed raw CoMo-SWCNTs, indicating the non-selective chiral indices in raw sample.

**Figure S6.** Raman spectra of sorted \{PW_{12}\}-CoMo-SWCNTs and raw CoMo-SWCNTs. The spectra are normalized with the $G$ bands.
Figure S7. UV–Vis–NIR absorption spectra, deconvolution curves, and fitting spectra of PCz sorted raw SWCNTs (a) and {PW12}-SWCNTs (b).

Table S1. Fitted and calculated relative abundance of \((n,m)\) in PCz sorted {PW12}-SWCNTs from absorption spectra.

| \((n,m)\) | Wavelength (nm) | Peak Area | Relative Abundance (%) |
|----------|-----------------|-----------|------------------------|
| (6,4)    | 891             | 0.27      | 5.9                    |
| (6,5)    | 992             | 4.14      | 90.6                   |
| (7,5)    | 1028            | 0.01      | 0.2                    |
| (7,6)    | 1146            | 0.15      | 3.3                    |

Table S2. Fitted and calculated relative abundance of \((n,m)\) in PCz sorted raw SWCNTs from absorption spectra.

| \((n,m)\) | Wavelength (nm) | Peak Area | Relative Abundance (%) |
|----------|-----------------|-----------|------------------------|
| (6,4)    | 899             | 0.42      | 2.7                    |
| (9,1)    | 935             | 0.55      | 3.6                    |
| (8,3)    | 970             | 1.34      | 8.8                    |
| (6,5)    | 992             | 1.85      | 12.1                   |
| (7,5)    | 1048            | 3.49      | 22.9                   |
| (7,6)(8,4)(9,4) | 1125-1160     | 5.54      | 36.3                   |
| (8,6)    | 1200            | 1.47      | 9.6                    |
| (8,7)    | 1265            | 0.30      | 2.0                    |
| (10,3)   | 1292            | 0.31      | 2.0                    |

Three types of adsorption sites of {PW12} on a (8,4) SWCNT were used. The smallest \(O_{\text{cluster}}-\text{CNT}\) inter-distance was found to be 1.44, 2.44, and 3.41 Å (Figure
S8a–c), respectively. The optimized configuration by DFT calculations is determined to be 3.40 Å (Figure S8d).

![Figure S8](image)

**Figure S8.** a–c, Different adsorption sites of \{PW_{12}\} on (8,4) SWCNT before optimization. The smallest inter-distances (O-C) 1.44 (a), 2.44 (b), and 3.41 Å (c) are labelled. d, Optimized configuration of \{PW_{12}\}/(8,4) SWCNT in tri-adsorption site with an inter-distance of 3.40 Å.

![Figure S9](image)

**Figure S9.** DFT calculations: iso-surface plots of electron density differences for \{PW_{12}\} on outside SWCNTs with different chirality/diameter: (8,3), (7,5), (8,4), and (7,6). The corresponding electron transfer (|e|) is indicated.
**Figure S10.** a–c, HAADF-STEM images of {PW\textsubscript{12}}-SWCNT residue after the sorting and centrifugation, showing lots of {PW\textsubscript{12}} clusters adsorbed on outside SWCNTs.

**Figure S11.** Normalized absorption spectra of PCz sorted {PW\textsubscript{12}}-SWCNTs under different sonication time: 50, 150, and 300 min.
**Figure S12.** Raman spectrum showing the $D$, $G$ bands of sorted SWCNTs via different sonication time.

**Figure S13.** SEM image (a) and length distribution (b) of (6,5) SWCNTs sonicated by 300 min. Tube counts: $N = 124$. Average length: $1.75 \pm 0.71 \, \mu m$.

**Figure S14.** a, b, TEM images of Pd nanoparticles with a size of ~1-2 nm.
**Figure S15.** Cyclic voltammogram of different polyoxometalates in Na$_2$SO$_4$ solution (0.5 mol·L$^{-3}$) using a 3 mm-diameter glass carbon electrode, a carbon rod counter electrode, and a saturated calomel electrode (SCE) reference electrode.

**Figure S16.** Cyclic voltammogram of CoMo-SWCNT thin film in Na$_2$SO$_4$ solution (0.5 mol·L$^{-3}$) using a 3 mm-diameter glass carbon electrode, a carbon rod counter electrode, and a Ag/Ag$^+$ reference electrode. The potential (V vs. Ag/Ag$^+$) of voltammogram of SWCNTs was converted to the potential (V vs. SCE) by subtracting 45 mV. The key features of the cyclic voltammogram are labeled.