Supporting Information

Synthesis of Rigid and Stable Large-Inner-Diameter Multiwalled Carbon Nanotubes

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1. Syntheses of materials

Synthesis of LID-MWCNTs: Typically, 0.5 g cetyltrimetylammonium bromide (CTAB) was dissolved in 10.0 mL water and 0.6766 g ammonium metatungstate hydrate was dissolved in 230 mL water. The aqueous CTAB solution was added drop-wise into the ammonium metatungstate solution with vigorous stirring. The produced white solid ($[(CTA)_6H_2W_{12}O_{40}]_n$) was collected by filtration, washed with copious water and ethanol, dried under vacuum at 353 K overnight. $[(CTA)_6H_2W_{12}O_{40}]_n$ was transferred into a quartz tube. The tube was purged with Ar several times and sealed with high vacuum (13.33 Pa) inside. The quartz tube with sample inside was heated to 1273 K at 1.0 K/min and kept at 1273 K for 2 hours before cooled down to room temperature naturally. Black powder inside the tube reactor was confirmed as large-inner-diameter multiwalled carbon nanotubes (LID-MWCTNs) by different analytic methods.

Synthesis of surface-coated WO_3 nanowires: The quartz tube with $[(CTA)_6H_2W_{12}O_{40}]_n$ inside was sealed with high vacuum (13.33 Pa) inside, heated to 1273 K at 1.0 ^{K}/min and kept at 1273 K for 2 hours before cooled down to room temperature naturally. Black powder at the bottom of the tube reactor was confirmed as surface-coated WO_3 nanowires.

Synthesis of amorphous carbon/WC composite from WC nanoparticles and CTAB: WC nanoparticles (50 – 100 nm in diameter) and CTAB with W/C ratio at 1/60, same as that for LID-MWCNTs synthesis described above, were mixed into a quartz tube reactor and sealed under high vacuum at 13.33 Pa. The reactor was heated to 1273 K at 1.0 K/min and kept at 1273 K for 2 hours before cooled down to room temperature naturally.

Synthesis of graphene/WC composite from WO_3 nanoparticles and CTAB: Here, LID-MWCTNs were heated to 573 K slowly at 0.5 K/min in air. After 2 hours at 573 K, WO_3 nanoparticles with diameter of 20 -30 nm were formed. WO_3 nanoparticles and CTAB with W/C ratio at 1/60, same as that for LID-MWCNTs synthesis described above, were mixed into a quartz tube reactor and sealed under high vacuum (13.33 Pa). The reactor was heated to 1273 K at 1.0 K/min and kept at 1273 K for 2 hours before cooled down to room temperature naturally.

2. Characterizations of materials

Large-angle X-ray diffraction (XRD) patterns were recorded on a Phillips Norelco powder diffractometer using Cu K radiation (40 kV, 40 mA) at the rate of 0.6^{o} min^{-1} over the range $2\theta = 20.0 – 80.0^{o}$. SEM images were measured using JSM-7400F field emission scanning electron microscope. JOEL JEM-2010F transmission electron microscope with a 200 kV acceleration voltage was used to collect TEM and HRTEM images.

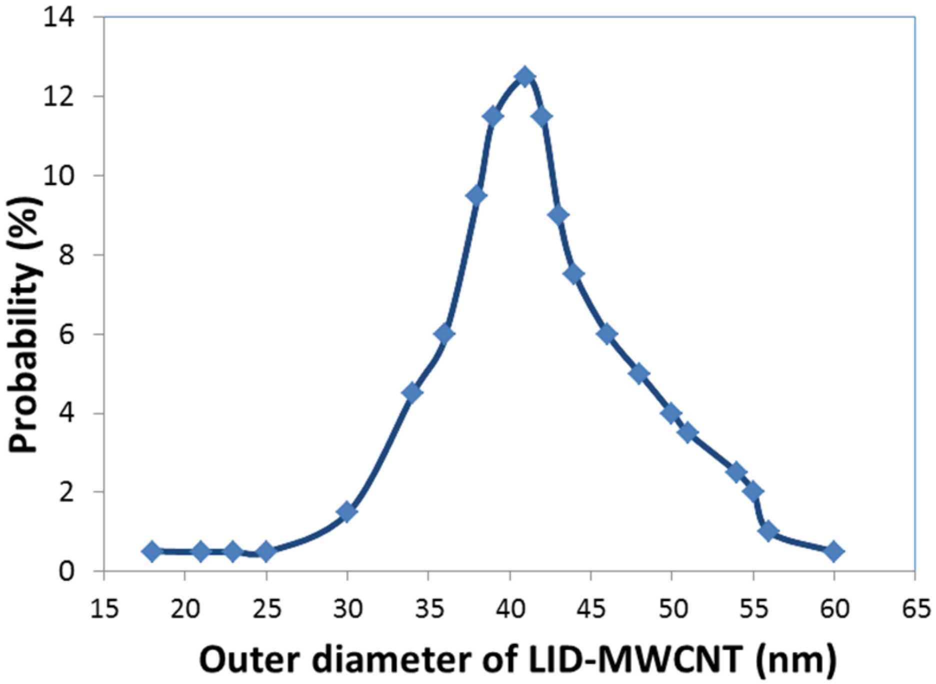

Figure S1. The distribution of outer diameters of LID-MWCNTs.

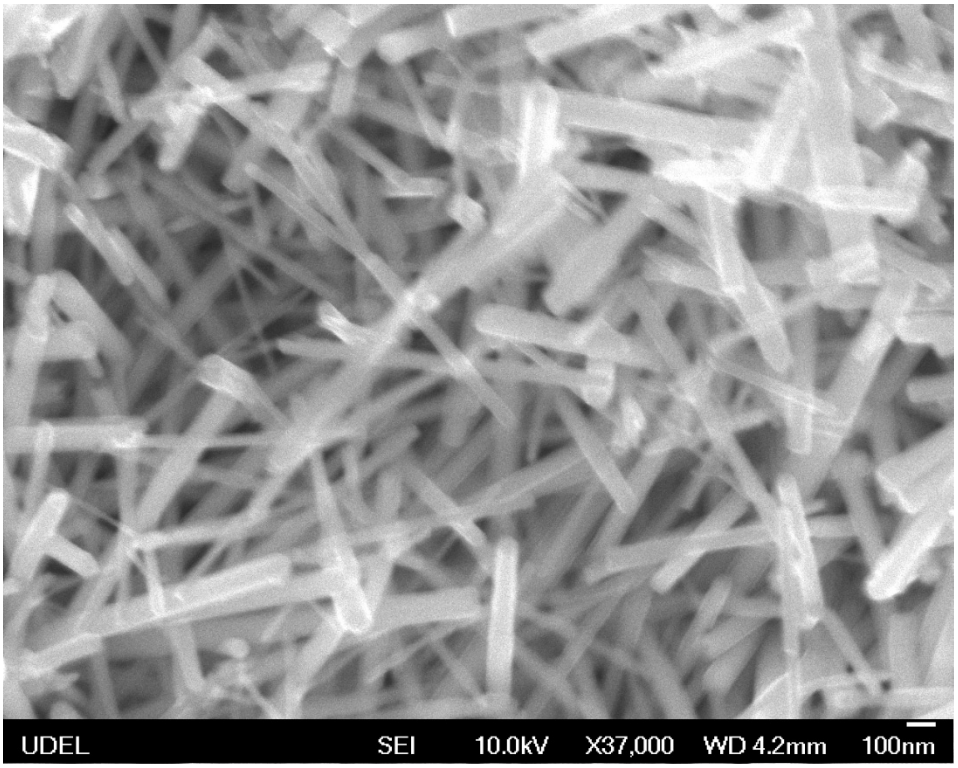

Figure S2. SEM images of LID-MWCNTs before the removal of WC nanoparticles.

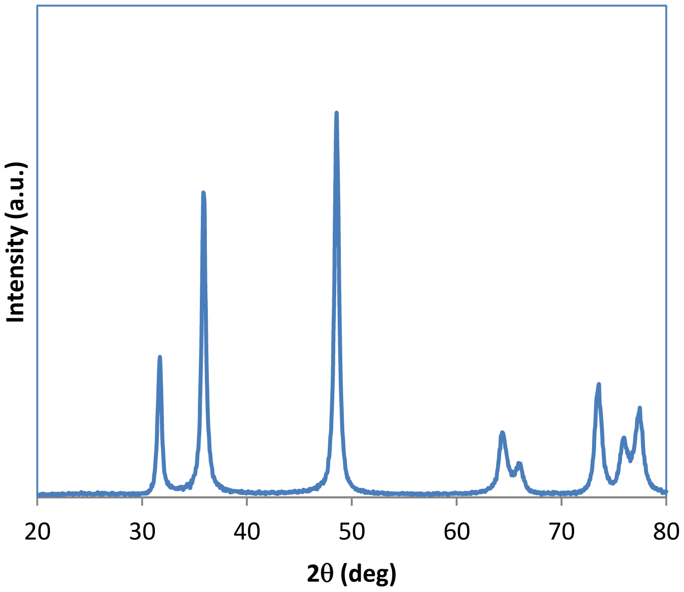

Figure S3. XRD of WC nanoparticles inside LID-MWCNTs.

(Figure S3 indicates a pure hexagonal WC phase inside LID-MWCNTs. The 2θ of 31.54, 34.84, 48.48, 64.16, 64.58, 73.28, 75.62 and 75.86^{o} with *d* values of 0.2838, 0.2574, 0.1879, 0.1451, 0.1291, 0.1255, 0.1237 nm correspond to (001), (100), (101), (110), (002), (111), (200) and (102) planes of the pure hexagonal WC.)

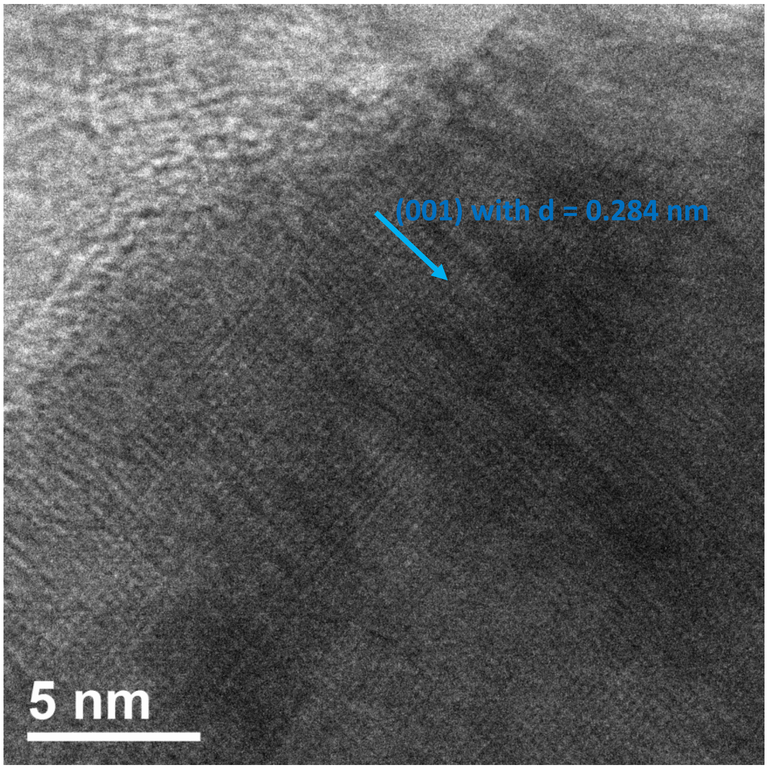

Figure S4. HRTEM of WC nanoparticle inside of LID-MWCNT.

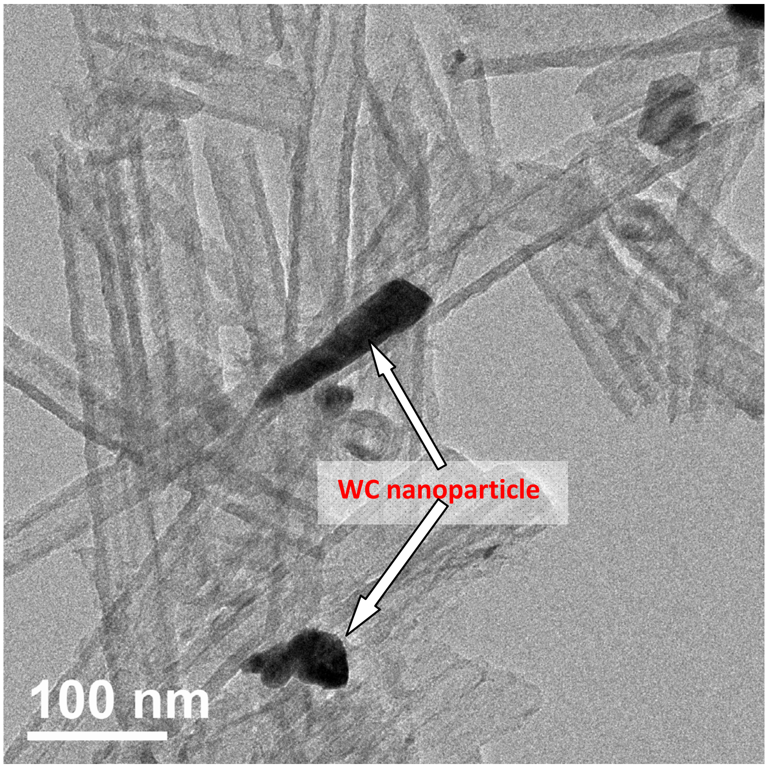

Figure S5. TEM images of LID-MWCNTs after partially removal of WC.

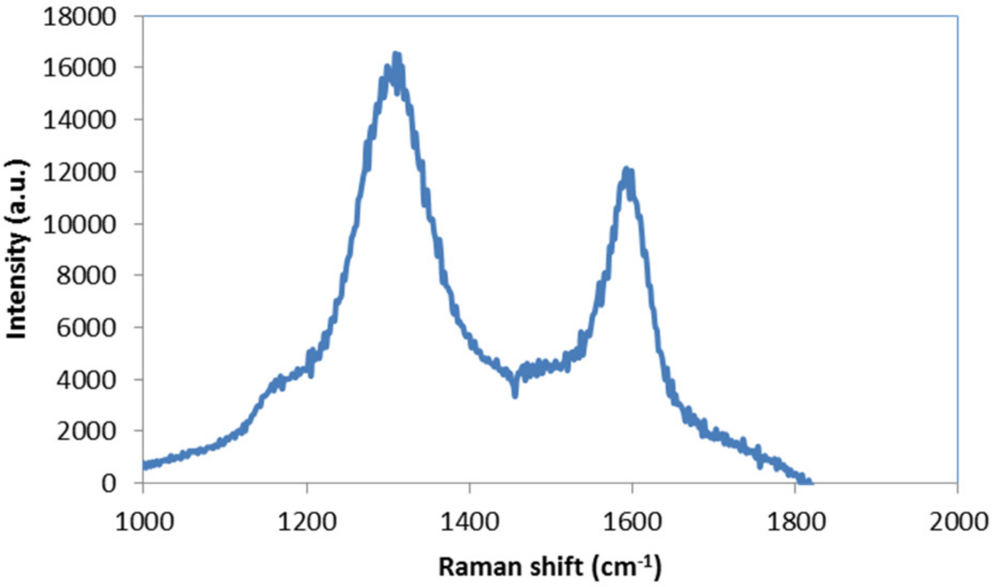

Figure S6. Raman spectrum of LID-WMCNTs.

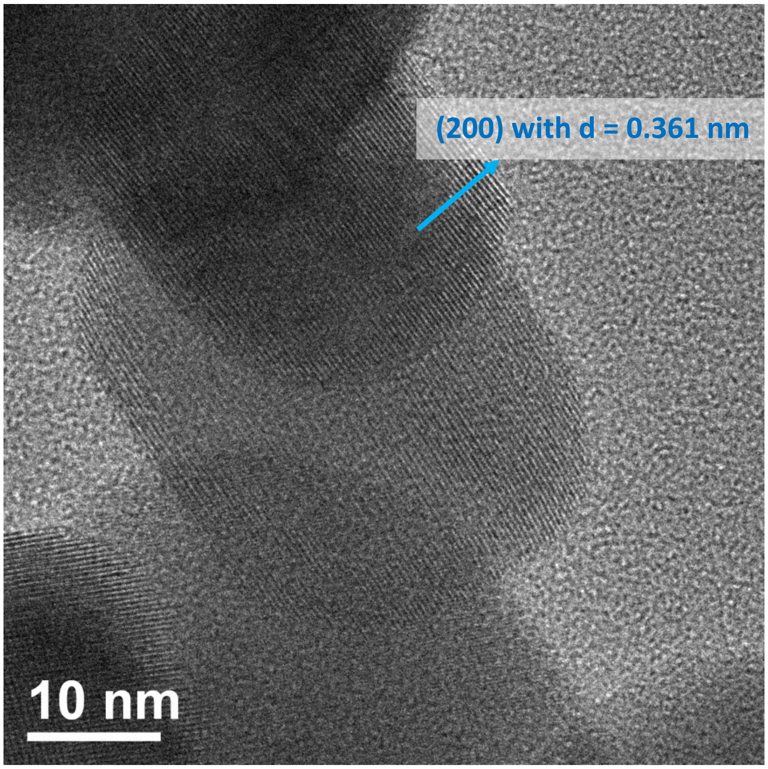

Figure S7. TEM images of WO_3 nanoparticles with diameter of 20 - 30 nm. (The lattice structure of WO_3 can be clearly seen. The lattice fringes were about 0.361 nm, corresponding to the interplanar spacing of (200) planes of triclinic WO_3 (JCPDS card No. 01-083-0947).)

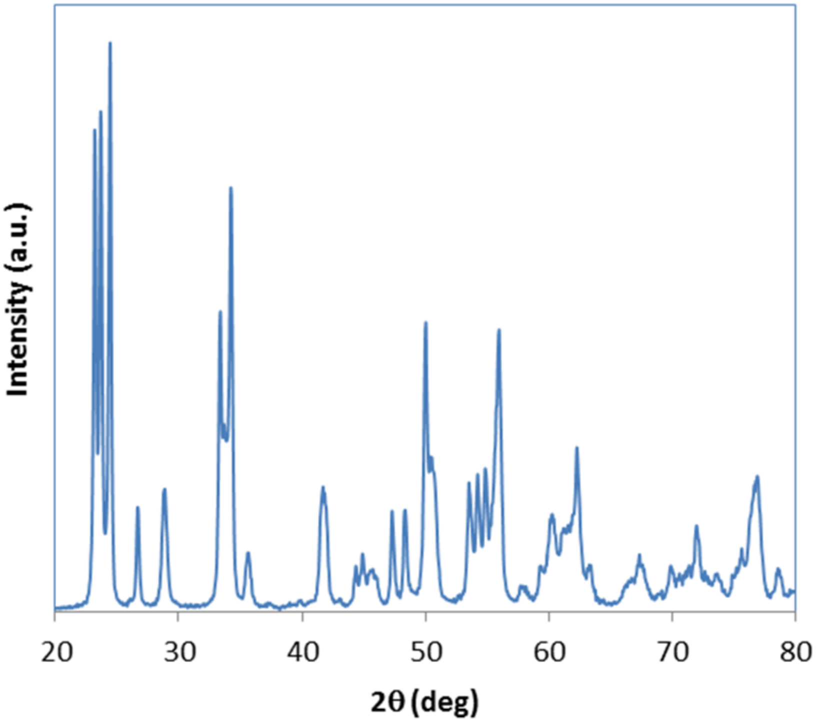

Figure S8. Large-angle X-ray diffraction of of WO_3 nanoparticles with diameter of 20 - 30 nm.

(This XRD pattern matches with the reported in JCPDS card No. 01-083-0947.)

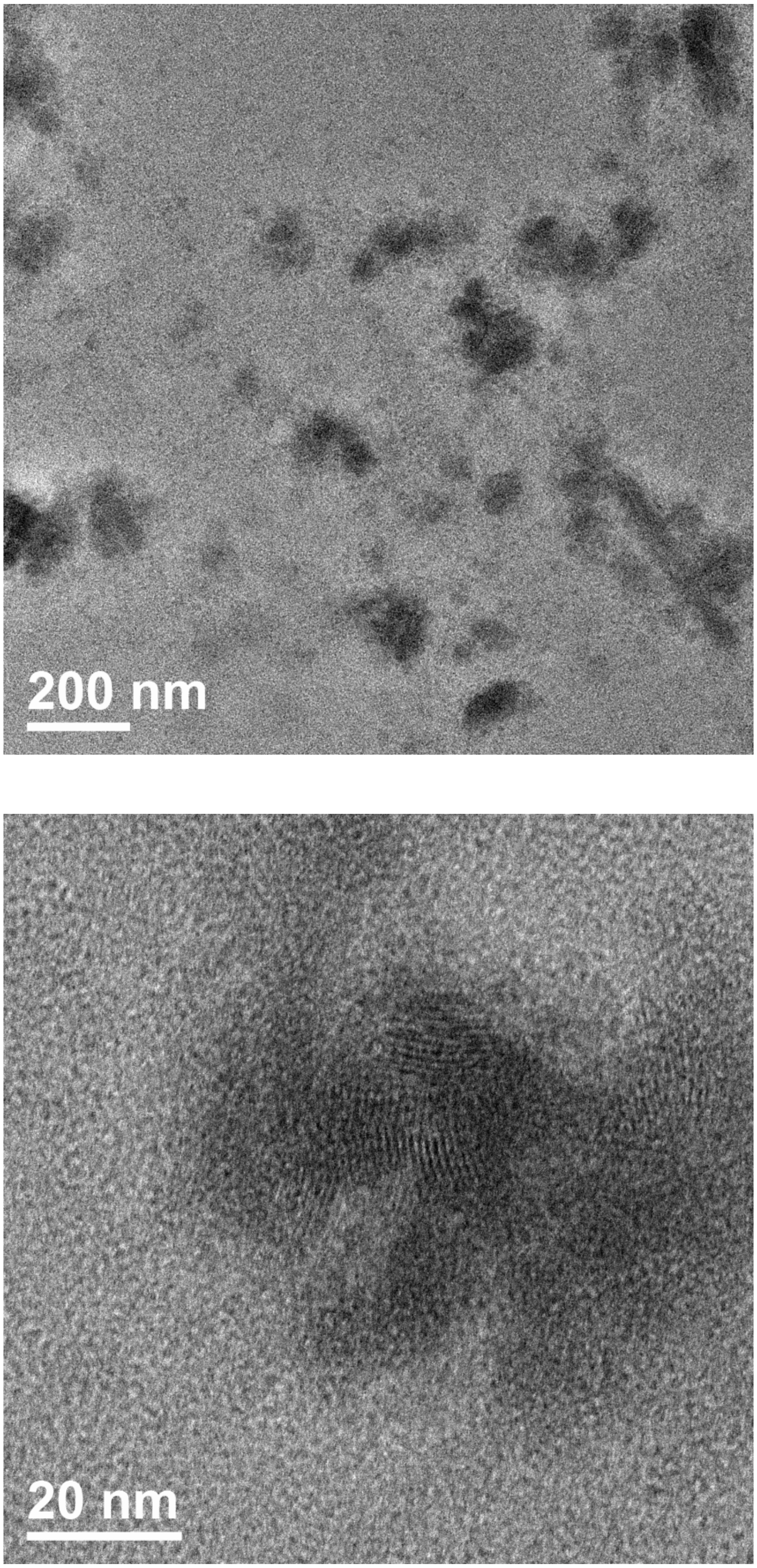

Figure S9. TEM images of $CTA^+/H_2W_{12}O_{40}{}^{6-}$.

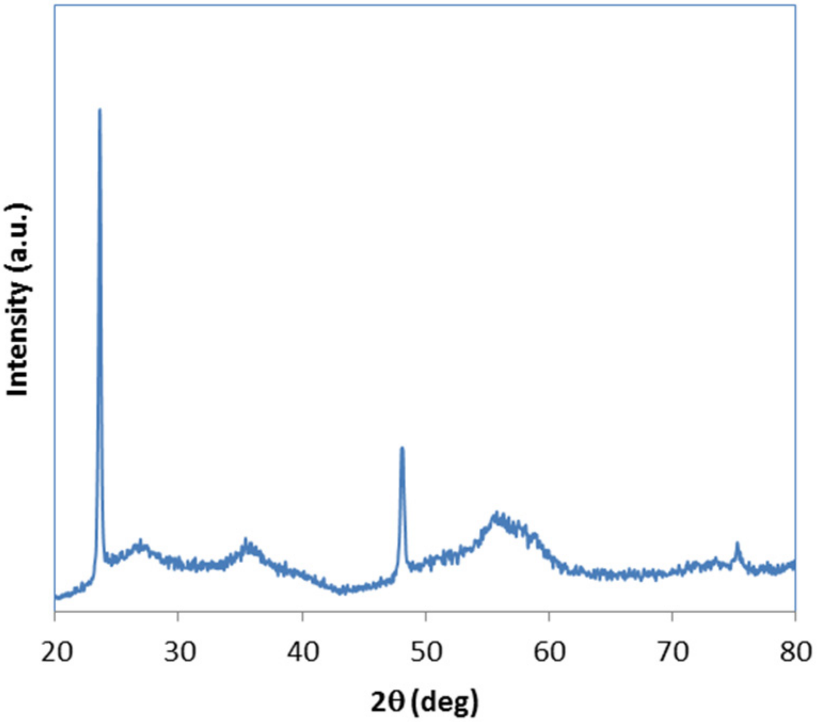

Figure S10. XRD of polymer-coated WO_3 nanowires.

(The 2θ of 23.6 and 55.22^{o} correspond to (002) and (440) planes of WO_3. The other peaks at 25.40, 31.40, 54.56 and 75.2^{o} are broadened and could not be assigned to some specific peaks.)

Table S1. Elemental analysis of different materials.

	Reaction temp. (K)	H/C molar ratio	Sample composition
1	none	2.2	$[(CTA)_6H_2W_{12}O_{40}]_n$ (starting material)
2	573	1.8	Polymer-coated WO_3 nanowires
3	673	1.3	Polymer-coated WO_3 nanowires
4	773	1.0	Polymer-coated WO_3 nanowires
5	873	0.3	Polymer/carbon-coated WO_3 nanowires
6	973	0	Carbon-coated WO_3 nanowires
4	1273	0	WC/LID-MWCNTs