Supporting Information (SI) for:

Carbon-protected bimetallic carbide nanoparticles for highly efficient alkaline hydrogen evolution reaction

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Table S1. Comparison of the electrocatalytic activity of C-CWC under basic conditions *vis-à-vis* some representative solid-state HER catalysts recently reported for basic solutions.

Catalyst	Loading density(mg/cm^2)	Current density (j)	Overpotential at the corresponding j	Reference
C-CWC	**0.28 mg/cm^2**	**1 mA/cm^2**	**33 mV**	**this work**
		10 mA/cm^2	**73 mV**	
Ni-Mo-alloy on Ti foil	1 mg/cm^2	10 mA/cm^2	80 mV	ACS Catal. 2013, *3*, 166.
30 wt.% Ni loading-Mo_2C nano-rod	—	10 mA/cm^2	130 mV	*Appl. Catal. B: Environ.* **2014**, *154–155*, 232.
Mo_2C nano-rod		10 mA/cm^2	150 mV	
CoP nanowire array	0.92 mg/cm^2	10 mA/cm^2	209 mV	*J. Am. Chem. Soc.* **2014**, dx.doi.org/10.1021/ja503372r
Co-NRCNTs	0.28 mg/cm^2	1 mA/cm^2 10 mA/cm^2	160 mV 370 mV	*Angew. Chem. Int. Ed.* **2014**, *53*, 4372.
Mo_2C	0.8 mg/cm^2	6 mA/cm^2	250 mV	*Angew. Chem. Int. Ed.* **2012**, *51*, 12703.
MoB	2.3 mg/cm^2	5 mA/cm^2	250 mV	*Angew. Chem. Int. Ed.* **2012**, *51*, 12703.
Ni wire	—	10 mA/cm^2	320 mV	*ACS Catal*. **2013**, *3*, 166.
MoS_2 nanosheets on 3D graphene/nickel structure	—	1 mA/cm^2	310 mV	*Adv. Funct. Mater.* **2014**. DOI: 10.1002/adfm.201401328
Electrodeposited cobalt-sulfide	0.123 mg/cm^2	1 mA/cm^2	480 mV	*J. Am. Chem. Soc.* **2013**, *135*, 17699.
Nitrogen and phosphorus dual-doped graphene	—	1 mA/cm^2	500 mV	*ACS Nano* **2014**. DOI: 10.1021/nn501434a
Amorphous MoS_x	—	10 mA/cm^2	540 mV	*Chem. Sci.* **2011**, *2*, 1262.

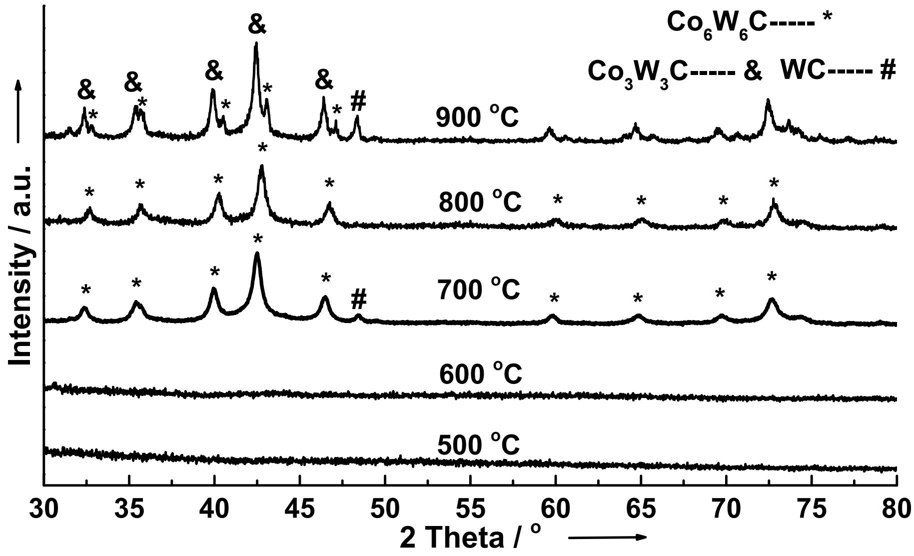


Figure S1. XRD patterns of the as-obtained samples that are synthesized *via* simple thermal treatment of a mixture of dicyandiamide, cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) and ammonium tungstate hydrate ($(NH_4)_5H_5[H_2(WO_4)_6] \cdot H_2O$) under N_2 atmosphere at different temperatures (*i.e.*, 500, 600, 700, 800 or 900 °C). Details of experimental procedures are provided in experimental section. From the Figure S1, it is seen that the lowest temperature for the formation bimetallic Co-W carbide is 700 °C. The samples obtianed at 700 and 800 °C are dominated by the cubic Co_6W_6C phase, whereas the sample obtianed 900 °C contians both Co_6W_6C and Co_3W_3C. Due to the similar catalytic activities of the samples obtianed at 700, 800, or 900 °C (see their catalytic activities in the main text), our work in this paper is focused on the sample abtained at 700 °C (*i.e.*, C-CWC).

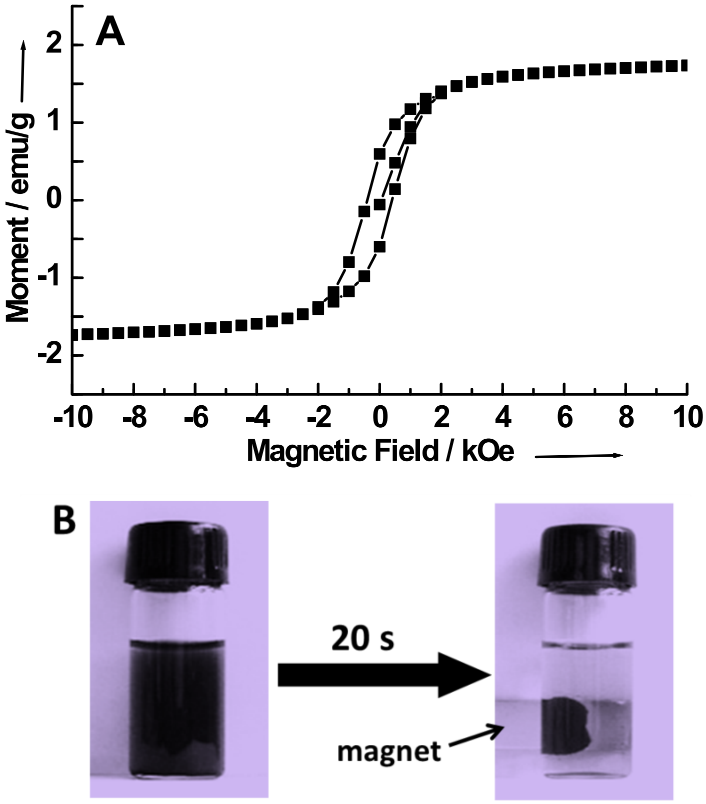


Figure S2. (A) Magnetization as a function of applied magnetic field at 300 K for the C-CWC material. A typical magnetic hysteresis loop with the saturation magnetization of ~1.5 emu/g was observed at 300 K, confirming the ferromagnetism of the C-CWC material at room temperature. (B) Photographs showing that the C-CWC material in water can be easily separated by a magnet.

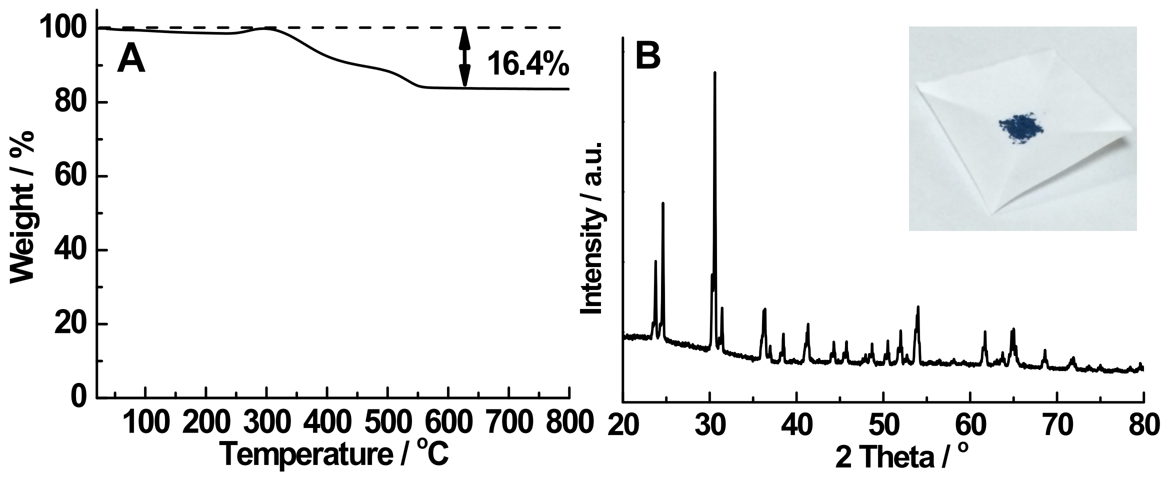


Figure S3. (A) TG curve measured in air for the C-CWC material; (B) XRD pattern of the sample collected after TG measurement with a sample photograph shown in the inset.

A representative method of evaluating the amount of carbon in the CWC@NC sample was given below:

From a TGA plot, we can obtain the initial amount of the sample = a (in g)
and the final amount of the sample = b (in g)

Since, the solid product left after TGA only corresponds to $CoWO_4$, the mol amount (x) of Co or W present in the sample can be calculated as,

mol of Co (x) = b (g)/306.8 (g/mol) where 306.8 (g/mol) = MW of $CoWO_4$

Since Co and W can only come from the initial material, the mol of Co and W in the initial material should also be x.

If the molar composition of the initial material to be x/6(Co_6W_6C)@yC (where x is already known from previous calculation), the mol (y) of C present in the material can be calculated as,

mol of C (y) = {a (g) – [1470 (g/mol)*x/6 (mol)]}/12.01 (g/mol)

where 1470 (g/mol) and 12.01 (g/mol) are the atomic weights of Co_6W_6C and C, respectively.

Based on the above results, we can obtain the weight percent of C in the material is about **(12.01*y/a)*100%.**

[Because of the similarity in the atomic weights between C and N, as well as the low N amount in the material, the contribution of nitrogen-dopant is expected to be very small to the above calculation, and hence is ignored for simplification.]

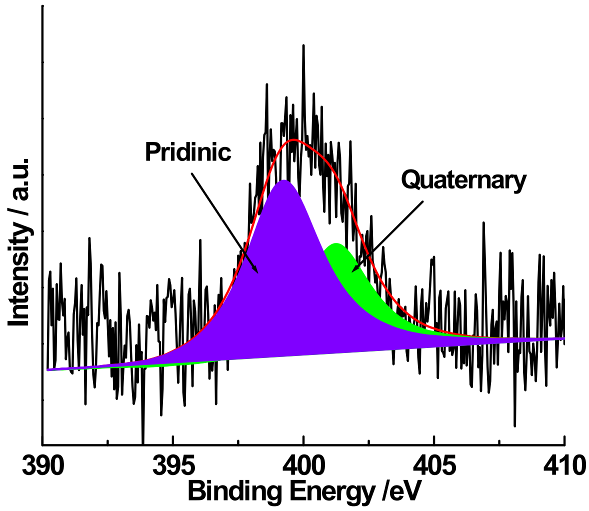


Figure S4. N1s XPS spectrum of C-CWC. In the XPS spectrum, the raw curve (black) is peak-fitted into two curves (indicated by violet and green shaded areas) that correspond to two different types of N species (pyridinic and quaternary), and the sum of the two peak-fitted curves is shown with the red curve.

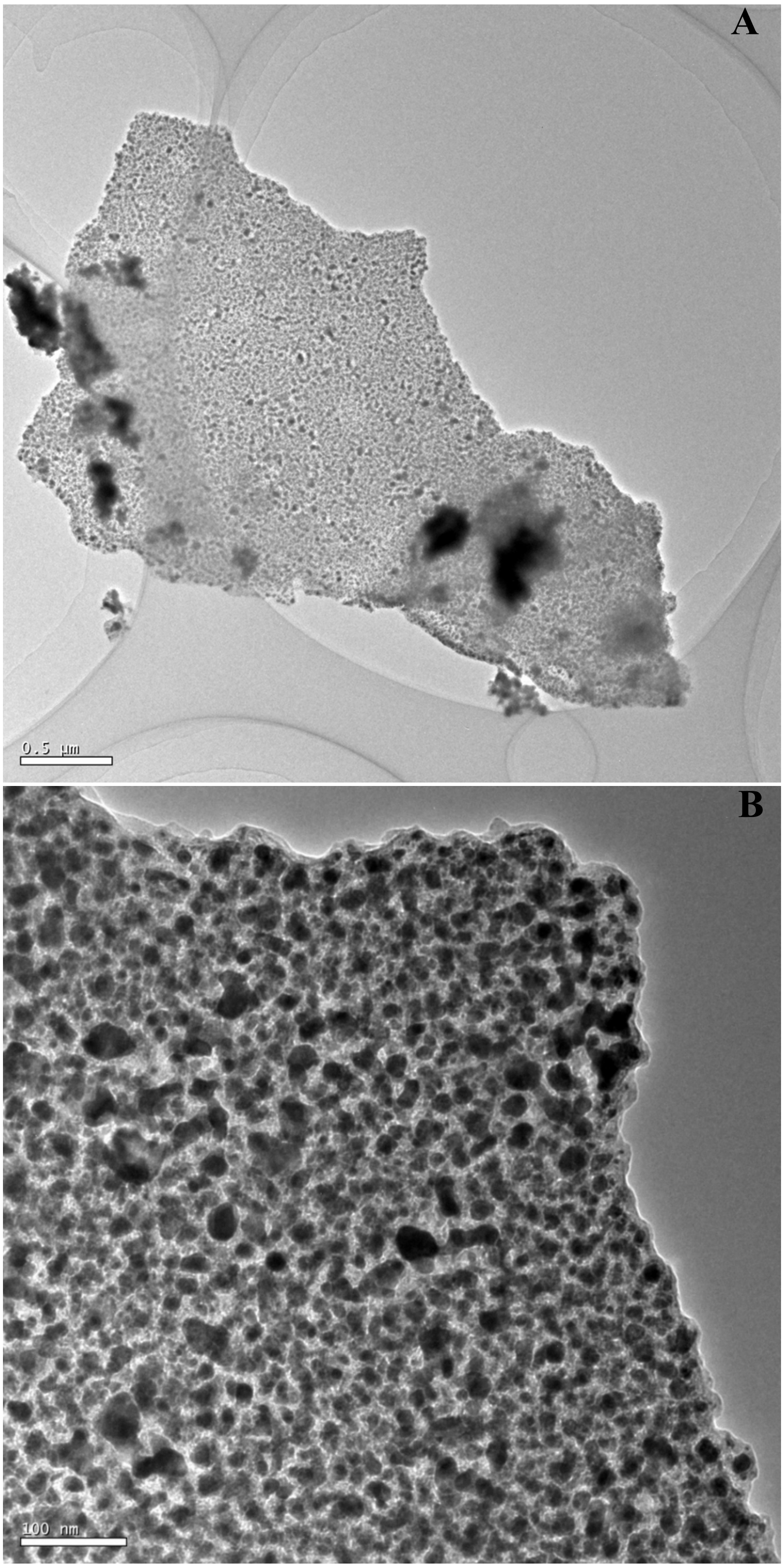


Figure S5. TEM images of the C-CWC material.

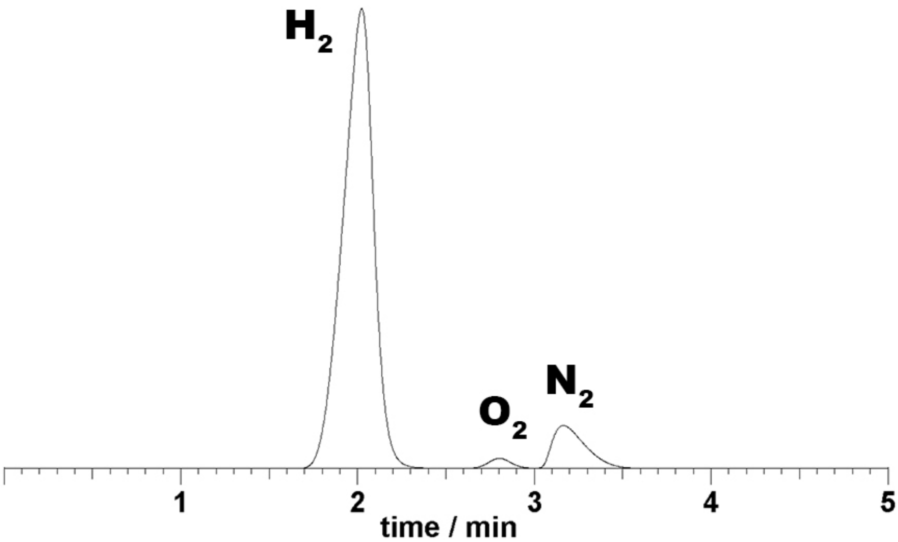


Figure S6. A representative GC result demonstrating the generation of H_2 during catalysis. The detected O_2 and N_2 originate from the air.

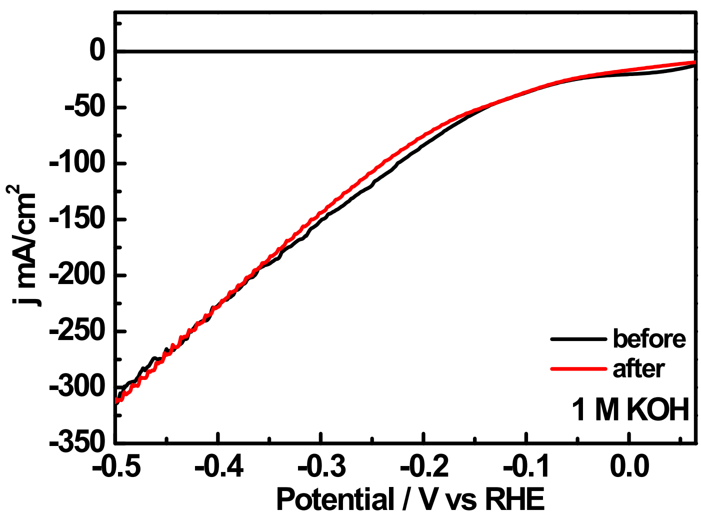


Figure S7. Linear sweep voltammetry (LSV) curves obtained with the C-CWC, before (black curve) and after (red curve) 18-hour use under the current−time measurement shown in Figure 4A. The sample loading on the GCE is ~0.28 mg/cm^2 in all the cases, and the obtained current densities are all normalized with the surface area of the GCE.

Table S2. Comparison of the electrocatalytic activity of C-CWC under acidic conditions *vis-à-vis* some representative solid-state HER catalysts recently reported for acidic solutions.

Catalyst	**Current density (*j*)**	**Overpotential at the corresponding *j***	**Reference**
CoP nanoparticles	10 mA/cm^2	70-85 mV	*Angew. Chem. Int. Ed.* **2014.** DOI: 10.1002/ange.201402646
Ni_2P	10 mA/cm^2	100 mV	*J. Am. Chem. Soc.* **2013**, *135*, 9267.
Carbon fiber paper-supported $CoSe_2$ nanoparticles	10 mA/cm^2	130 mV	*J. Am. Chem. Soc.* **2014**, *136*, 4897.
MoS_2/Graphene	10 mA/cm^2	150 mV	*J. Am. Chem. Soc.* **2011**, *133*, 7296**.**
Oxygen-incorporated or defect-rich MoS_2 nanosheets	10 mA/cm^2	180 mV	*J. Am. Chem. Soc.* **2013**, *135*, 17881. *Adv. Mater.* **2013**, *25*, 5807.
C-CWC	**10 mA/cm^2**	**200 mV**	**this work**
Amorphous MoS_x	10 mA/cm^2	200 mV	*ACS Catal.* **2012**, *2*, 1916.
MS_2 films (M=Fe, Co, $Fe_{0.43}Co_{0.57}$)	1 mA/cm^2 10 mA/cm^2	160-210 mV 190-270 mV	*Energy Environ. Sci.* **2013**, *6*, 3553.
Exfoliated WS_2/MoS_2 nanosheets	10 mA/cm^2	187-210 mV	*Nature Mater.* **2013**, *12*, 850; *Nano Lett.* **2013**, *13*, 6222; *J. Am. Chem. Soc.* **2013**, *135*, 10274.
$Co_{0.6}Mo_{1.4}N_2$	10 mA/cm^2	200 mV	*J. Am. Chem. Soc.* **2013**, *135*, 19186.
MoB	10 mA/cm^2	215 mV	*Angew. Chem. Int. Ed.* **2012**, *51*, 12703.
Mo_2C	10 mA/cm^2	215 mV	*Angew. Chem. Int. Ed.* **2012**, *51*, 12703.
$Mo_{0.06}W_{1.94}C$/CB	10 mA/cm^2	220 mV	*Angew. Chem. Int. Ed.* **2014**, *53*, 5131
MSe_2 films (M=Fe, Co, $Fe_{0.43}Co_{0.57}$)	1 mA/cm^2 10 mA/cm^2	170-230 mV 230-250 mV	*Energy Environ. Sci.* **2013**, *6*, 3553.
g-C_3N_4/N-doped graphene	10 mA/cm^2	240 mV	*Nature Chem.* **2014**, *5*, 3783.
N-rich tungsten carbonitride	10 mA/cm^2	250 mV	*Angew. Chem. Int. Ed.* **2013**, *52*, 13638.
Co-NRCNTs	10 mA/cm^2	260 mV	*Angew. Chem. Int. Ed.* **2014**, *53*, 4372.
WS_2/rGO hybrid nanosheets	10 mA/cm^2	260 mV	*Angew. Chem. Int. Ed.* **2013**, *52*, 13751.
Analytical grade WC	10 mA/cm^2	300 mV	*Appl. Catal. B: Environ.* **2012**, *126*, 225.
$NiMoN_x$	1 mA/cm^2	150 mV	*Angew. Chem. Int. Ed.* **2012**, *51*, 6131.

Table S3. Comparison of the electrocatalytic activity of C-CWC under neutral conditions *vis-à-vis* some representative solid-state HER catalysts recently reported for neutral solutions.

Catalyst	Current density (*j*)	Overpotential at the corresponding *j*	Reference
CoP nanowire array	2 mA/cm^2 10 mA/cm^2	65 mV 106 mV	*J. Am. Chem. Soc.* **2014**, dx.doi.org/10.1021/ja503372r
Electrodeposited cobalt-sulfide	2 mA/cm^2 10 mA/cm^2	85 mV 160 mV	*J. Am. Chem. Soc.* **2013**, *135*, 17699.
C-CWC	**1 mA/cm^2** **2 mA/cm^2** **10 mA/cm^2**	**75 mV** **100 mV** **224 mV**	**this work**
Fe, Co, or Ni-doped amorphous MoS_2	1 mA/cm^2	200-300 mV	*Chem. Sci.* **2012**, *3*, 2515.
$CuMoS_4$	2 mA/cm^2	210	*Energy Environ. Sci.* **2012**, *5*, 8912
Amorphous MoS_2	2 mA/cm^2	280 mV	*Chem. Sci.* **2011**, *2*, 1262
Co-NRCNTs	1 mA/cm^2 10 mA/cm^2	330 mV 540 mV	*Angew. Chem. Int. Ed.* **2014**, *53*, 4372.
Metallic cobalt@cobalt-oxo/hydroxo phosphate	2 mA/cm^2	385 mV	*Nature Mater.* **2012**, *11*, 802
Mo_2C	1 mA/cm^2	200 mV	*Angew. Chem. Int. Ed.* **2012**, *51*, 12703.
MoB	1 mA/cm^2	250 mV	*Angew. Chem. Int. Ed.* **2012**, *51*, 12703.

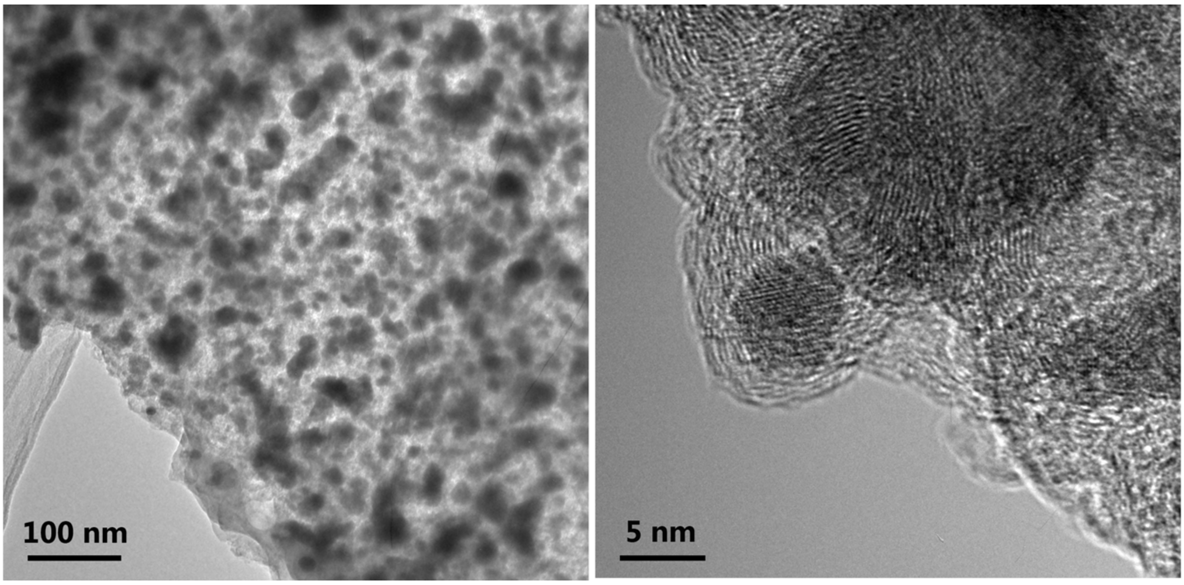
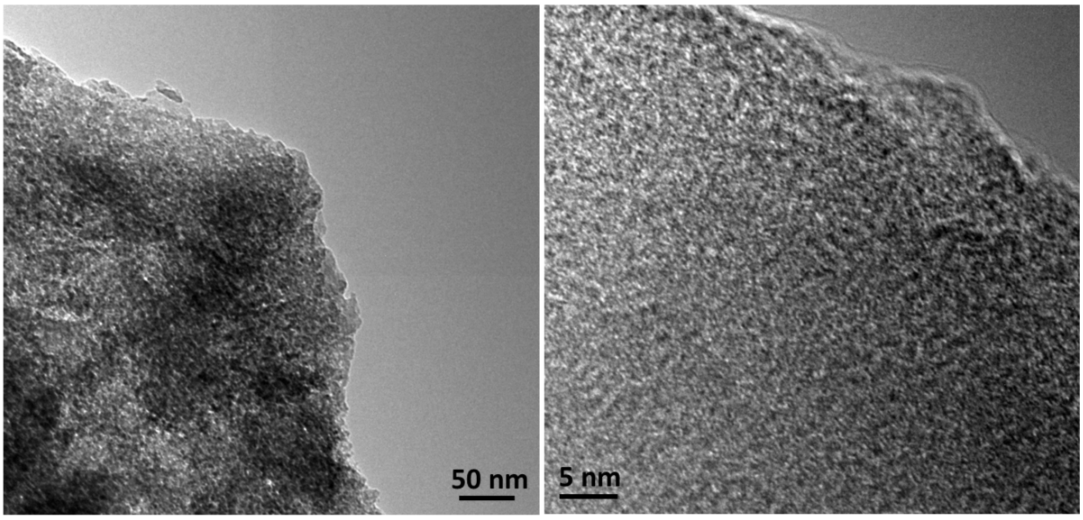
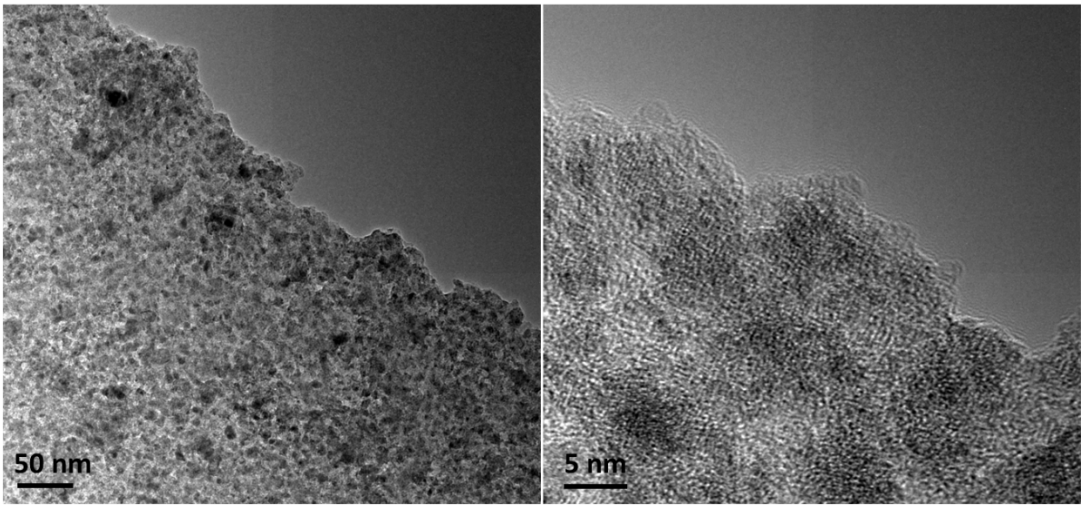


Figure S8. TEM images of the sample after stability test.

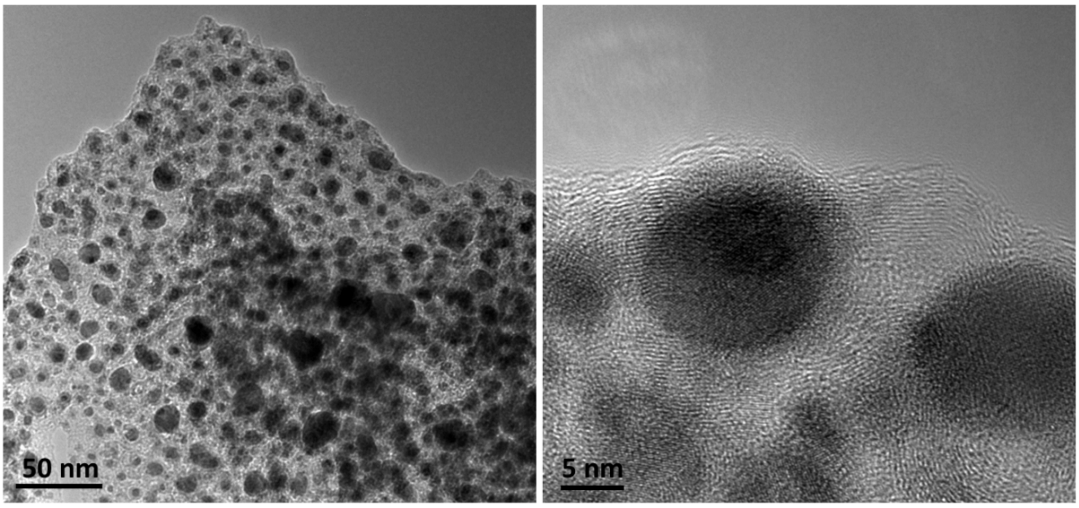
500 °C



600 °C



800 ^oC



900 ^oC

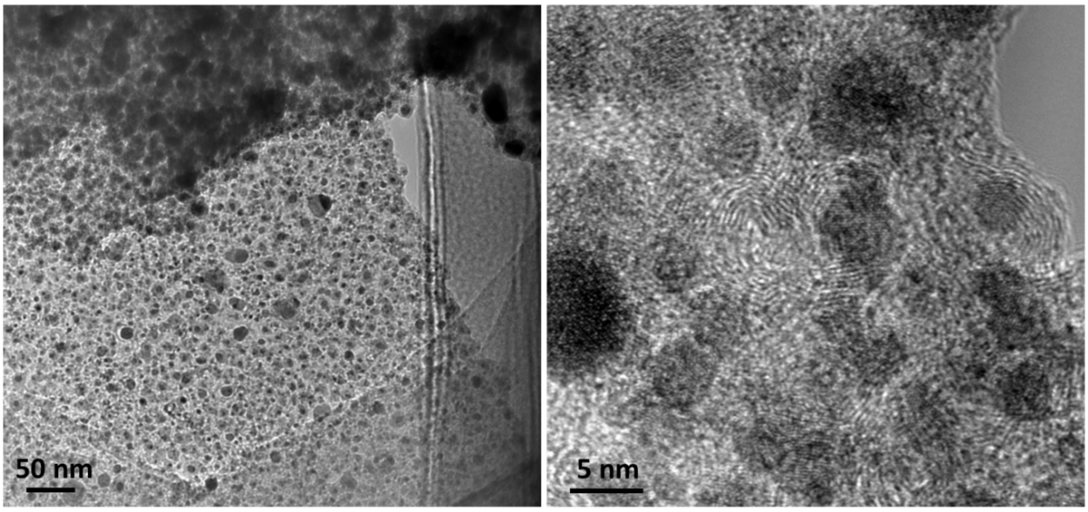


Figure S9. TEM images of the samples obtained at 500, 600, 800 and 900 ^oC.

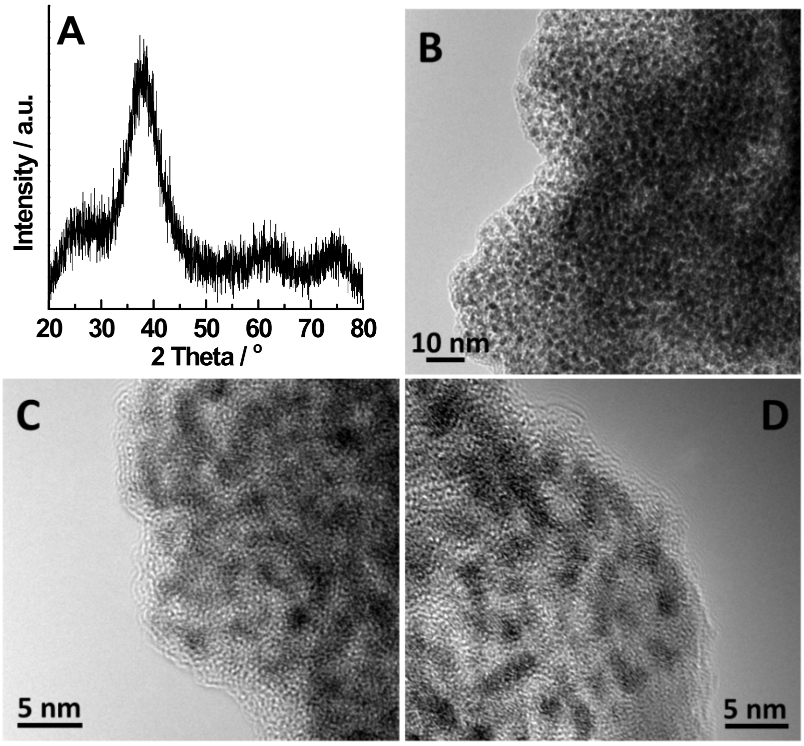


Figure S10. (A) XRD pattern, and (B-D) TEM images of the C-W_2C material.

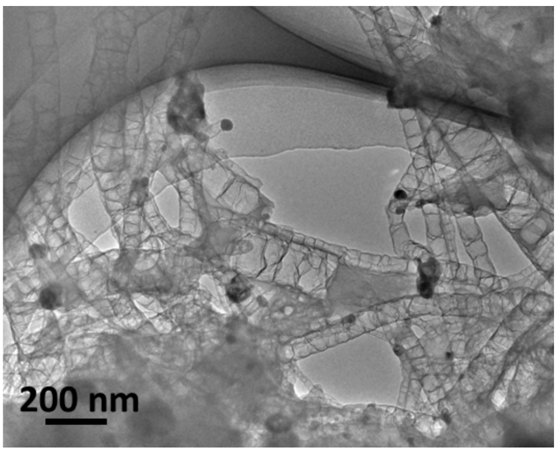


Figure S11. A typical TEM image of the Co-NRCNTs. The more detailed characterization on this material can be seen in our previous report (*Angew. Chem.* **2014**, *126*, 4461-4465).

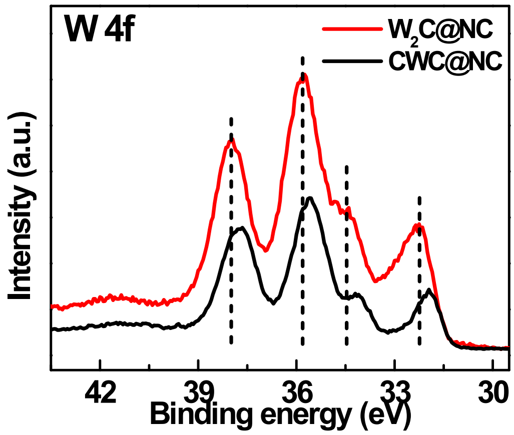


Figure S12. W4f XPS spectra of C-CWC and C-W_2C.

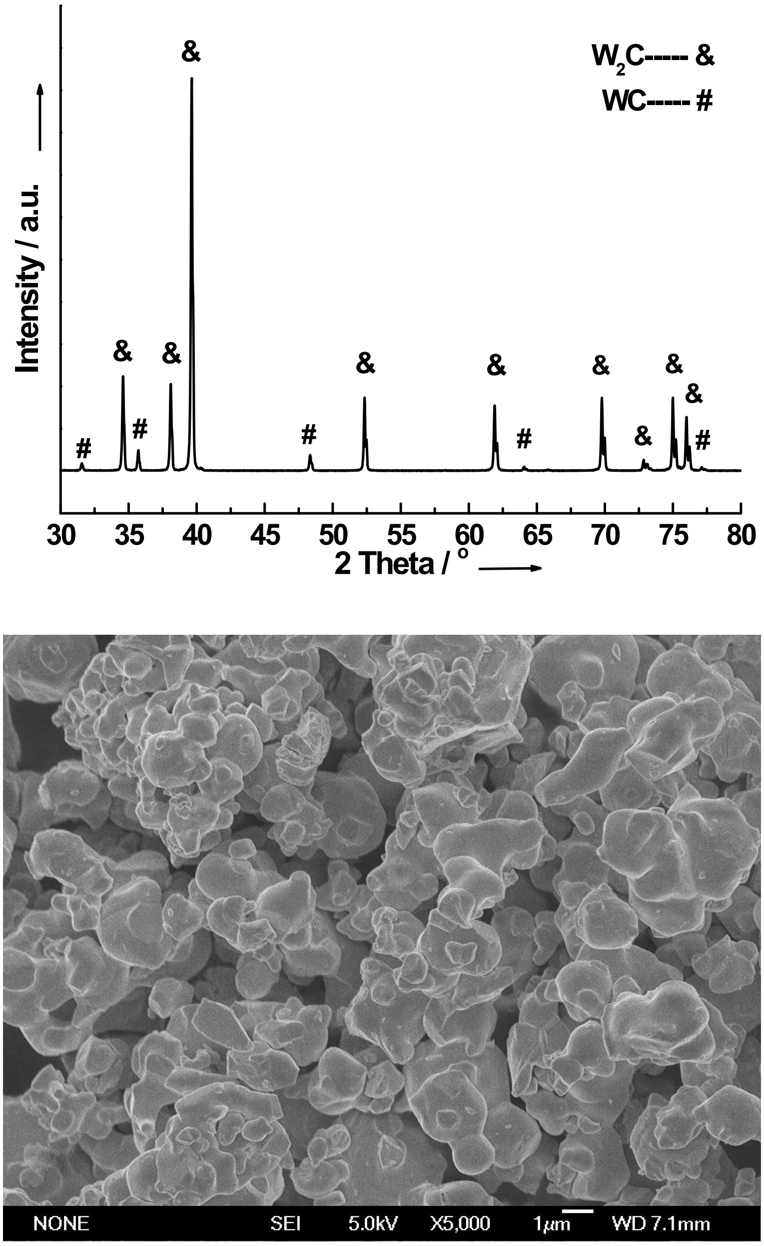


Figure S13. XRD pattern (top) and SEM image (down) of com-W_2C. The XRD analysis shows that the com-W_2C is dominated by the W_2C phase, with a small amount of WC in the material. In addition, the SEM image of com-W_2C shows that this material is composed of micrometer-sized particles.