Electronic Supplementary Information

Co-MoC$_x$ supported on N-doped CNT for efficient hydrogen evolution reaction under alkaline medium

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S1. Experimental Details

S1.1 X-ray diffraction

X-ray diffraction (XRD) patterns were recorded on a Rigaku Smartlab instrument, using a Cu Kα monochromatized radiation source at 1.54056 Å. Diffraction patterns were collected in ranges of 2θ from 10°-80° with a step size of 0.02 and a dwell time of 0.25 second per step. The receiving slit (RS), scattering prevention slit (SS) and divergence slit (DS) were 1/2°, 10 mm and 10 mm, respectively.

S1.2 Raman spectroscopy

Raman spectra were recorded at room temperature on a HORIBA LabRAM HR Evolution Raman Microscope (manufactured in France SAS) equipped with a liquid-nitrogen cooled multiple detectors including charge coupled device (CCD) detector and a confocal microscope. The line at 532 nm Ar laser was used as an excitation source and the scanning range was 50-3500 nm^{-1}. The laser was focused on the sample under a microscope with the diameter of the analysed spot being ~1 μm. The wavenumber values reported were accurate to within 2 cm^{-1}.

S1.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectra (XPS) were measured using a photoelectron spectrometer (XPS, PHI 5600) with a monochromatic Al K α X-ray source. The binding energy was preliminarily calibrated using the peak positions of the adventitious carbon (C 1s, 284.6 eV). The composition of Co oxidation states was estimated by the deconvolution of Co 3d doublet. Relative element concentrations of N and C were determined by the integral areas of the core-level spectra. After the background was subtracted according to the Shirley method, the spectra were fitted into several peaks using a convolution of Gaussian and Lorentzian functions.

S1.4 Scanning electron microscope

Scanning electron microscope (SEM) morphological images of the catalyst samples were obtained on a FE-SEM (Hitachi S-4800) electron microscope with a voltage range of 0.5–30 kV.

S1.5 Transmission electron microscopy

The microstructure and element distributions were carried out using transmission electron microscope (TEM, JEM2100+, JEOL) operated at 200 keV. The Co/CoN$_x$-CNT sample particles were ground between two glass slides, and dispersed on the copper grid.

S1.6 Specific surface area measurement (BET)

The specific surface areas and pore size distributions of catalysts samples were analyzed at liquid nitrogen temperature by the Brunauer–Emmett–Teller (BET) and Barrett-Joyner-Halenda (BJH) methods (Micromeritics, ASAP2020). The samples were degassed with a vacuum at 350ºC for 12 hours before conducting nitrogen adsorption-desorption isotherm at liquid nitrogen temperature.

Table S1. Comparison of the electrochemical performances

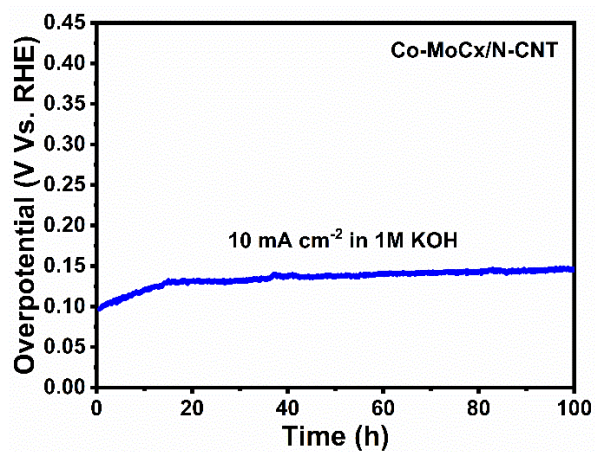|	Reaction media	Overpotential (η_{10})	Tafel slope (mV dec^{-1})	Reference
Co NPs/N-CNT	0.1M NaOH	337	N/A	[1]
Pt$_1$/carbon matrix	1.0M KOH	139	73.6	[2]
Co/N-CNT	1.0M KOH	143	152.05	This work
Co-MoC$_x$/N-CNT	1.0M KOH	130	156.08	This work
Co-Cu/N-CNT	1.0M KOH	161	182.75	This work
Co-Mn$_x$N$_y$/N-CNT	1.0M KOH	135	175.94	This work
Co$_1$/CN	1.0M KOH	138	N/A	[3]
Co$_1$/PCN	1.0M KOH	89	59	[3]
Mo doped Co$_1$-N$_4$	1.0M KOH	44	N/A	[4]

Figure S1 Chronopotentiometry curves of Co-MoC$_x$/N-CNT at constant current density of 10 mA cm^{-2}.
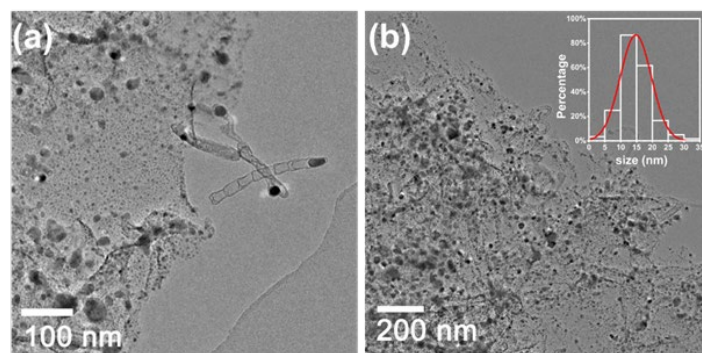
Figure S2 TEM images, inset is size distribution of Co-MoC$_x$ nanoparticles.

References

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