Chemical Communications

Electronic Supplementary Information (ESI) for

A high efficiency $CoCr_2O_4$/carbon nanotubes nanocomposite electrocatalyst for dye-sensitised solar cells

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Experimental Section

Synthesis of $Co_xCr_yO_4$/CNTs: $Co_xCr_yO_4$/CNTs samples were fabricated as follows: 0.2 g $Co(NO_3)_2 \cdot 6H_2O$ (*Kang Pu Hui Wei Technology Co., Ltd., Beijing*) was firstly dissolved in 20 mL of distilled water, and $Cr(NO_3)_3 \cdot 9H_2O$ (*Kang Pu Hui Wei Technology Co., Ltd, Beijing*) with different amounts was dissolved in another 20 mL of distilled water. After 30 min, the above two solutions were mixed under stirring in the presence of 0.2 g multiwalled carbon nanotubes (CNTs) (*Nanotech Port Co., Ltd, Shenzhen*). The formed mixtures with different molar ratios of cobalt and chromium precursors were placed for 12 h in room temperature in dark condition and then dried at 110 °C for 5 h in atmosphere to obtain solid product. To improve crystallinity, the resulting products were calcined at 500 °C for 30 min in N_2. Cr_2O_3/CNTs and Co_xO_y/CNTs samples were obtained with a similar synthetic process of $Co_xCr_yO_4$/CNTs, but only containing 0.2 g cobalt or chromium precursor and 0.2 g CNTs. All fabricated samples were preserved for further characterisation and use. To

obtain meaningful comparison, the commercially available Pt counter electrodes were purchased from Wuhan Geao Science Instrument Co., Ltd (China).

Preparation of TiO_2 films: TiO_2 photoanode films were fabricated as follows: 20 nm-sized TiO_2 nanoparticles (*P25, Degussa, Germany*) were loaded on FTO conductive glass substrate by doctor-blading technique to form a TiO_2 nanoparticle layer with a thickness of 12 μm. After sintering at 200 °C for 30 min, the obtained nanoparticle layer was further coated with a 4 μm thick light scattering layer composed of 160 nm-sized TiO_2 particles (*ST-41, Ishihara, Japan*), and then the obtained TiO_2 film was further thermally treated at 500 °C for 90 min in air. The resulting nanocrystalline TiO_2 films with light scattering layer were immersed in a 5×10^{-4} M dye N719 (*Solaronix SA, Switzerland*) solution in acetonitrile/tert-butyl alcohol (V:V=1:1) for 12 h. The obtained N719 sensitised TiO_2 films were used as photoanodes for DSSCs measurements.

Fabrication of $Co_xCr_yO_4$/CNTs counter electrodes: 0.5g of the prepared $Co_xCr_yO_4$/CNTs was firstly dispersed in 5 mL of isopropanol by ultrasonic bath to obtain spray paste. A certain amount (2.0 mL) of the prepared $Co_xCr_yO_4$/CNTs paste was then sprayed onto five pieces of cleaned FTO conductive glass substrates using an air brush each experiment. The $Co_xCr_yO_4$/CNTs coated FTO substrates were further calcined at 500 °C for 30 min in N_2 to obtain counter electrodes in this work. Similar preparation procedures were also adopted to obtain Cr_2O_3/CNTs and Co_xO_y/CNTs counter electrodes.

Characterisation: X-ray diffraction (XRD) measurements were carried out using an automatic X-ray powder diffractometer (D/Max-Ultima, RIGAKU). The morphologies of the samples were characterised by field emission scanning electron

microscopy (FESEM, ZEISS SUPRA 55 SAPPHIRE) and transmission electron microscopy (TEM, G2 F30, Tecnai).

The XRD diffraction peak data of Cr_2O_3, Co_xO_y, $CoCr_2O_4$ and carbon from Fig. 1A in manuscript are as below:

Rhombohedral Cr_2O_3 (JCPDS No. 70-3766): The diffraction peaks at 24.486°, 33.558°, 36.175°, 41.457°, 50.189°, 54.820°, 63.418°, 65.061° are assigned to the (012), (104), (110), (113), (024), (116), (214), (300) planes, respectively.

Co_xO_y: The diffraction peaks at 42.485°, 61.646°, 74.858°, 77.738° are ascribed to the (200), (220), (311), (222) planes of cubic CoO (JCPDS No. 70-2856), correspondingly, while more diffraction peaks at 19.000°, 31.272°, 36.848°, 38.549°, 44.811°, 55.657° , 59.358°, 65.237°, 77.344° are attributed to the (111), (220), (311), (222), (400), (422), (511), (440), (533) planes of cubic Co_3O_4 (JCPDS No. 73-1701), respectively.

Cubic $CoCr_2O_4$ (JCPDS No. 80-1668): The diffraction peaks at 18.426°, 30.312°, 35.707°, 37.352°, 43.400°, 53.853°, 57.412°, 63.055° are due to the (111), (220), (311), (222), (400), (422), (511), (440) planes, correspondingly.

Carbon (JCPDS No. 75-0444): The intense diffraction peak at 26.309° is assigned to the (111) plane of graphitic carbon.

Measurements: A series of DSSCs were fabricated with traditional sandwich type configuration by using a dye-anchored TiO_2 photoelectrode, a $CoCr_2O_4$/CNTs counter electrode, and an electrolyte containing 0.06 M LiI, 0.6 M 1-butyl-3-methylimidazolium iodide, 0.03 M I_2, 0.5 M 4-tert-butyl pyridine and 0.1 M guanidinium thiocyanate in acetonitrile. The DSSCs measurements were carried out under a simulated AM1.5 illumination (100 mW/cm^2, Solar Light Co., INC., USA) with an illumination active area of 0.2 cm^2. Photocurrent-photovoltage curves of the

DSSCs were performed with a Keithley digital source meter (Keithley 2601, USA). The EIS experiments were measured with dummy cells in the dark by using an electrochemical workstation (Zenium Zahner, Germany). The frequency range of EIS experiment was from 100 mHz to 1 MHz with an AC modulation signal of 10 mV and a DC bias of 0.60 V. The obtained EIS curves were further fitted by the Zview software. Cyclic voltammetry (CV) was carried out in a three-electrode system in an Ar-purged acetonitrile solution containing 0.1 M $LiClO_4$, 10 mM LiI, and 1.0 mM I_2 at a scan rate of 100 mV/s using a BAS 100B/W electrochemical analyser. Pt mesh and Ag/AgCl electrode were used as counter electrode and reference electrode, respectively. Tafel polarisation curves were obtained using symmetrical cells, at a scanning rate of 10 mV/s, using an electrochemical workstation (Zenium Zahner, Germany).

Table S1 Photovoltaic parameters of the DSSCs made of $Co_xCr_yO_4$/CNTs counter electrodes (CEs) with different molar ratios of cobalt and chromium precursors and the parameters of the dummy cell assembled with two identical CEs.

CEs	V_{oc} ***(V)***	J_{sc} ***(mA/cm²)***	***FF***	η ***(%)***	R_s ***(Ω cm²)***	R_{ct} ***(Ω cm²)***
1:3	0.70	19.03	0.58	7.73	15.59	1.67
1:1.5	0.71	18.92	0.60	8.06	13.28	2.32
1:1	0.75	18.98	0.59	8.40	12.35	1.12
1.5:1	0.71	18.69	0.59	7.83	13.85	1.58
3:1	0.70	19.23	0.55	7.40	16.06	2.21

Table S2 Photovoltaic parameters of the DSSCs assembled with $CoCr_2O_4$/CNTs, Cr_2O_3/CNTs, Co_xO_y/CNTs and Pt counter electrodes. Parallel three samples for DSSCs measurements under each experimental condition.

CEs	*Sample No.*	V_{oc} (*V*)	J_{sc} (*mA/cm*^{2})	*FF*	η (%)
$CoCr_2O_4$/CNTs	1	0.73	19.51	0.55	7.83
	2	0.75	18.98	0.59	8.40
	3	0.75	19.47	0.60	8.76
	Average	0.74 ± 0.01	19.32 ± 0.30	0.58 ± 0.03	8.33 ± 0.47
Cr_2O_3/CNTs	1	0.71	16.34	0.52	6.03
	2	0.71	15.74	0.53	5.92
	3	0.72	16.68	0.50	6.00
	Average	0.71 ± 0.01	16.25 ± 0.48	0.52 ± 0.02	5.98 ±0.06
Co_xO_y/CNTs	1	0.71	15.64	0.47	5.22
	2	0.72	14.65	0.47	4.96
	3	0.71	19.80	0.38	5.34
	Average	0.71±0.01	16.70 ± 2.73	0.44 ± 0.05	5.17 ± 0.19
Pt	1	0.76	18.52	0.61	8.59
	2	0.70	21.51	0.58	8.73
	3	0.76	18.73	0.61	8.68
	Average	0.74 ± 0.03	19.59 ± 1.67	0.60 ± 0.02	8.67 ± 0.07

Note: all underlined data were chosen and shown in Table 1 in manuscript.

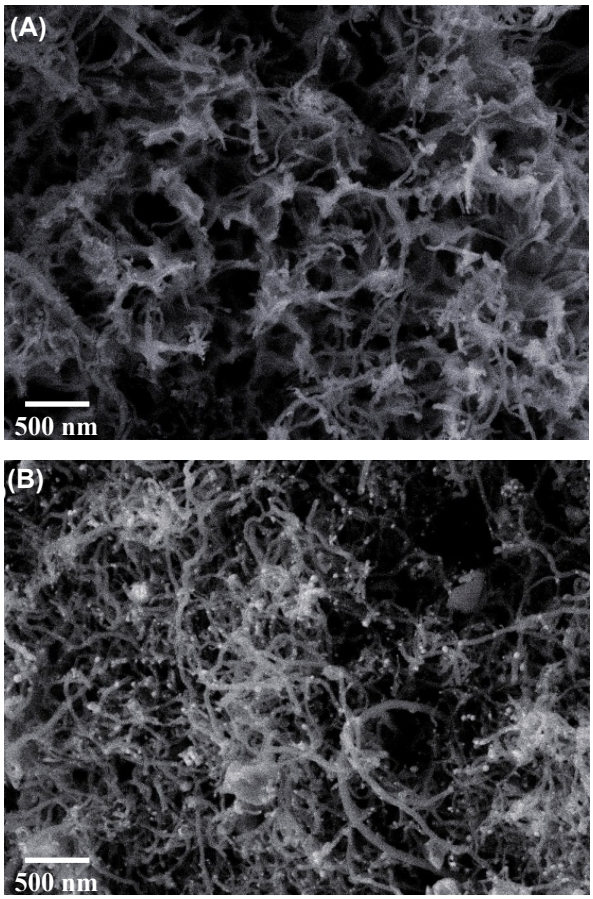

Fig. S1 SEM images of (A) Cr_2O_3/CNTs and (B) Co_xO_y/CNTs (Co_xO_y represents a mixture of CoO and Co_2O_3).

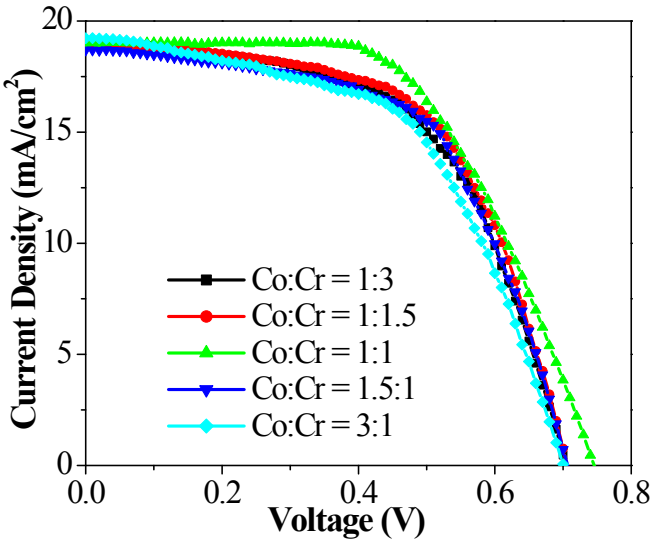

Fig. S2 *I-V* characteristics of the DSSCs made of $Co_xCr_yO_4$/CNTs counter electrodes with different molar ratios of cobalt and chromium precursors.

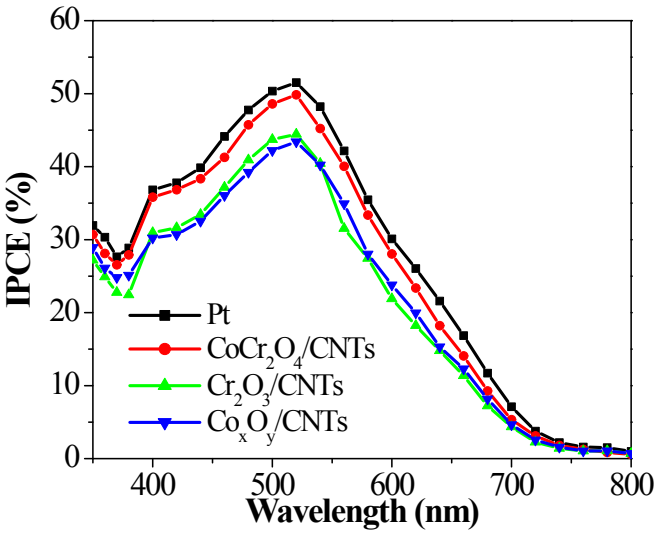

Fig. S3 Incident photon to current conversion efficiency (IPCE) curves of the DSSCs assembled with $CoCr_2O_4$/CNTs, Cr_2O_3/CNTs, Co_xO_y/CNTs and Pt counter electrodes.

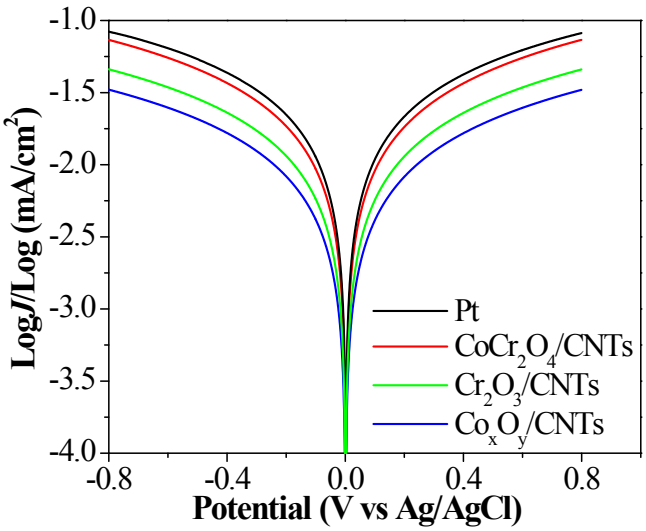

Fig. S4 Tafel polarisation curves of the $CoCr_2O_4$/CNTs, Cr_2O_3/CNTs, Co_xO_y/CNTs and Pt counter electrodes.

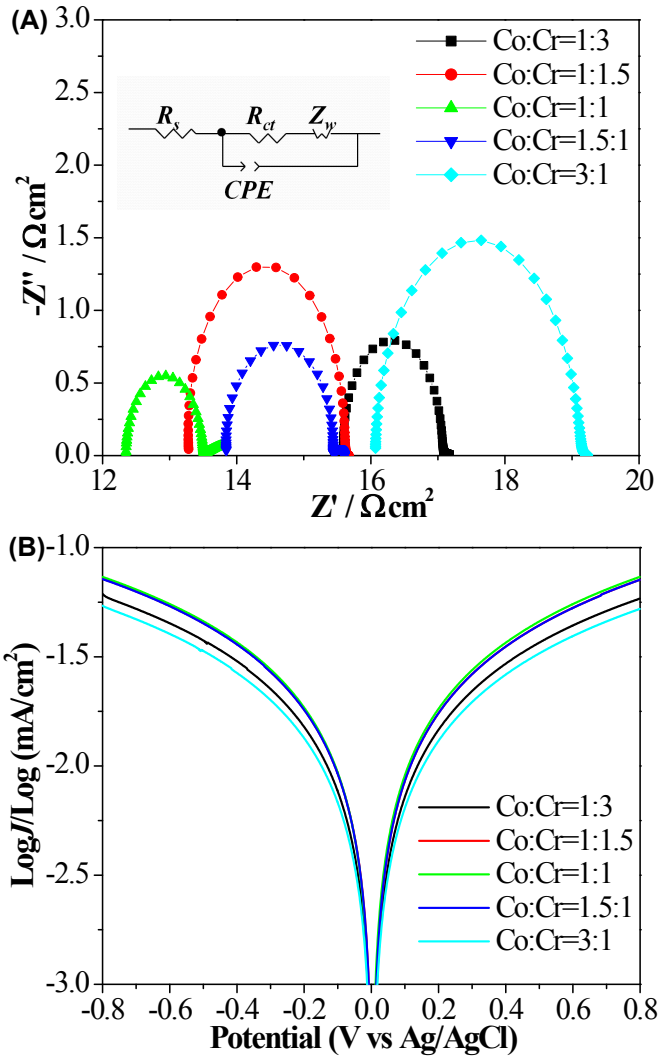

Fig. S5 (A) Nyquist plots of the dummy cells fabricated with two identical $Co_xCr_yO_4$/CNTs electrodes with different molar ratios of cobalt and chromium precursors in I_3^-/I^- electrolyte. (B) Tafel polarisation curves of the $Co_xCr_yO_4$/CNTs electrodes with different molar ratios of cobalt and chromium precursors.