Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Optimization of the Facet Structure of Cobalt Oxide Catalysts for Enhanced Hydrogen Evolution Reaction

Minghong Wu[a,b], Shuqiang Ke[a], Wenqian Chen[a,c]*, Shaomei Zhang[a], Min Zhu[a], Yu Zhang[a], Maw Lin Foo[d], Liang Tang[a,b]*

[a] School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, PR China

[b] Key Laboratory of Organic Compound Pollution Control Engineering, Ministry of Education, Shanghai 200444, PR China

[c] Shanghai Institute of Applied Radiation, Shanghai University, 20 Chengzhong Road, Shanghai 201800, PR China

[d] Department of Chemistry, National University of Singapore, 117543, Singapore

* Corresponding authors: wenqianchen@shu.edu.cn, tang1liang@shu.edu.cn

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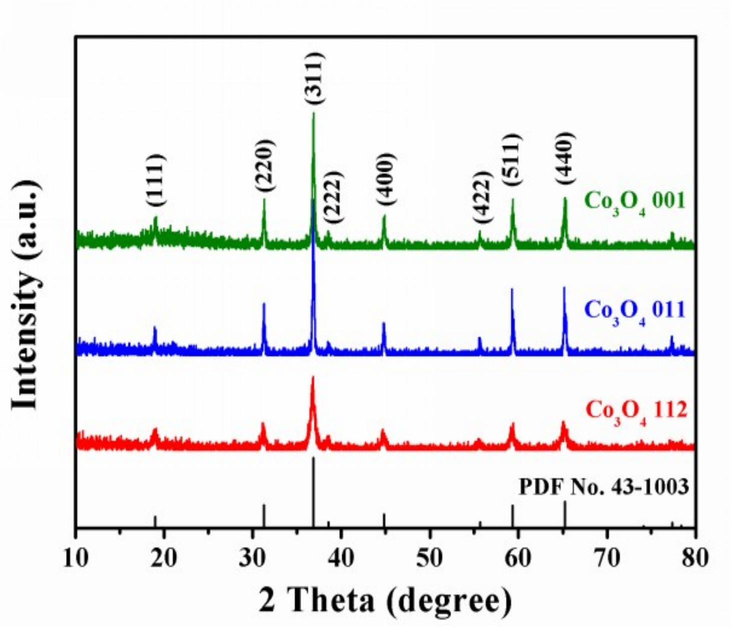


Figure S1. XRD patterns of Co_3O_4 112 , Co_3O_4 011 and Co_3O_4 001.

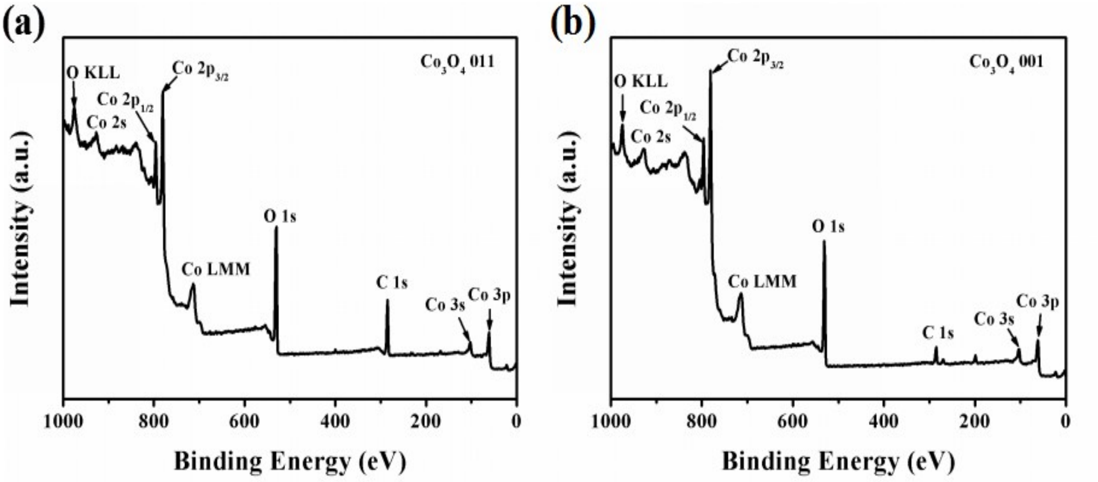


Figure S2. XPS survey spectrum of (a) Co_3O_4 011 and (b) Co_3O_4 001. Both the XPS results show the signal of C, Co, and O without any other impurities.

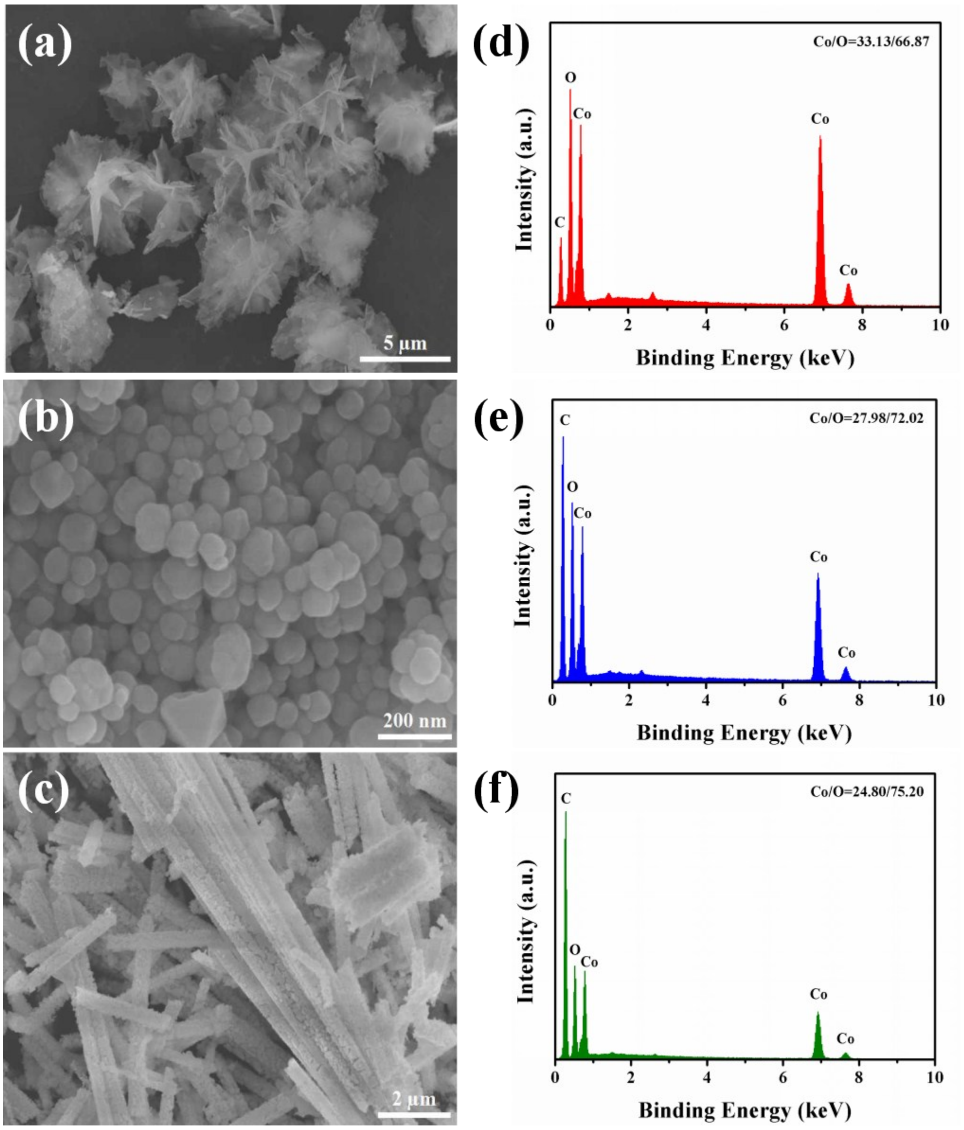


Figure S3. SEM images and EDS spectra of (a, d) Co_3O_4 112, (b, e) Co_3O_4 011, and (c, f) Co_3O_4 001.

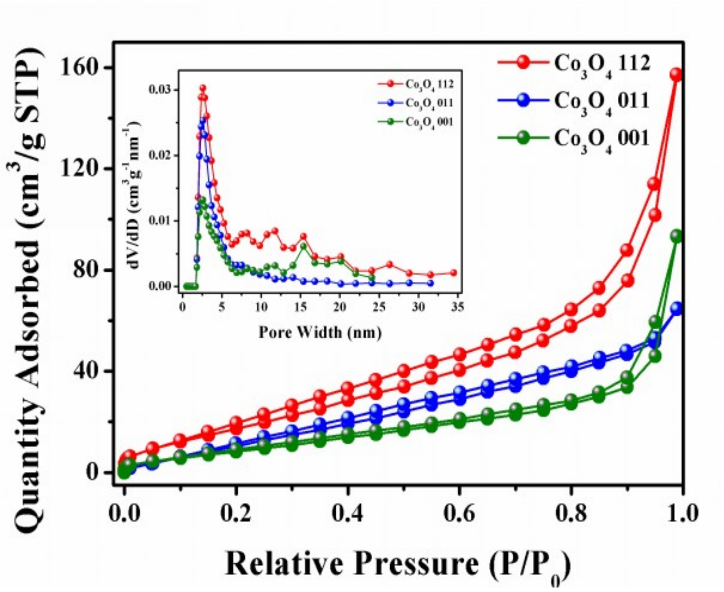


Figure S4. Nitrogen adsorption-desorption isotherms and the corresponding pore-size distribution curves (inset) of Co_3O_4 112, 011 and 001 samples.

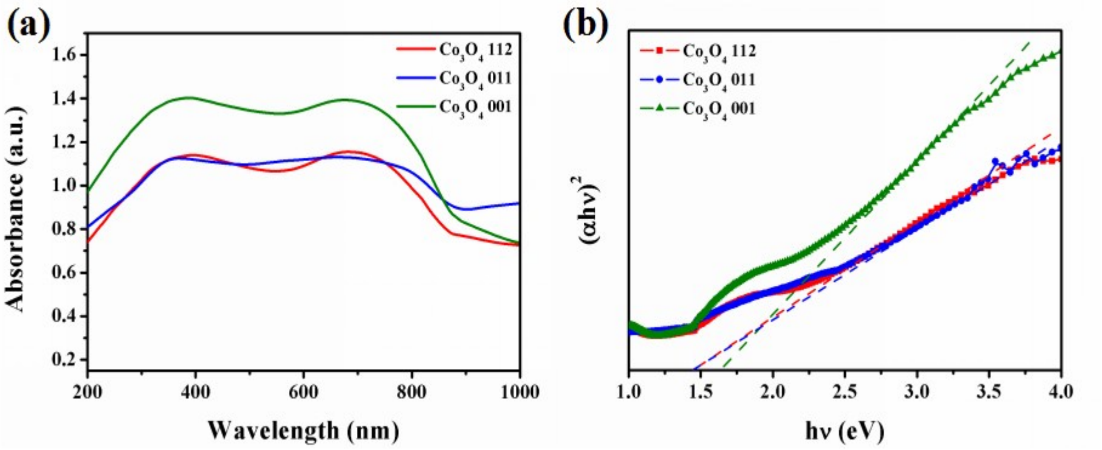


Figure S5. (a) UV-vis diffuse reflectance spectra (DRS) and (b) $(\alpha h\nu)^2$-$h\nu$ curve of Co_3O_4 112, 011 and 001 samples. The band gap energy (E_g) of a semiconductor can be calculated by the Tauc drawing method：$\alpha h\nu = A(h\nu - E_g)^{n/2}$, where h, ν, α, and A respectively represent the Planck constant, light frequency, the absorption coefficient and a constant. The inherent optical transition characteristics of the semiconductors *determine the value of n, where n = 1 for direct transitions and n = 4 for indirect transitions.*

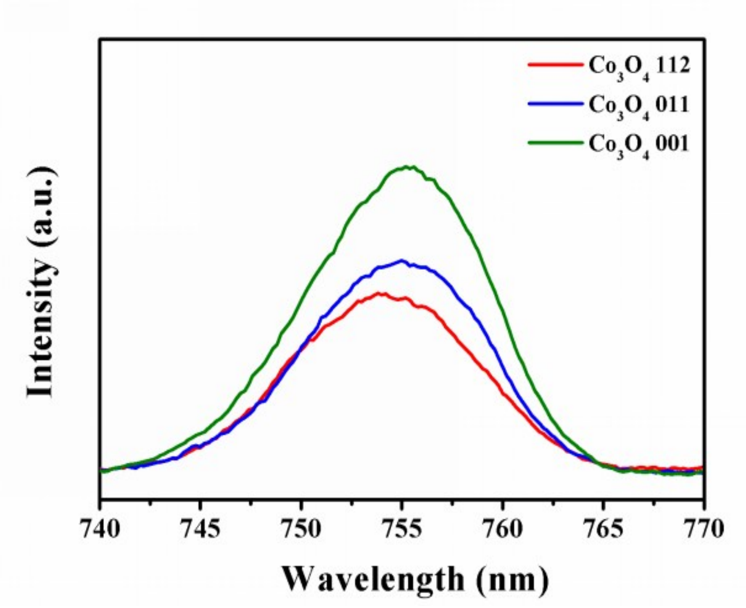


Figure S6. PL spectra of Co_3O_4 112 , 011 and 001 at an excitation wavelength of 500 nm.

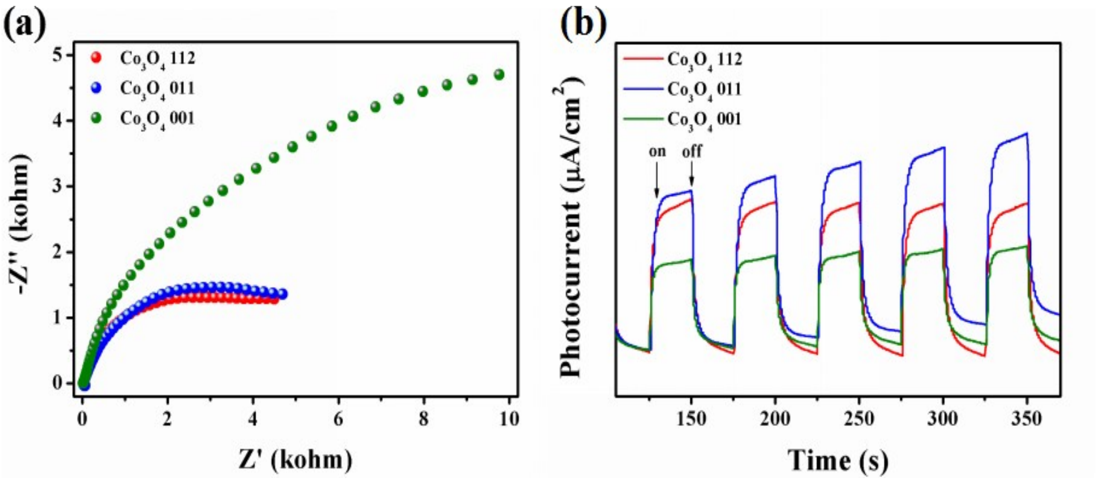


Figure S7. (a) Electrochemical impedance spectroscopy (EIS) and (b) transient photocurrent response under visible light irradiation of Co_3O_4 112, 011 and 001 samples.

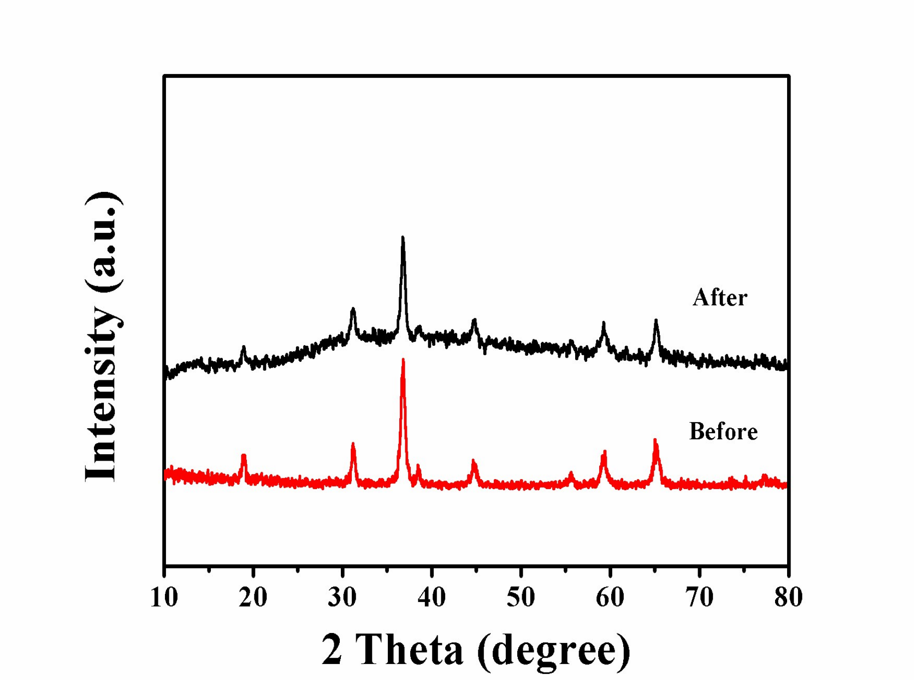


Figure S8. XRD patterns of Co_3O_4 112 after 20 hours of photocatalytic hydrogen evolution.

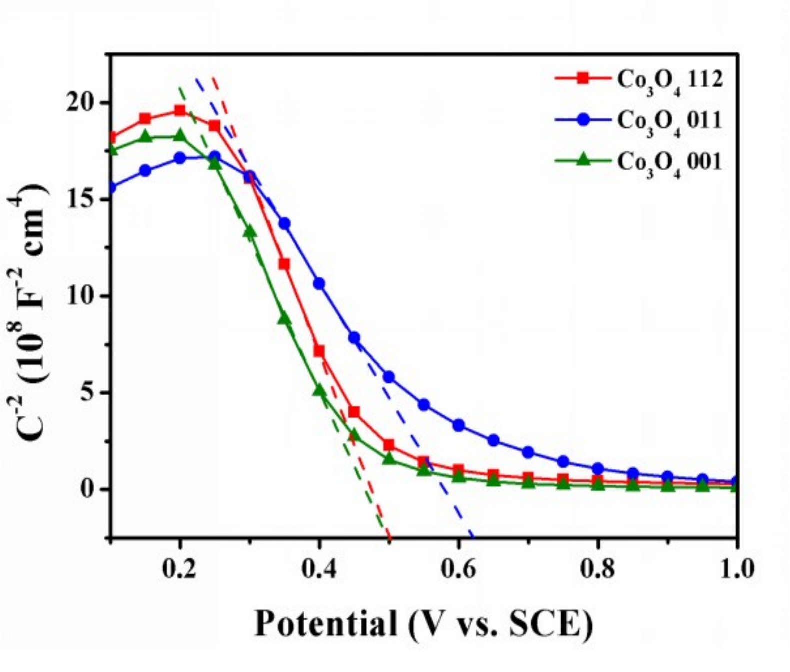
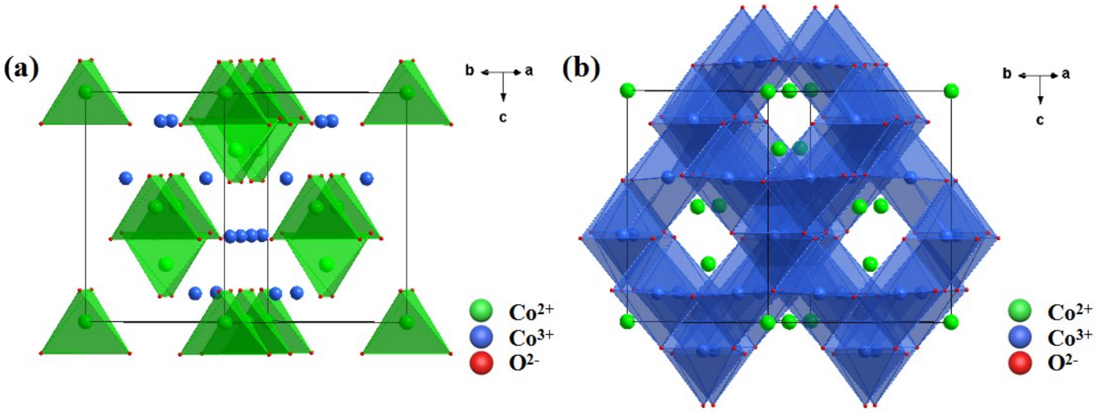
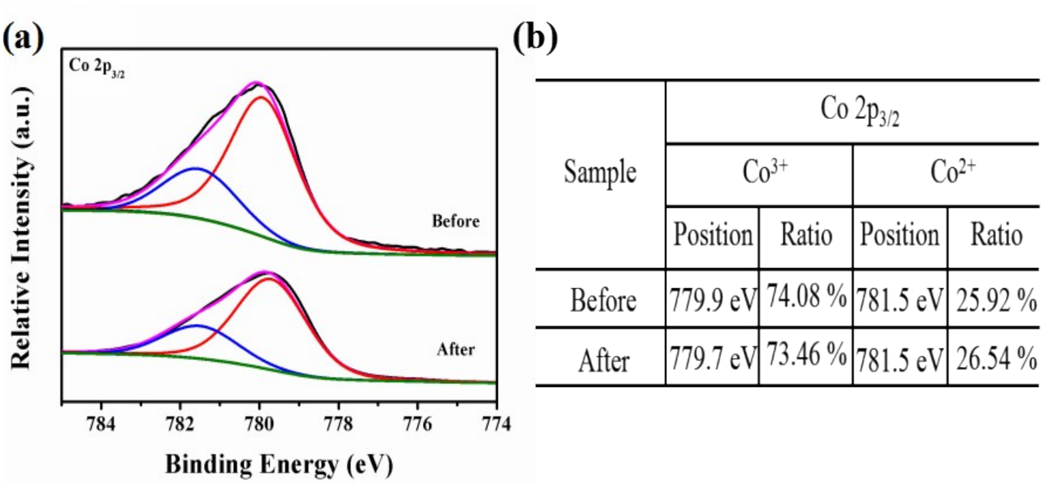


Figure S9. Mott-Schottky curves of Co_3O_4 112, 011 and 001 samples with frequencies of 1.0kHz. The flat band potential (E_{fb}) of Co_3O_4 112 and 001 are 0.50 V versus SCE, and Co_3O_4 011 is 0.62 V. It is generally considered that the E_{VB} of the p-type *semiconductor is higher 0.1 or 0.2 V than* E_{fb}*,*[1] *so the* E_{VB} *of* Co_3O_4 *112 and 001 are roughly estimated to be 0.60 V vs. SCE, and* Co_3O_4 *011 is 0.72 V. According to the equation:* $E_{NHE} = E_{SCE} + 0.241$*, the* E_{VB} *of* Co_3O_4 *112 and 001 are roughly estimated to be 0.841V vs. NHE, while* Co_3O_4 *011 is 0.961V.*



Co^{2+}-O_4 tetrahedron **Co^{3+}-O_6 octahedron**

Figure S10. The crystal structure of spinel Co_3O_4 *(*$Co^{2+}Co^{3+}{}_2O_4$*). (a)* Co^{2+} *ion in the unit cell occupies the tetrahedral site, (b)* Co^{3+} *ion occupies the octahedral site.*



Sample	Co $2p_{3/2}$			
	Co^{3+}		Co^{2+}	
	Position	Ratio	Position	Ratio
Before	779.9 eV	74.08 %	781.5 eV	25.92 %
After	779.7 eV	73.46 %	781.5 eV	26.54 %

Figure S11. (a) Co 2p spectra of Co_3O_4 *112 after 20 hours of photocatalytic hydrogen evolution. (b) Detailed peak positions in (a).*

Table S1. Elemental compositions of prepared three Co_3O_4 samples.

Samples	C (at%)	Co (at%)	O (at%)
Co_3O_4 112	9.64	65.67	24.69
Co_3O_4 011	41.51	16.73	41.75
Co_3O_4 001	21.05	29.05	49.90

Table S2. Detailed peak position and corresponding area percentage of the Co $2p_{3/2}$ and O 1s spectra of prepared three Co_3O_4 samples.

Samples	Co $2p_{3/2}$				O 1s			
	Co^{3+}		Co^{2+}		–OH		absorbed H_2O	
	Position (eV)	Area (%)	Position (eV)	Area (%)	Position (eV)	Area (%)	Position (eV)	Area (%)
Co_3O_4 112	779.9	74.08	781.5	25.92	531.3	91.72	533.2	8.28
Co_3O_4 011	779.9	71.02	781.4	28.98	531.3	91.12	533.2	8.88
Co_3O_4 001	780.1	56.11	781.7	43.89	531.3	81.34	533.2	18.66

Table S3. Porous structure parameters of prepared three Co_3O_4 samples

Samples	BET surface area (m^2/g)	Mean pore width (nm)	Pore volume (cm^3/g)
Co_3O_4 112	74.439	2.6	0.079
Co_3O_4 011	62.117	2.8	0.072
Co_3O_4 001	35.922	2.6	0.034

References

1. X. Li, J. Yu, J. Low, Y. Fang, J. Xiao and X. Chen, Engineering heterogeneous semiconductors for solar water splitting, *J. Mater. Chem. A*, 2015, **3**, 2485-2534.