Electronic Supplementary Material

Co_3O_4 Quantum Dots: Reverse Micelle Synthesis and Visible-light-driven Photocatalytic Overall Water Splitting

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Experimental Section

Preparation of samples: All reagents were of analytical purity and used as received from Sinopharm Chemical Reagent Co., Ltd. All experiments were conducted using ultrapure water (pH, 5.6; resistivity, 18.2 MΩ cm) produced from a Milli-Q (Millipore, USA) water purifying system. Co_3O_4 quantum dots were prepared via a facile reverse micelle method with microwave-assisted solvothermal process (see Fig. S1) as follows. $Co(NO_3)_2 \bullet 6H_2O$ (1 mmol) was dissolved in butanol (1 mL) to form solution A, which was then mixed with dodecanol (39 mL) in a Teflon-lined autoclave (100 mL) to form a clear precursor solution of reverse micelles. The Teflon-lined autoclave was then sealed and transferred into a microwave reactor (MDS-10, SINEO, China) with a program of heating to 170^{o}C in 7 minutes and keeping this temperature for 30 s, and then cooling to room temperature. The solid product of Co_3O_4 quantum dots was separated out by centrifugation. In order to remove organic molecules absorbed on the surface of Co_3O_4 quantum dots, the solid product was washed with absolute ethanol in an ultrasonic bath and separated out by centrifugation for three cycles. Finally, the solid product was dried in vacuum at 200^{o}C for 3 h and designated as Co_3O_4-QDs. For comparison, the sample designated as Co_3O_4-SSR was prepared by a solid-state reaction, i.e., directly calcining $Co(NO_3)_2 \bullet 6H_2O$ at 500^{o}C for 3 h.

Characterization of samples: Crystal structures and phase composition of the samples were determined by using a powder X-ray diffractometer (X'Pert PRO MPD, PANalytical, the Netherlands) with (θ/2θ) Bragg–Brentano geometry. The powder X-ray diffraction (PXRD) patterns were collected in the range 2θ=25–75^{o} (40 kV, 40 mA; Cu Kα radiation, λ=1.541874Å; Ni filter; realtime multiple strip (RTMS) detector, X'Celerator). Surface chemical components and states of the products were studied using a X-ray photoelectron spectrometer (AXIS Ultra DLD, Shimadzu/Kratos Analytical, Japan) with monochromatic Al Kα radiation (150 W, 15 kV, 1486.6 eV) and with pressure under high vacuum ($< 3\times10^{-9}$ Torr). Binding energies of X-ray photoelectron spectroscopy (XPS) were calibrated relative to the C 1s peak (284.8 eV) from hydrocarbons adsorbed on the surface of samples. Particle size and morphology were confirmed by a transmission electron microscope that was operated at 200 kV (JEM-2100F, JEOL, Japan). Samples for transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analysis were ultrasonically dispersed in absolute ethanol, and then, by dipping and drying process, were deposited on copper grids, which were coated with holey or lacey amorphous carbon support films. Raman spectra was obtained on a spectrometer (LabRAM HR 800, Horiba/Jobin Yvon, France) using 514.5 nm irradiation from an argon ion laser at 20 mW. Brunauer-Emmett-Teller (BET) surface areas of samples were deduced from N_2 adsorption-desorption isotherms at 77 K, and determined by using an Accelerated Surface Area and Porosimetry Analyzer (ASAP 2020, Micromeritics, USA) after degassing the samples at 150°C for 24 h. UV-Vis spectra of the photocatalysts were measured on a spectrophotometer (UV4100, HITACHI, Japan) employing a labsphere diffuse reflectance accessory. The obtained data were transformed to absorption spectra according to the Kubelka–Munk function (F(R)),[1] and bandgaps of samples were estimated on the basis of the Tauc equation.[2] Both

Co_3O_4-QDs and Co_3O_4-SSR were considered as direct allowed transition semiconductors.[3] The analysis of photoluminescence (PL) spectra was carried out at room temperature using a fluorescence spectrophotometer (QuantaMaster 40, PTI, Canada). The excitation wavelength is 420 nm. Fourier transform infrared spectra (FTIR) were collected on a spectrophotometer (Vextex 70, Bruker, Germany) under a transmittance mode. Specimens were prepared by thoroughly dispersing samples into KBr powder and then pressing them into pellets. The spectra were collected between 4000 and 400 cm^{-1} with 64 scans and resolution of 4 cm^{-1}.

Evaluation of photocatalytic activities: UV-driven photocatalytic H_2 evolution was performed in a 130 mL Pyrex glass cell, which had a flat, round side-window (7.09 cm^2) for external light incidence with a 300 W high-pressure mercury lamp (CEL-LAM500, AULTT, China). The irradiance of incident light is 54 mW cm^{-2}. The amount of photocatalyst was 0.010 g and reactant solution was 100 mL 50% ethanol aqueous solution.

Visible-light-driven photocatalytic H_2 evolution was performed in a 130 mL Pyrex glass cell, which had a flat, round side-window (7.09 cm^2) for external light incidence. A 300 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Technology Co., Ltd, China) with a series of UV cut-off filters (i.e., 380 , 400 and 420 nm) was used as the light source. The irradiance of incident light is 180 mW cm^{-2}. The amount of photocatalyst was 0.010 g and reactant solution was 100 mL 50% ethanol aqueous solution.

The visible-light-driven photocatalytic overall water splitting on Co_3O_4-QDs was evaluated in pure water on a differential auto-test system. Argon was chosen to be the purge gas. The reactor was a 130 mL Pyrex glass cell, which had a flat, round side-window (7.09 cm^2) for external light incidence. A 300 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Technology Co., Ltd, China) with a UV cut-off filter (> 420 nm) was used as the light source. The irradiance of incident light is 180 mW cm^{-2}. The average intensity of incident light was measured with a spectroradiometer (AvaSpec-2048-USB2, Avantes, Netherland) and equal to 300 mW cm^{-2}, and the irradiated area was 3.14 cm^2. The amount of catalyst was 0.010 g and reactant solution was 100 mL pure water.

For all photocatalytic tests, the reactor with reactant solution was purged with Ar for 20 min to eliminate O_2 before light irradiation. Temperature of the system during photocatalytic reaction was maintained by thermostatic circulating water at around 30°C. The evolved gas was detected with a gas chromatograph (GC, SP-2100, Beijing Beifen-Ruili Analytical Instrument (Group) Co., Ltd, China), which was equipped with a thermal conductivity detector (TCD), TDX-01 column, and Ar carrier gas.

Calculation of turnover number

The turnover number (TON), which is generally employed to judge whether the reactions proceeded photocatalytically,[4] was calculated according to Equations (1) and (2). Co_3O_4-QDs exhibited visible-light-driven photocatalytic activity with stable H_2 (0.79 μmol h^{-1}) and O_2 (0.40 μmol h^{-1}) evolution rate for 244 h.

$$TON = \frac{\text{Molar amount of H}_2\text{ evolved} \times 2}{\text{Molar amount of photocatalyst}}$$

$$= \frac{0.79 \mu mol \bullet h^{-1} \times 244 h \times 2}{0.010 g / (240.8 \times 10^{-6} g \bullet \mu mol^{-1})} = 9.3 \qquad (1)$$

$$TON = \frac{\text{Molar amount of } \mathrm{O_2} \text{ evolved } \times 4}{\text{Molar amount of photocatalyst}}$$

$$= \frac{0.40 \mu mol \bullet h^{-1} \times 244 h \times 4}{0.010 g / (240.8 \times 10^{-6} g \bullet \mu mol^{-1})} = 9.4 \qquad (2)$$

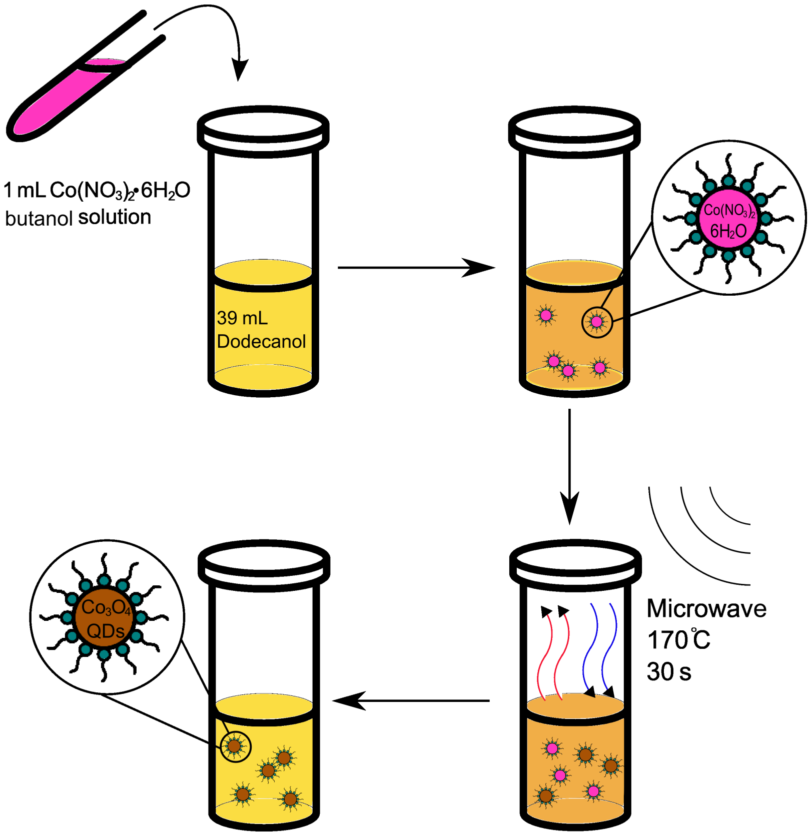

Fig. S1 Synthetic route of Co_3O_4-QDs.

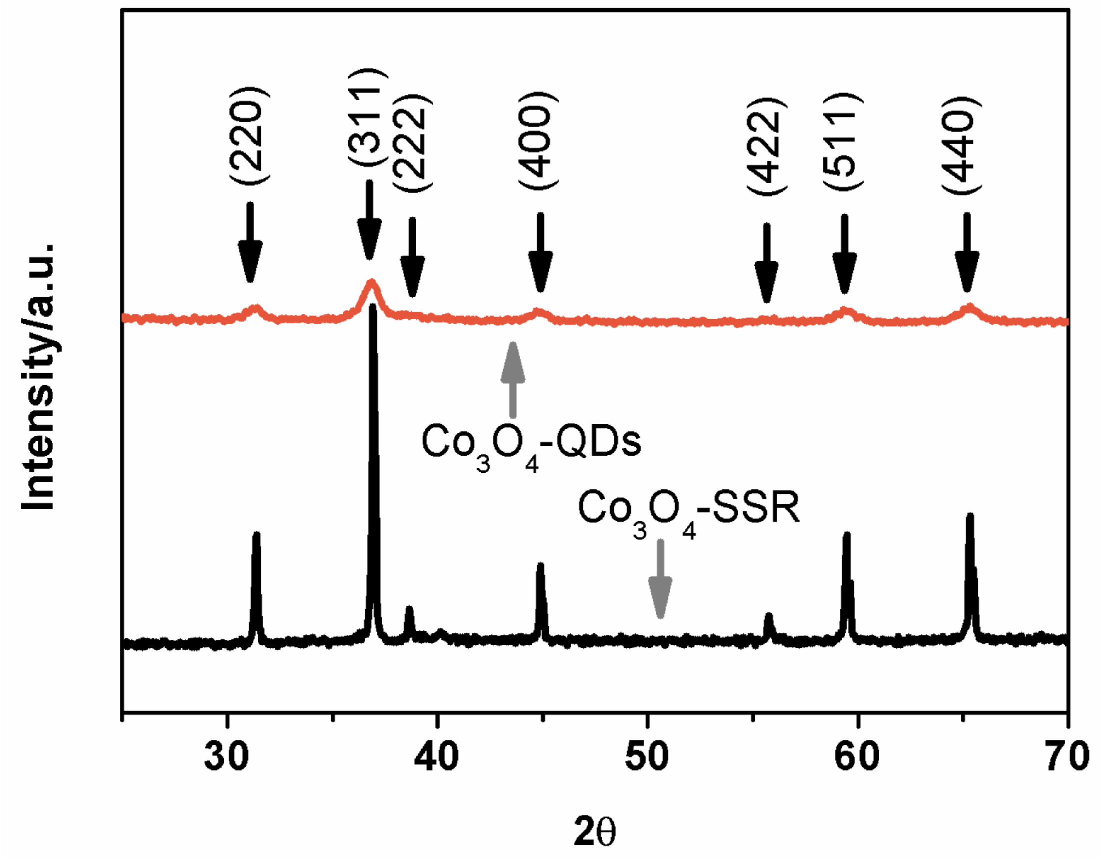

Fig. S2 PXRD spectra of Co_3O_4-QDs and Co_3O_4-SSR.

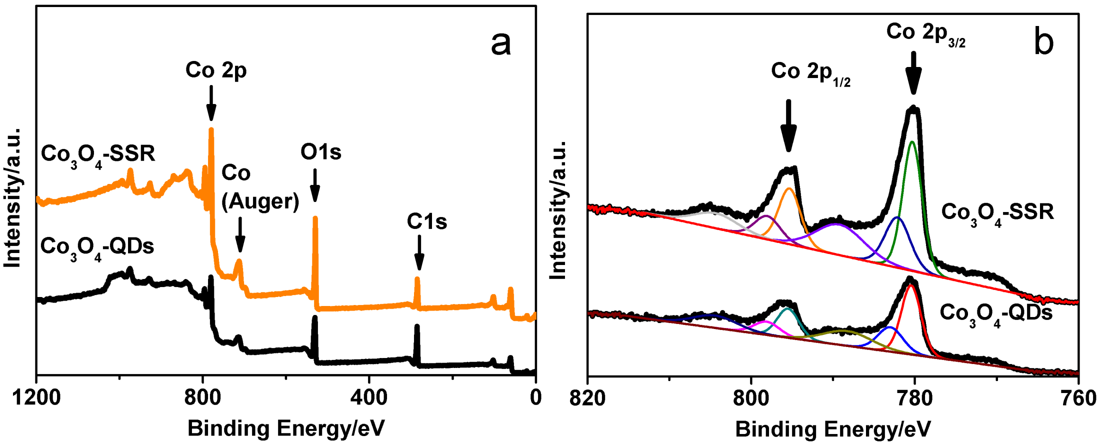

Fig. S3 (a) Survey-scan XPS spectra and (b) High-resolution XPS spectra of Co 2p for Co_3O_4-QDs and Co_3O_4-SSR.

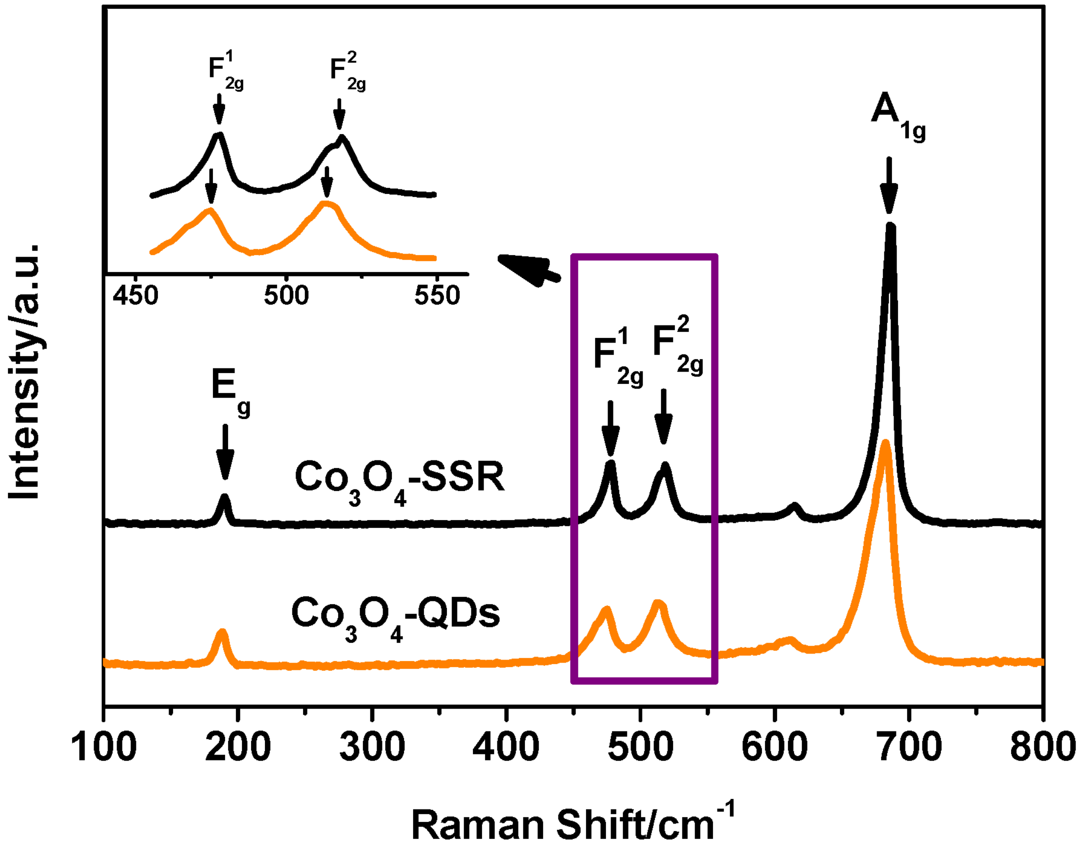

Fig. S4 Raman spectra of Co_3O_4-QDs and Co_3O_4-SSR.

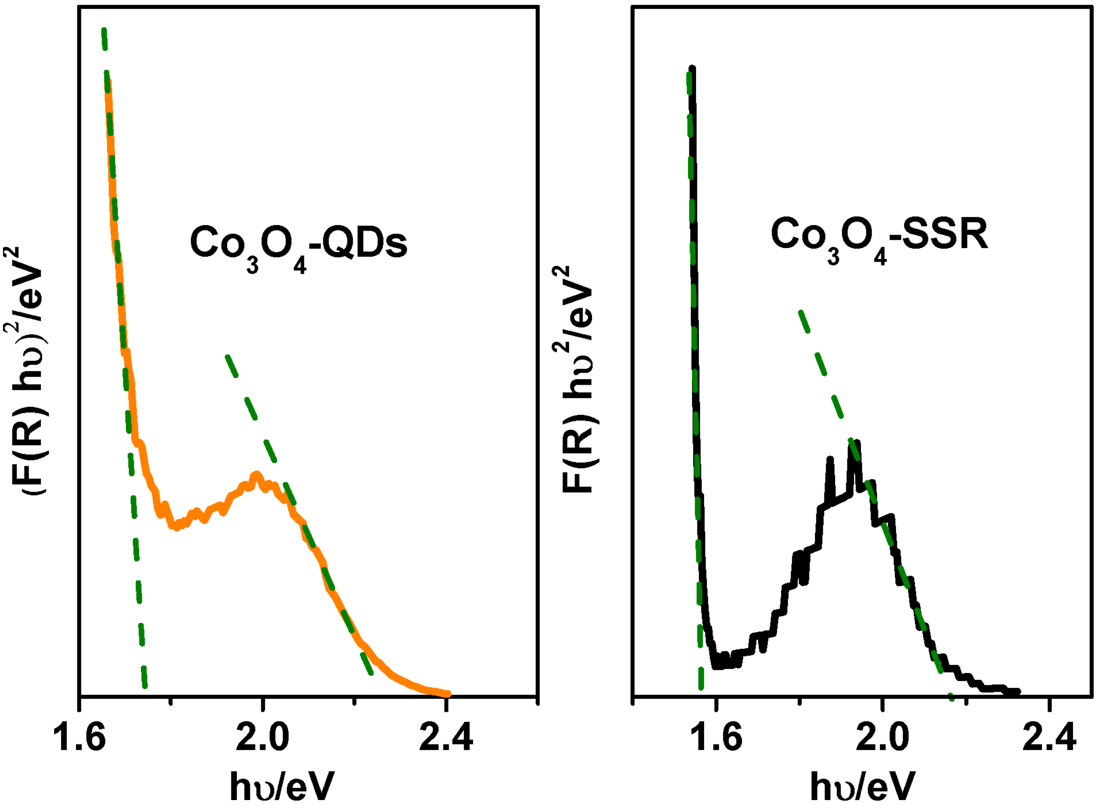

Fig. S5 Tauc plots ($(F(R)\ h\nu)^2$ vs. hν) of Co_3O_4-QDs and Co_3O_4-SSR.

Table S1 Crystal size, bandgap, BET surface area, and photocatalytic activity under visible-light irradiation in pure water for Co_3O_4-QDs and Co_3O_4-SSR.

Photocatalyst	Crystal size (nm)	Bandgap (eV)[a]		BET surface area ($m^2\ g^{-1}$)[b]	Rate of gas evolved under visible-light irradiation in pure water (μmol h^{-1})	
		E_{g1}	E_{g2}		H_2	O_2
Co_3O_4-SSR	20~60	1.57	2.15	9.6	0	0
Co_3O_4-QDs	3~4	1.74	2.26	147.8	0.79	0.40

[a] calculated by K-M method. [b] determined from N_2 adsorption-desorption isotherms.

Table S2 Photocatalytic H_2-prodution rate over Co_3O_4-QDs and Co_3O_4-SSR with different UV cutoff filters.

Photocatalyst	Photocatalytic H_2-production rate (μmol h^{-1})			
	UV[a]	380 nm[b]	400 nm[b]	420 nm[b]
Co_3O_4-SSR	3.03	0.11	0	0
Co_3O_4-QDs	5.46	1.92	1.61	1.10

[a] 300 W high-pressure mercury lamp. [b] 300 W Xe arc lamp with a series of UV cut-off filters.

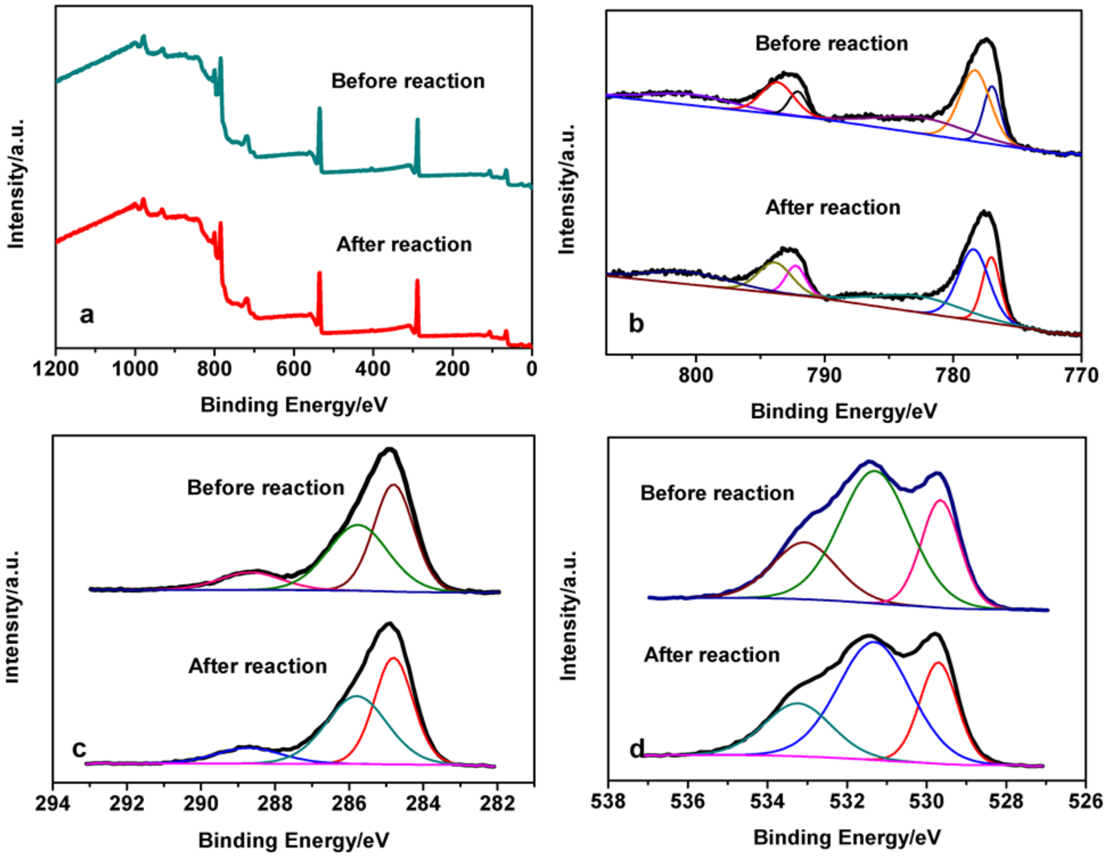

Fig. S6 (a) Survey scan XPS spectra and high-resolution XPS spectra in (b) Co 2p, (c) C 1s and (d) O 1s of Co_3O_4-QDs before and after reaction.

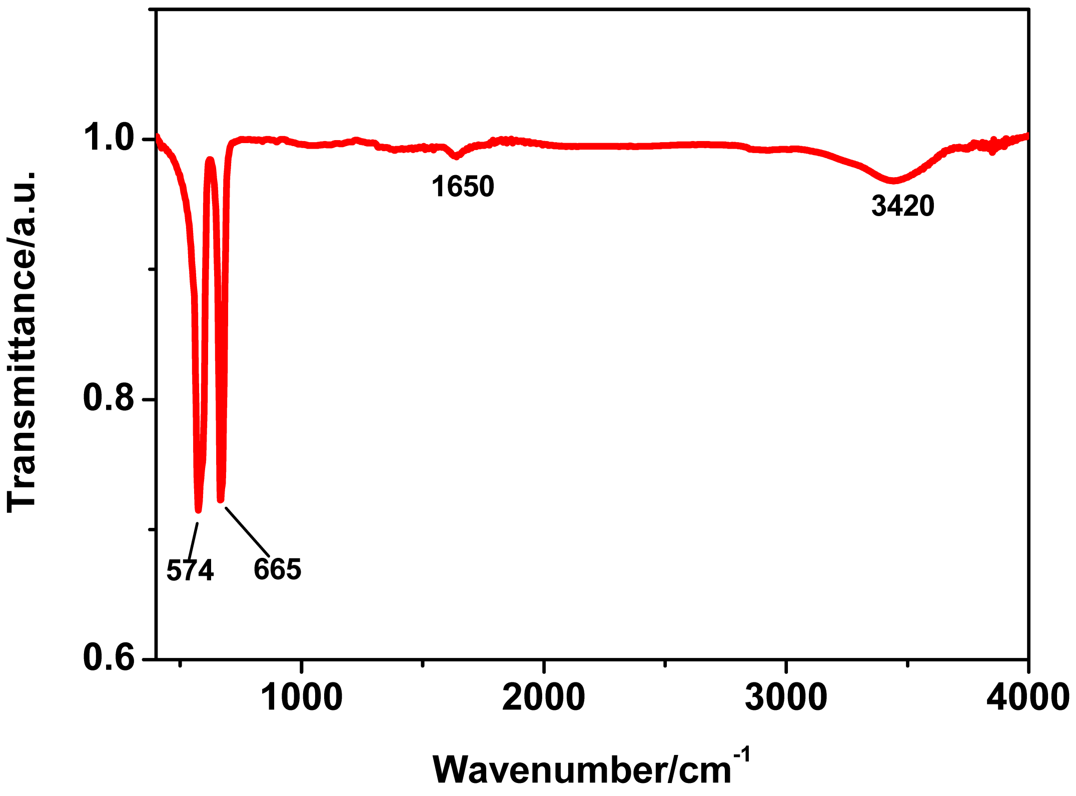

Fig. S7 FTIR spectrum of Co_3O_4-QDs.

FTIR in **Fig. S7** was collected to detect the surface ligands on Co_3O_4-QDs. Two strong bands centered at around 574 and 665 cm^{-1} were attributed to ν(Co-O) modes of Co_3O_4.[5] Bands at 1650 and 3420 cm^{-1} were assigned to H_2O absorbed on the surface.[6] No other bands could be obviously observed, thereby demonstrating that no surface ligands existed on Co_3O_4-QDs. This result further excluded the influence of surface ligands on water-splitting process assisted by Co_3O_4-QDs. The absence of surface ligands might be attributed to the heat-treatment at 200°C in vacuum.

Notes and references

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