

## Supporting information

### Experimental Section

**Chemicals:** Cobalt(II) acetate (99.995% trace metal basis), benzyl alcohol puriss. (99-100.5% GC), ammonium hydroxide solution puriss.p.a. (~25% NH<sub>3</sub> basis), were purchased from Sigma-Aldrich. Benzylamine (>=99.0%) was purchased from Fluka-Chemie AG. 10-30 nm cobalt (II,III) oxide nanopowder (99% metals basis) was purchased from Alfa Aesar. All the chemicals were used as received.

#### Synthesis of Co<sub>3</sub>O<sub>4</sub> quantum dots

**4.5 nm BA-Co<sub>3</sub>O<sub>4</sub> quantum dots:** 160 mg Co(II) acetate was added into 7 ml benzyl alcohol. The mixture was stirred at room temperature for 2 hours. Later, 7 ml ammonium hydroxide (25%) solution was dropwise added into the open vessel under vigorous stirring. The vessel with reddish-brown solution was put into an oil bath set at 165 °C. The solution was boiled immediately with substantial bubbles. After about 5 minutes, reddish-brown solution with much reduced volume was obtained. The reaction was kept at 165 °C for 2 hours under continuous stirring. Afterwards, a black suspension was obtained. After adding diethyl ether in the reaction solution, the black precipitate was collected by centrifugation and washed with ethanol twice.

**6 nm BL-Co<sub>3</sub>O<sub>4</sub> quantum dots:** 160 mg Co (II) acetate was dissolved into 7 ml benzylamine under stirring. Later, 9 ml ammonium hydroxide (25%) was added into the open vessel. The mixture was kept at 165 °C for 3 hours under continuous stirring. After centrifugation and washing, the cube-shaped, 6 nm Co<sub>3</sub>O<sub>4</sub> quantum dots were harvested.

#### Characterization

The powder X-ray diffraction patterns (PXRD patterns) were recorded in Bragg-Brentano mode and in  $\theta$ - $2\theta$  geometry with Cu K $\alpha$  radiation on a PANalytical X'Pert PRO diffractometer equipped with a secondary monochromator. The field emission scanning electron microscope (FESEM) image was performed with a Hitachi S-4800. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained using a JEM-2100F instrument operated at 200 kV. Brunauer-Emmett-Teller (BET) surface area measurements were performed at 77 K on a Micromeritics ASAP 2010 adsorption analyzer in N<sub>2</sub>-adsorption mode. The sample was degassed at 150°C for 24 h under vacuum prior to the measurements. The UV-vis absorption spectra was conducted on a Shimadzu UV-2450 Uv-vis spectrophotometer in the range from 250 nm to 900 nm. The FTIR spectroscopy measurement was recorded on a Bruker EQUINOX 55 instrument. The X-ray photoelectron spectroscopy (XPS) was measured on a Thermo ESCALAB 250 spectrometer with monochromatized Al K $\alpha$  X-rays (hv=1486.6 eV) at a pass energy of 30 eV. The C 1s peak of contaminant carbon was calibrated to 284.8 eV.

#### Photocatalytic Oxygen Evolution.

Photocatalytic oxygen evolution activities were evaluated in a well-established [Ru(bpy)<sub>3</sub>]<sup>2+</sup>-persulfate system by using a Clark electrode for 120 seconds reaction. In a typical Clark electrode experiment, water oxidation was carried out in a 10 mL headspace sealed with an aluminum crimp cap and a rubber septum (PTFE). Reaction mixtures were prepared in a glass vessel under dark

conditions as follows: 8 mL of buffered solution (0.1 M  $\text{K}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$  buffer with a pH value of 7.0) containing 8 mg  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ , 50 mg  $\text{Na}_2\text{S}_2\text{O}_8$  and 10 mg catalyst. The suspension was then deaerated by helium (6.0 purity) for 30 min to remove the oxygen both in solution and head vial. Afterwards, a baseline was recorded for each test to make sure that no oxygen leakage or side reaction occurred. Oxygen evolution was continuously monitored by the Clark electrode system for at least 120 s after it was exposed to a 300 W Xe lamp with a 420 nm cutoff filter. Constant temperature was maintained by a mineral insulated thermosensor (2 mm tip diameter, TP2000, Unisense). Oxygen evolution was monitored in solution by an Oxygen Sensor (OX-N) Clark electrode (Unisense).

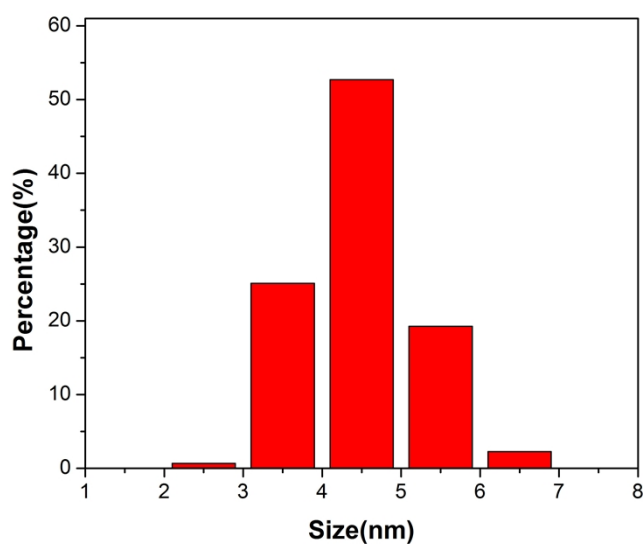


Figure S1. Size distribution histogram of BA-Co<sub>3</sub>O<sub>4</sub> quantum dots.

Figure S2. SEM image of BA-Co<sub>3</sub>O<sub>4</sub> quantum dots.

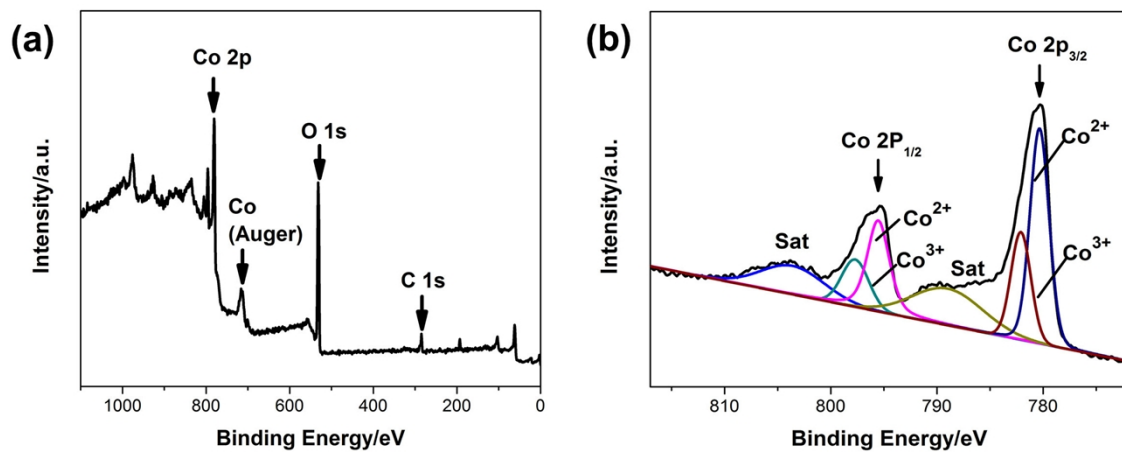


Figure S3. (a) Survey-scan XPS spectrum of BA-Co<sub>3</sub>O<sub>4</sub> quantum dots, and (b) high-resolution XPS spectrum of Co 2p.

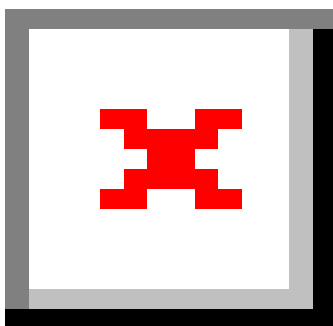


Figure S4. UV-Vis spectrum of BA-Co<sub>3</sub>O<sub>4</sub> quantum dots. Inset: Photograph of BA-Co<sub>3</sub>O<sub>4</sub>.

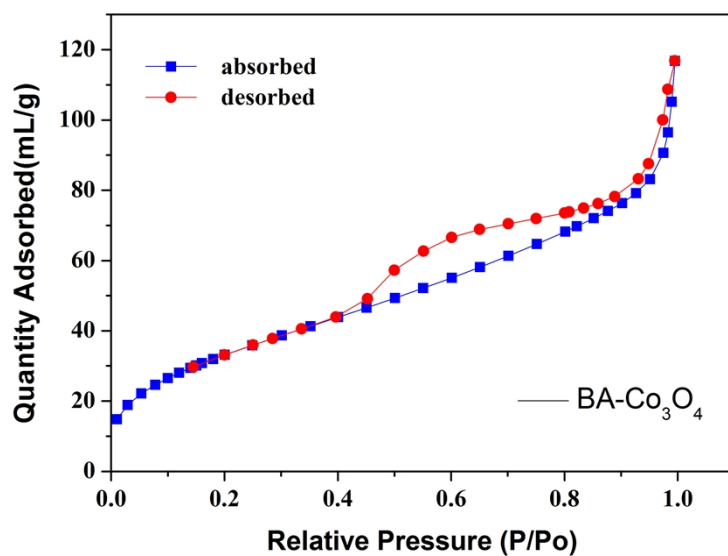


Figure S5. N<sub>2</sub> adsorption-desorption isotherms for BA-Co<sub>3</sub>O<sub>4</sub> quantum dots.

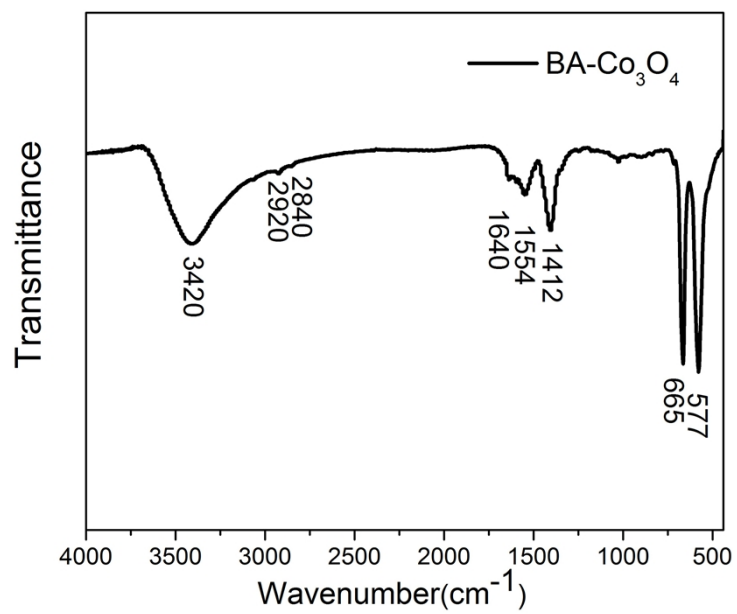


Figure S6. FTIR spectrum for BA-Co<sub>3</sub>O<sub>4</sub> quantum dots.

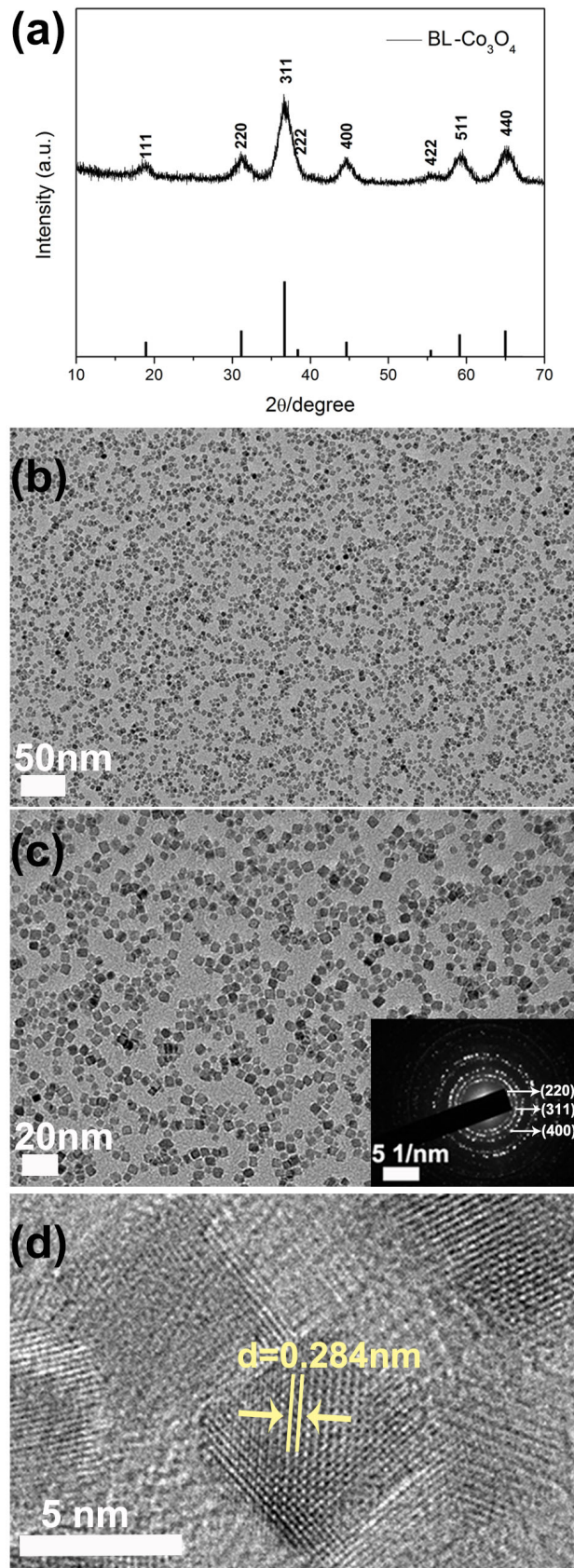


Figure S7. (a) PXRD pattern of BL-Co<sub>3</sub>O<sub>4</sub> quantum dots, (b) overview TEM image, (c) magnified TEM image, and (d) HRTEM image of BL-Co<sub>3</sub>O<sub>4</sub> quantum dots. The inset in (c) shows the corresponding SAED pattern.