

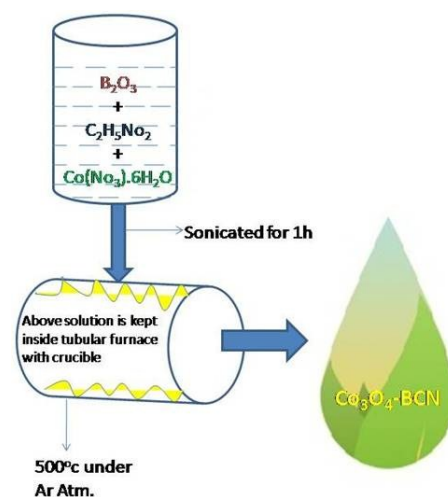
BCN-Co₃O₄ hybrid - a highly efficient catalyst for oxygen evolution reaction and dye degradation

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Supporting information

Experimental

The Co₃O₄ containing BCN is prepared via simple solution combustion technique in which boron trioxide (source of boron), glycine (source of carbon and nitrogen) and cobalt nitrate (source of cobalt) were taken in the ratio of 1:2:2. The mixture is dissolved in water (10 ml) and sonicated for 30 min. Resultant solution is poured into the alumina boat and heated in a tubular furnace to 500°C with heat rate of 2° per min in argon atmosphere. During combustion, the temperature of the reaction mixer reaches very high temperature (>1000°C) which is the desired condition for formation of Co₃O₄-BCN structure as shown in scheme 1. The product is further annealed at the temperature of 500°C for the next 2 hours and then cooled down to room temperature. The synthesized product is well grinded into powder for the analysis.



Scheme 1: Schematic for the synthesis of Co₃O₄-BCN hybrid material

Characterization techniques

Structural analysis was performed with X-ray diffraction (XRD) patterns obtained from Bruker D8 Advance powder X-ray diffractometer with Cu K α radiation. Bonding characteristics of Cu-BCN were analysed with Fourier transform infrared spectrum (FTIR) using a Bruker TENSOR 27 with spectral resolution of 0.125 cm⁻¹. Chemical environment of an element was predicted using X-ray photoelectron spectroscopy (XPS) with Sigma probe X-Ray Photoelectron Spectrometer (Thermo Scientific, a MULTILAB 2000 Base system with X - Ray, Auger and ISS attachment) with Al K α as source of X-Rays. . The as-prepared samples in the solid state were used for XPS analysis. The surface morphology of synthesized material was observed using a scanning electron microscope (SEM) (Bruker, Tescan vega3) with an accelerating voltage between 0.3 - 30 kV using SE detector. Energy-Dispersive X-ray (EDX) for elemental analysis was obtained with an EDAX detector installed on the SEM. The as-prepared samples in the solid state were used for SEM analysis. The graphitic layered structure and selected area electron diffraction (SAED) pattern were acquired from a transmission electron microscope (TEM) (FEI make, model Tecnai 20 G2). The samples for TEM were prepared by placing a drop of the as-prepared solution (measured quantity of Co₃O₄-BCN dispersed in water via sonication) on carbon-coated copper grids followed by drying. The optical absorption of dye is measured from UV-VIS-NIR double beam spectrometer (Cary 500 scan, VARIAN) with wavelength range from 200 to 800 nm. The liquid samples for UV-vis were prepared by dispersing measured quantity of Co₃O₄-BCN/Co₃O₄ in water via sonication. The Brunauer-Emmett-Teller (BET) analysis for as-prepared material in solid state was performed with Quantachrome® ASiQwin™ © 1994-2012, Quantachrome Instruments v2.02 and nitrogen (N₂) gas is used as an adsorptive for the determination of the surface area.

Sunlight source

The samples were irradiated with direct sunlight and irradiation was conducted under similar conditions on sunny days in Karaikudi town (geographical location 10.07° North and 78.78° east) between 1:00 p.m. and 3:00 p.m. (outside temperature, 29-31°C).

For degradation with UV filter the samples were irradiated with direct sunlight and irradiation was conducted with and without UV filter under similar conditions on sunny days in July 2016 in Karaikudi town (geographical location 10.07° North and 78.78° east) between 1:00 p.m. and 3:00 p.m. (outside temperature, 29-31°C).

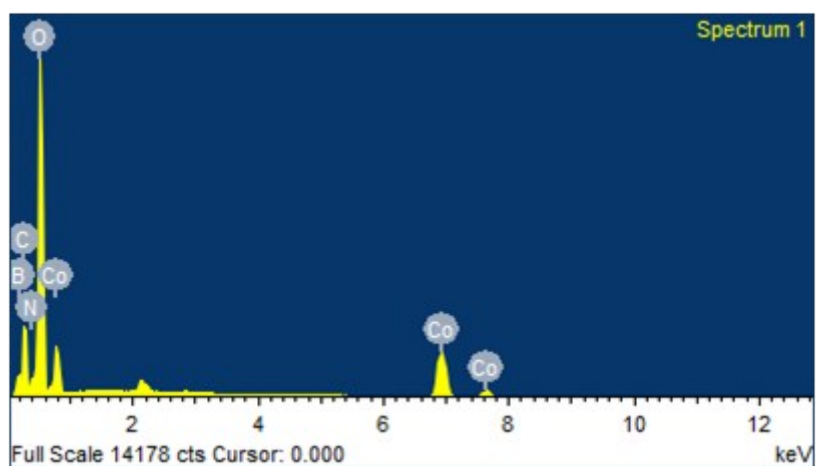


Figure S1: EDX spectra of BCN-Co₃O₄

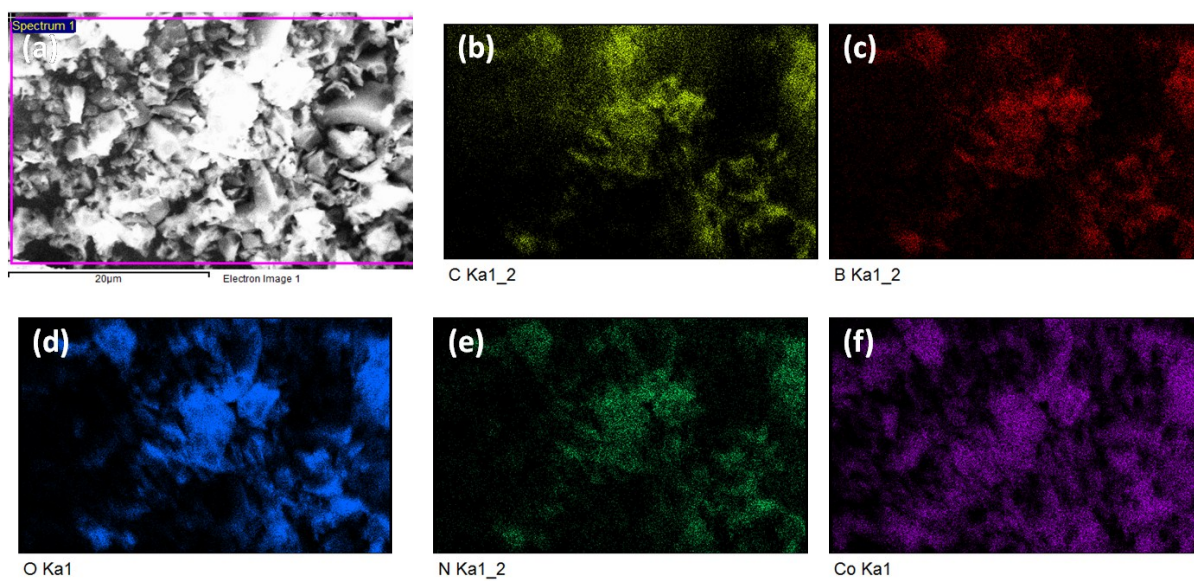


Figure S2: FE-SEM image of (a) BCN-Co₃O₄ and the corresponding EDX (b-f)maps of C,B,O,N, and Co

S3: The rate of the reaction is determined by calculating rate constant using the following relation, $\ln (C_t / C_0) = (-K_{app})t$

where C_0 – Initial concentration of the dye solution,

C_t – Concentration of the solution at time (t)

and K_{app} – is the rate constant of the reaction.

The plot of $-\ln (C_t/C_0)$ versus time is a straight line as in the Figure S4 and the slope of the line (linear fitting) gives rate constant. Fig S4 shows the obtained rate constant values are $1.99 \times 10^{-2}/\text{min}$ (methylene blue) and $1.03 \times 10^{-2}/\text{min}$ (methyl orange) for photocatalysis.

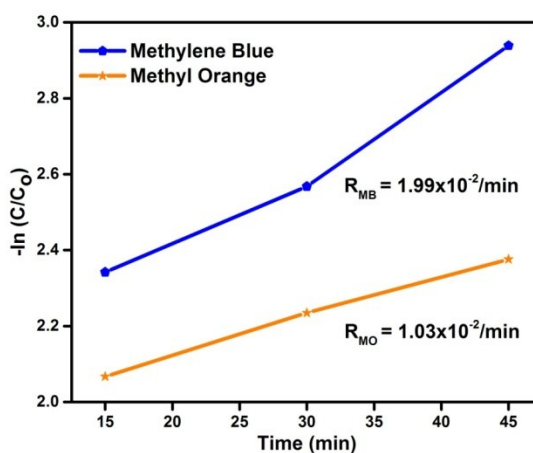


Figure S3. Rate Constant of Methylene Blue and Methyl Orange

S4: Effect of UV filter on the degradation efficiency of MB and MO

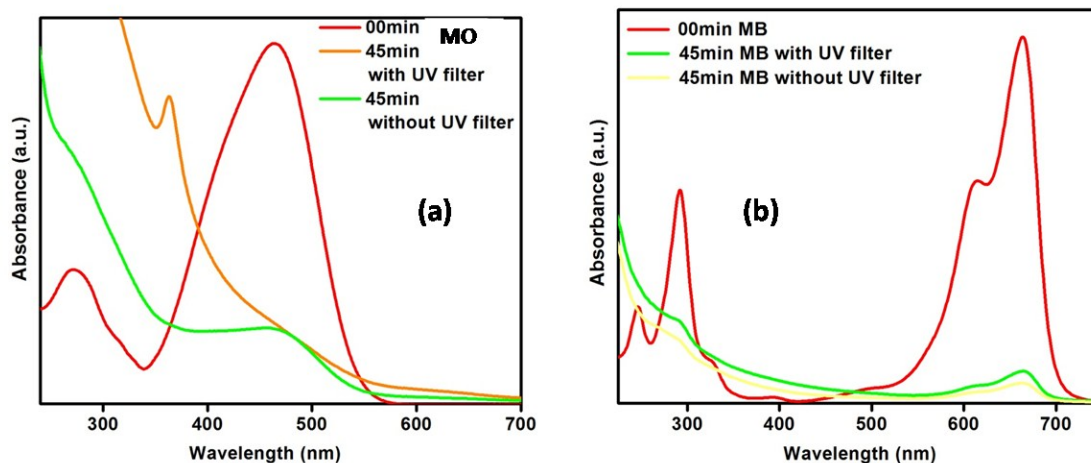


Figure S4. U.V Spectra of Degradation of Methyl orange (a) and Methylene Blue (b).

MO with UV filter Degradation efficiency	=	90.7%
MB without UV filter Degradation efficiency	=	94.22%
MO with UV filter Degradation efficiency	=	82%
MO without UV filter Degradation efficiency	=	86.56%

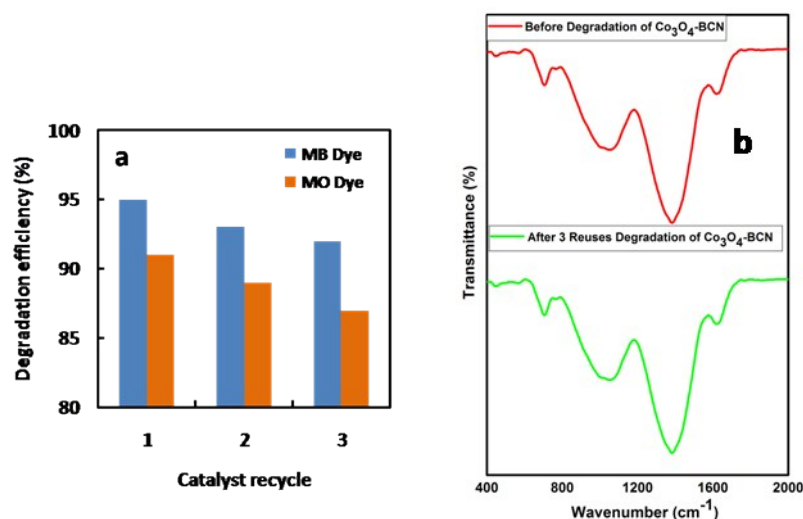


Figure S5 (a) Reusability of the Co₃O₄-BCN; **(b)** Co₃O₄-BCN before and after 3 cycles of dye degradation