Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Novel hetero-bimetallic coordination polymer as a single source of highly dispersed Cu/Ni nanoparticles for efficient photocatalytic water splitting

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Characterization

Single Crystal X-ray diffraction data were collected using the MX1 beamline at the Australian Synchrotron operating at 17.4 keV (λ = 0.7107 Å) [1]. The data collection temperature was maintained at 100 K using an open-flow N_2 cryostream. Data collection was conducted using the program Blu-Ice.[1] Initial data reduction was carried out using the XDS package.[2] The structure was solved by direct methods using SHELXS-2013.[3] Least-squares refinement against F^2 was conducted using SHELXL-2013 using the program X-Seed as a graphical interface.[4] All non-H atoms were refined using an anisotropic model. H atoms were placed in idealized positions and refined using riding models. H atoms of the lattice water molecules were located from the Fourier difference map and refined using distance restraints. Powder XRD patterns were collected on Bruker D8 Advance X-ray powder diffractometer equipped with a Cu sealed tube (λ = 1.54178 Å) at a scan rate of 2 ° min^{-1}. The Fourier transform infrared (FTIR) spectra were studied with Bio-Rad FTS-3500 ARX FTIR spectrometer. Thermogravimetric studies (TGA) were carried out using a Shimadzu DTG-60AH in the temperature range of 25 to 800 °C under flowing air (30 mL min^{-1}) and a heating rate of 10 °C min^{-1}. UV-vis absorbance spectra of the photocatalysts were collected over the wavelength range of 200–800 nm using a Thermo Fisher Scientific UV-vis spectrophotometer equipped with a praying mantis diffuse reflectance accessory. Field-emission transmission electron microscopy (FE-TEM) was conducted on a JEOL-JEM 2100F transmission electron microscope (200 kV). X-ray photoelectron spectroscopy (XPS) experiments were done with a Kratos AXIS Ultra DLD surface analysis instrument using a monochromatic Al Kα radiation (1486.71 eV) at 15 kV as the excitation source. The take-off angle of the emitted photoelectrons was 90° (the angle between the plane of sample surface and the entrance lens of the detector). Peak position was calibrated by referencing the C 1s peak position of adventitious carbon for a sample (284.8 eV), and shifting all other peaks in the spectrum accordingly. Fitting was done using the program Casa XPS. Photoluminescence (PL) studies were done by using a Flau Time 300 (FT-300) steady-state and lifetime spectrometer, PicoQuant GmbH, Germany. The PL was measured by using a pulsed LED laser excitation source, PLS-300, centered at 305 nm with full-width half-maximum (FWHM) of ~ 416 ps and pulse energy 0.077 pJ. The PL curves were fitted by using Easy Tau and FluoFit software.

Hydrogen production experiments

5 mg of photocatalyst was dispersed in the Pyrex reactor (140 mL) containing 25 mL of glycerol/water mixture (20 vol. % glycerol) as sacrificial reagent. The suspension was purged with N_2 for 40 min in order to force out the dissolved and headspace oxygen otherwise oxygen can scavenge electrons from the C.B of TiO_2 and generate superoxide radicals which

react with sacrificial electron donor.[5] UV light excitation source [Spectroline model SB-100P/F lamp (100 W, 365 nm)] was placed at a distance of 10 cm from the reactor. The photon flux measured at the sample was ~6.5 mW cm^{-2} (comparable to UV flux in sunlight). H_2 evolution was checked by removing the gas head space samples (0.5 mL) at regular time intervals and injecting them into the GC (Shimadzu GC 2014) equipped with a TCD detector and molecular sieve capillary column (Length = 25 mm; ID = 0.32 mm; average thickness 0.50 μm). Volume of H_2 evolved during photoreaction was calculated against an internal calibration curve. The photocatalytic tests for each sample were repeated at least three times for accuracy. TiO_2, with band gap of 3.15eV, can only be excited by radiation below ca. 400 nm. The external quantum efficiency (EQE) was found to be 15.78% under similar photocatalytic reaction conditions using the following equation.[6]

$$\mathrm{EQE} = \frac{\mathrm{nH_2} \times N_A \times \mathrm{h} \times c \times 2}{t_{irr} \times \lambda \times I \times \mathrm{A}} \times 100$$

Where

$\mathrm{nH_2}$ = Number of moles of hydrogen produced

N_A = Avogadro's number

h = Plank's constant

c = speed of light

t_{irr} = Irradiation time

λ = Wavelength of incident light

I = Intensity of lamp

A = Illuminated area of photoreactor

Turnover Number (TON)

Activity of bulk = [mol(H_2) / g(bulk catalyst)]

Activity relative to proportion of metal = [mol(H_2) / (g(bulk catalyst) x wt.%(metal))]

TON relative to active metal = [mol(H_2)] / [(g(bulk catalyst) x wt.%(metal)) / Mr(metal)]

e.g. In the case of 1.0% Cu-Ni/TiO_2 composites, where a 1.0 wt. % Cu/Ni loading was done on TiO_2, the metrics for dihydrogen evolution are as following equation after 8 h.[7]

Activity of bulk = 73.88239×10^{-3} mol(H_2) g(bulk)$^{-1}$

Activity relative to proportion of metal = 73.88239×10^{-3} mol(H_2) g(bulk)$^{-1}$ / (1.0/100) wt. %

= 7.388239 mol(H_2) g(metal)$^{-1}$

TON = 7.388239 mol(H_2) g(metal)$^{-1}$x(63.546+58.69 gmol^{-1})

= 903.11

Turn of frequency (TOF)

TOF relative to active metal = TON h^{-1}

TOF = 903.11 / 8 h

= 112.89 h^{-1}

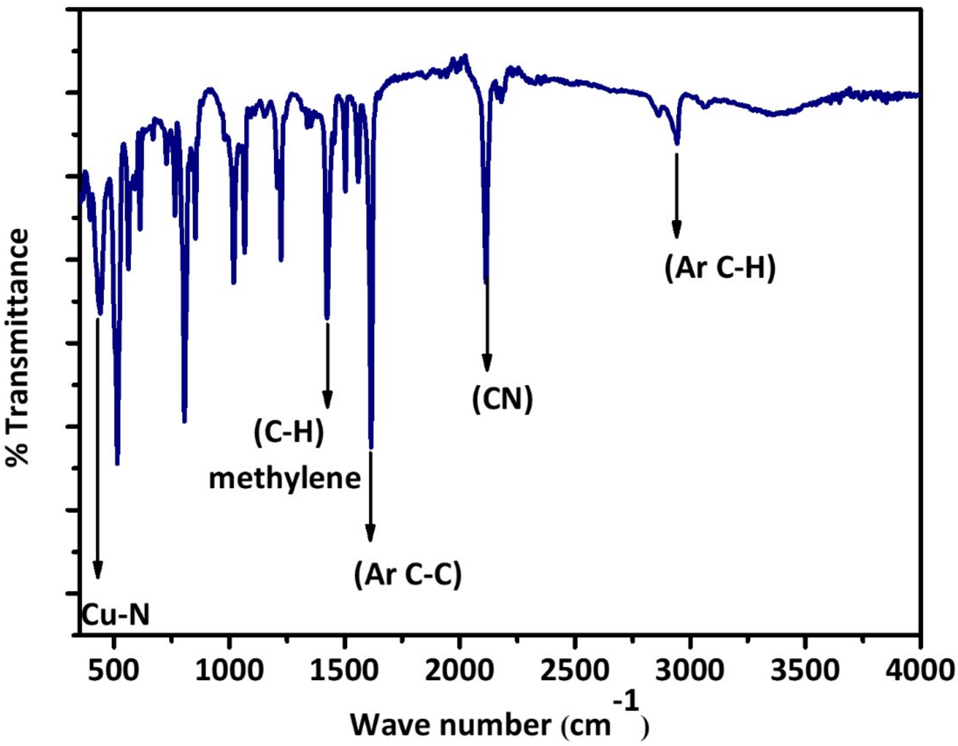

Figure S1. FTIR spectrum of **CP-1**

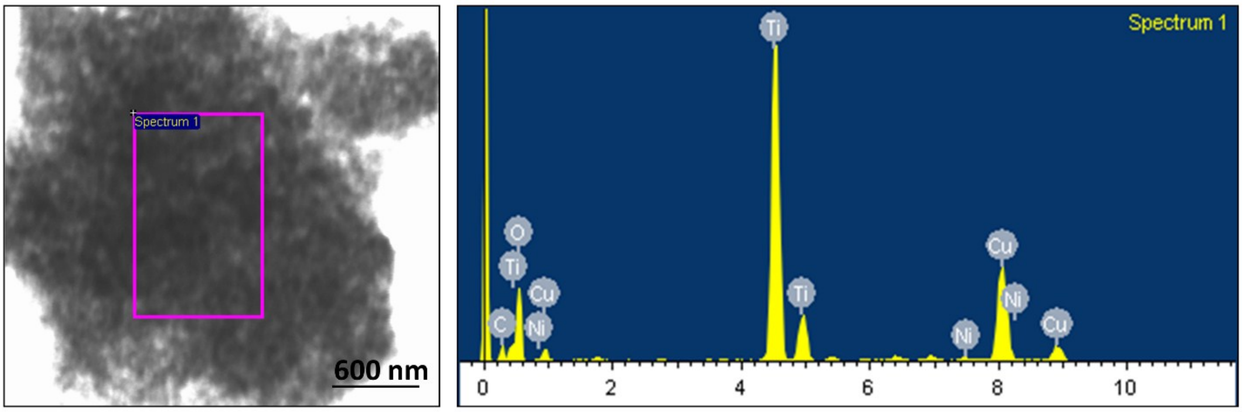

Figure S2. TEM EDX studies on 1%Cu-Ni/TiO_2-470 composite: (a) TEM image at 600nm; (b) spectrum indicates the presence of Ti, O, Ni and Cu.

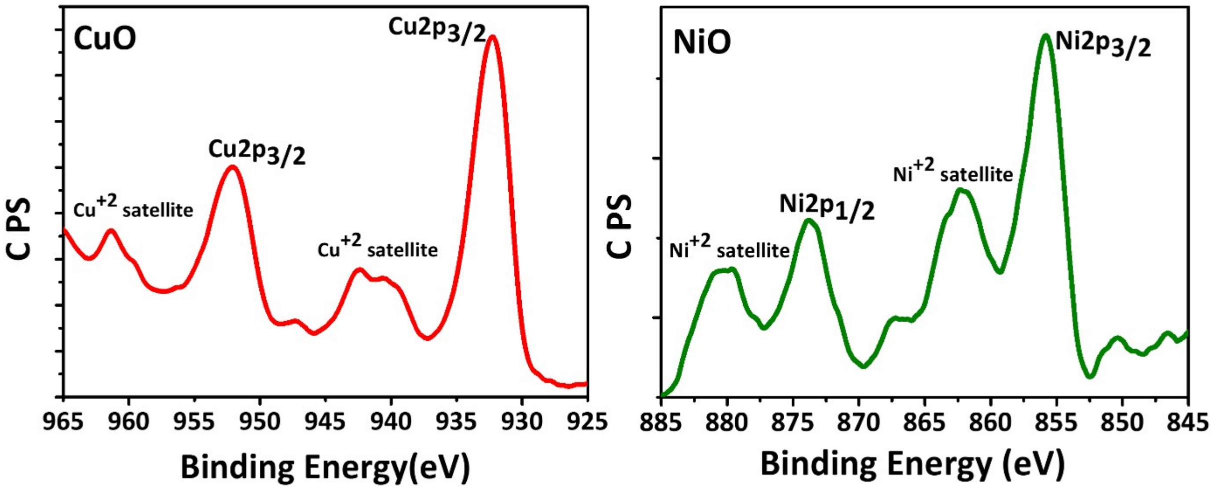

Figure S3. XPS spectra of Cu2p and Ni 2p for 1% CuO-NiO/TiO_2-470 photocatalyst

Table S1: Selected bond lengths and bond angles of **CP-1**

Bond lengths (Å)			
Cu1–N1	2.111(3)	Cu2–N9	2.005(3)
Cu1–N3	2.252(3)	Ni1–C27	1.844(3)
Cu1–N5	2.011(2)	Ni1–C28	1.869(3)
Cu2–N2	2.250(3)	Ni2–C29	1.837(4)
Cu2–N4	2.095(2)	Ni2–C30	1.868(3)
Cu2–N7	2.007(4)	Ni2–C31	1.833(4)
Bond angles (°)			
N1–Cu1–N1	180.00	N4–Cu2–N4	178.10(9)
N1–Cu1–N3	87.37(9)	N2–Cu2–N9	90.9(1)
N1–Cu1–N3	92.63(9)	N4–Cu2–N7	90.9(1)
N1–Cu1–N5	90.44(9)	N4–Cu2–N9	89.1(1)
N1–Cu1–N5	89.56(9)	N9–Cu2–N7	180.0(1)
N3–Cu1–N3	180.00	C28–Ni1–C28	180.00
N3–Cu1–N5	90.95(9)	C28–Ni1–C27	89.8(1)
N3–Cu1–N5	89.05(9)	C28–Ni1–C27	90.2(1)
N5–Cu1–N5	180.00	C27–Ni1–C27	180.00
N2–Cu2–N2	178.2(1)	C30–Ni2–C30	179.4(1)
N2–Cu2–N4	87.8(1)	C30–Ni2–C29	89.7(2)
N2–Cu2–N4	92.2(1)	C30–Ni2–C31	90.3(2)
N2–Cu2–N7	89.1(1)	C29–Ni2–C31	180.00

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