

Supporting Information

An innovative light assisted production of acetic acid from CO₂ and methanol: a first photocatalytic approach using reusable cobalt (II) molecular hybrid at atmospheric pressure

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1.0 Experimental details

Chemicals

Chemicals required for the synthesis of photocatalysts and reaction substrates, such as phthalic anhydride, cobalt chloride hexahydrate, urea, ammonium chloride, ammonium molybdate, sodium thiosulphate, methanol, N,N-dimethyl acetamide, ethanol, etc. were purchased from Alfa-Aesar. All the chemicals were used as received without further purification. Orthorhombic octasulfur (S_8) was prepared as per the existing literature procedure.¹

Preparation of cobalt phthalocyanine (CoPc) complex

Phthalic anhydride (4 g, 19.6 mmol), cobalt chloride salt (5.45 mmol), urea (48 g, 0.8 mmol), ammonium chloride (4.048 g, 75.7 mmol), and ammonium molybdate (0.44 g, 2.23 mmol) were crushed in a mortar, placed in a quartz vessel of 50 ml, and irradiated in a microwave oven at 440 W for 15-20 minutes. After that, the crude product was washed with deionized water, filtered, and dried under vacuum at 120° C. The crude product was added to 2% HCl, and the obtained mixture was heated to boil for 30 minutes. After filtering and drying the product, it was added to a 1% aqueous NaOH solution, boiled for 30 minutes, filtered, and dried. The acid/base washing procedure was repeated three times. Finally, the obtained dark colored solid was dried in an oven to get the metal phthalocyanine complex in a yield of 81-85%.

Attachment of CoPc complex to octasulfur S_8

In this synthetic procedure, 100 mg of CoPc complex (as synthesized in section 2.1.1) was dispersed in 10 mL ethanol with continuously vigorous stirring for 2 h at 25 °C in a beaker. In another beaker, 1 g of sulfur (S_8) was added to 10 mL of deionized H_2O , and the resulting mixture was sonicated for 2 h. After that, both the mixtures were combined and kept under stirring overnight or until the complete solvent evaporation occurred. The residue so formed

was thoroughly washed with ethanol and dried under reduced pressure at 60 °C. The cobalt content in the hybrid was found to be 5.9wt% as determined by ICP-AES.

2.0 Characterization Techniques

X-ray diffraction (XRD) pattern recorded to determine the crystallinity of the materials using Bruker D8 Advance diffractometer at 40 kV and 40 mA with Cu K α radiation ($\lambda=0.15418\text{nm}$). The scan range was $2\theta = 20^\circ$ to 70° with a scan rate of $0.02^\circ/\text{s}$ for analysis. Perkin Elmer Lambda 750 UV-VIS-NIR spectrophotometer with a 10-mm quartz cell recorded UV-VIS absorption spectra of the samples using BaSO $_4$ as a reference. A Field emission scanning electron microscope (FESEM) (JEOL JSM7610F) equipped with an EDS (Oxford Instruments) was used for the determination of the morphological features. High-resolution transmission electron microscopy (HR-TEM) was done using a JEM 2100 (JEOL, Japan) microscope by mounting the ethanol dispersed sample on a Lacey carbon-coated Cu grid. Fourier transform infrared spectroscopy (FT-IR) used to determine the stretching and bending vibrations and was recorded at RT in the range of $4000\text{--}400\text{ cm}^{-1}$ on an Alpha-Bruker FTIR spectrometer with a wave number resolution of 4 cm^{-1} in the transmission mode in spectroscopic grade KBr pellets for all the powders used to determine the stretching and bending vibrations on a Perkin-Elmer spectrum RX-1 IR spectrophotometer having potassium bromide window. All the samples were degassed at 200 °C for 3h under an N $_2$ atmosphere. X-ray photoelectron spectroscopy (XPS) analysis to determine the oxidation state and binding energy of elements in the photocatalysts was performed using KRATOS AXIS 165 with Mg K α irradiation.

3.0 Characterization of the recovered photocatalyst (CoPc/S8)

3.1 XRD

The X-ray diffraction pattern of the used photocatalyst recovered after the third recycling experiment is shown in Figure S1. All the characteristic peaks similar to the XRD of fresh photocatalyst are observed with slight decrease in intensity.

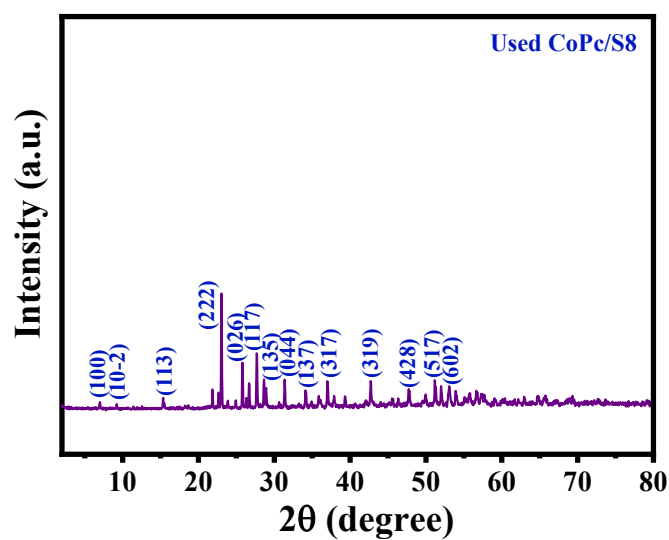


Figure S1. XRD pattern of the recovered photocatalyst CoPc/S8

3.2 SEM

The morphology and microstructure of the used photocatalyst CoPc/S8 are probed by scanning electron microscopy (SEM), as shown in Figure S2.

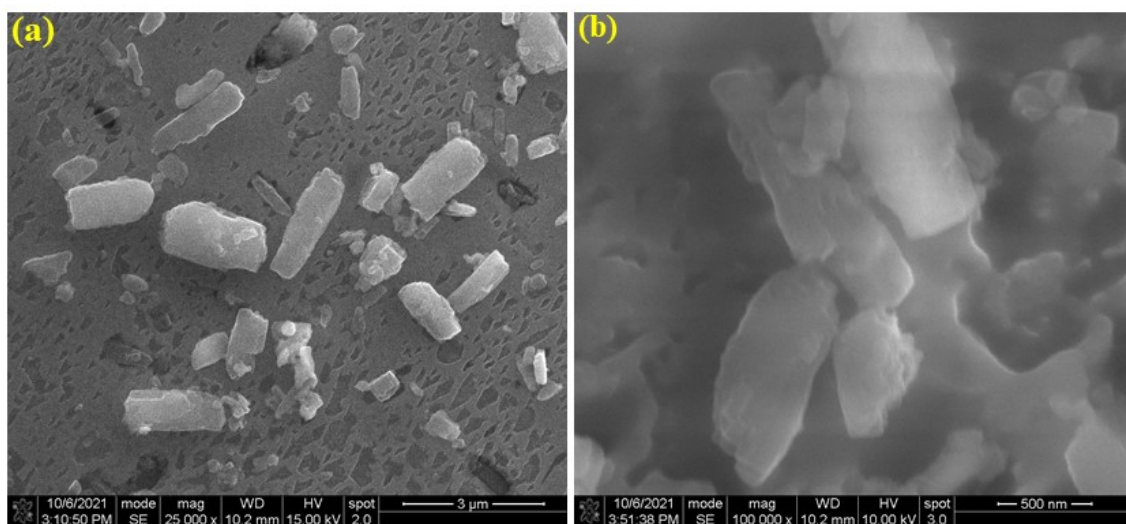


Figure S2. SEM images of used CoPc/S8 photocatalyst

3.3. XPS

The XPS spectra of the used photocatalyst CoPc/S8 is shown in Figure S3.

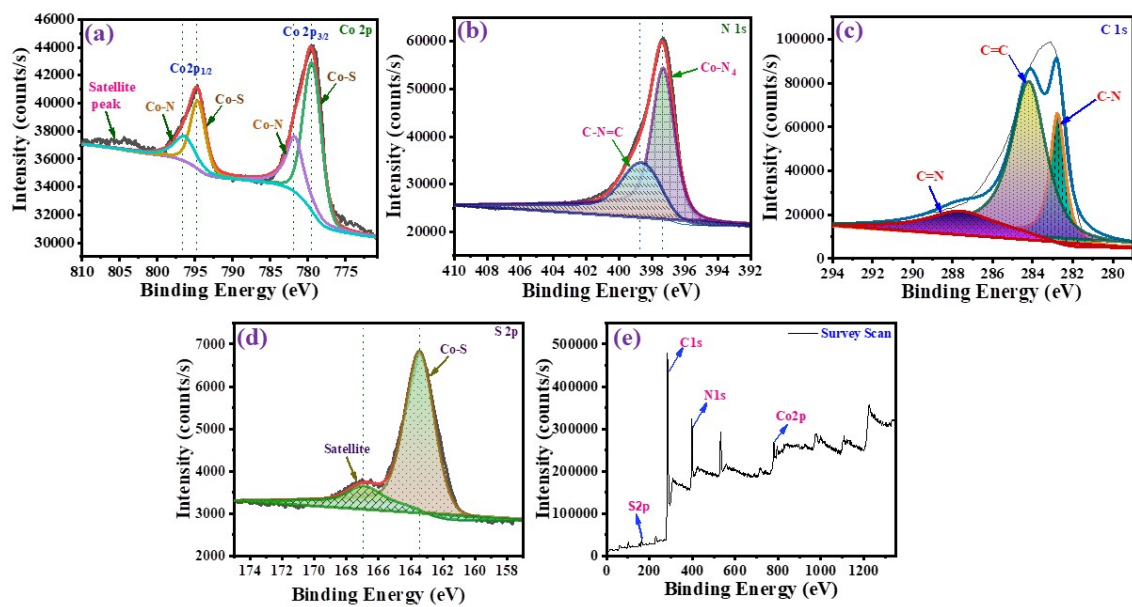


Figure S3. XPS plot of the used CoPc/S8 photocatalyst

4.0 Interaction of methanol and CO₂ with CoPc/S8

The optimized structures of CoPc and CoPc/S8 are shown in Figure S4. The activation of CO₂ and CH₃OH molecules on CoPc/S8 was studied using Gaussian 09. The interaction of CO₂ and CH₃OH on CoPc/S8 interface is shown in Figure S5. The higher interaction energy of methanol indicated the higher reactivity of CH₃OH towards CoPc-S₈ as compared to the CO₂. However, the adsorption configuration of CO₂ in Figure S5 indicated the transformation of CO₂ into CO and left an O atom linked to Co and neighbouring N sites having interaction energy 3.11 eV which is less than that of CH₃OH adsorption energy. So, it can be concluded that the reaction proceeded through the adsorption of CH₃OH to the CoPc/S8 and not *via* CO₂ adsorption. In order to explore the overall thermodynamics of reaction, free energy profile has been monitored in the present study. These interaction energies indicate the feasibility of substrates i.e. CO₂ and CH₃OH for adsorption on the catalyst surface. High interaction energies of CH₃OH indicated the higher reactivity of CH₃OH towards CoPc-S₈.

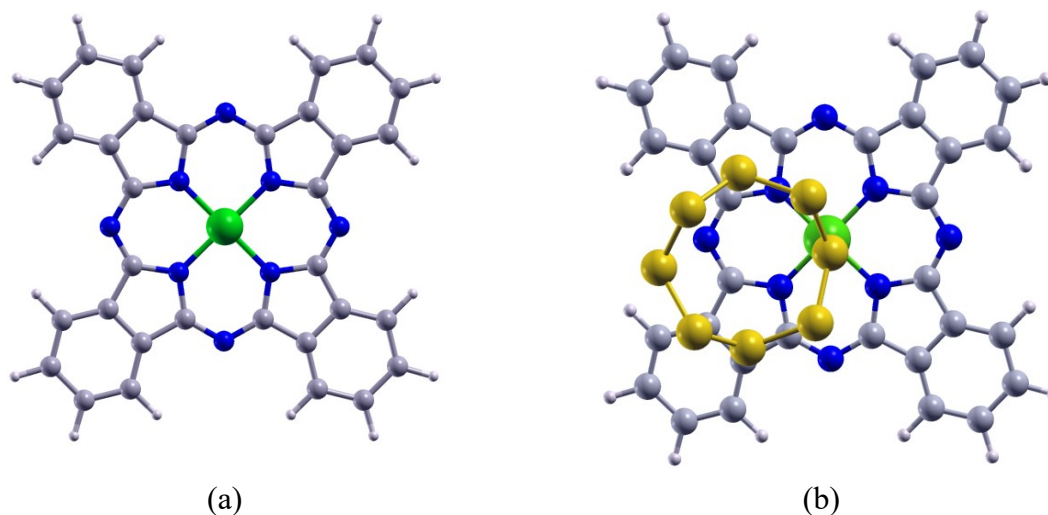


Figure S4: Optimized geometries of (a) CoPc and (b) CoPc/S8

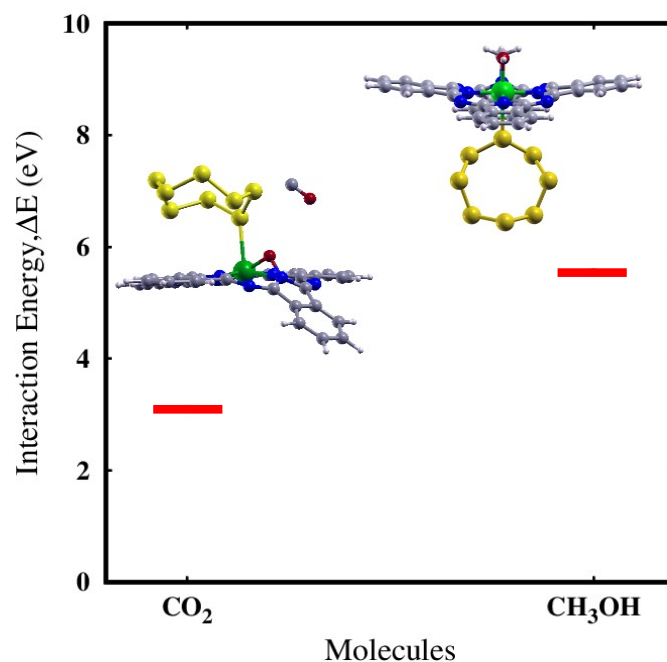


Figure S5: Interaction energies of CO₂ and CH₃OH on CoPc/S8

Furthermore the theoretical UV spectrum of CoPc/S8 (Fig. S6) showed a broad peak in the range of 400 nm and 500- 800 nm that confirmed the formation of combined system having the peak contributions from both S8 and CoPc systems, respectively. Experimental UV-Vis spectrum of S8 shows an absorbance around 450 nm, dedicated to the orthorhombic sulphur (Figure 10 in the main text). The same is indicated by a broad peak in between 400 - 500 nm for S8 in theoretical studies (Fig. S6). This validates the existence of sulfur with CoPc in CoPc/S8. Further, the UV-Vis spectrum of CoPc exhibited characteristic Q-band in the region 635-711 nm due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the phthalocyanine ring, respectively. The Q-band further splits into two wavelengths, one at 552 nm and the other at 757 nm that is elucidated by a broad peak obtained at 750 nm. Therefore, the theoretical UV spectrum of CoPc/S8 (Figure S6), showed a broad peak in the range of 400 nm and 500- 800 nm that confirmed the formation of combined system having the peak contributions from both S8 and CoPc systems, respectively. The highest peak in Figure S6 indicated the transition from HOMO to LUMO +2 corresponding to energy 1.65 eV at 750 nm and $f = 0.162$.

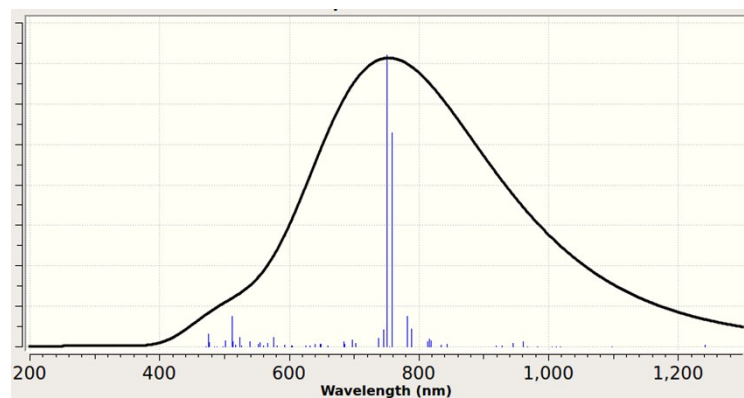


Figure S6: Theoretical UV spectrum of CoPc/S8

References

1. Liu G, Niu P, Yin L, Cheng H-M. α -Sulfur crystals as a visible-light-active photocatalyst. *J. Am. Chem. Soc.* **134**, 9070-9073 (2012).