Electronic Supplementary Information

Photocatalytic CO₂ Reduction using a Molecular Cobalt Complex Deposited on TiO₂ Nanoparticles

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1. Experimental Details

1.1. Materials

Triethylamine (\geq 99%), triethanolamine (TEOA, \geq 99%), acetonitrile (99.999%), hydrochloric acid (37%), tetrabutylammonium hexafluorophosphate (TBAH, \geq 99%), 1,4,8,11-tetraazacyclotetradecane (cyclam, 98%), and methylene blue were obtained from Sigma-Aldrich. Methanol (99.9%) was purchased from Fisher Scientific. Cobalt(II) chloride hexahydrate was obtained from J. T. Baker. N,N-dimethylformamide (DMF, 99.8%) was obtained from Acros Organics. Ethanol (95.0%) and chloroform (99.8%) were purchased from Parmo Products Inc. All reagents were used without further purification. P25 TiO₂ (specific surface area 57 m²/g, average particle size ~25 nm, phase composition ~80% anatase and ~20% rutile) and Silica nanoparticles (Aerosil 200, specific surface area ~200 m²/g, average primary particle size ~12 nm) obtained from Evonik were used as received. Anatase nanopowder (99.7% trace metal basis, specific surface area 20 m²/g, particle size ~10 nm × 40 nm) obtained from Sigma-Aldrich were used as received. Fluorine-doped tin oxide conductive glasses (FTO, Tec 8, light transmittance 77%) were purchased from Hartford Inc.

1.2. Catalyst Synthesis

Trans-[Co(cyclam)Cl₂]Cl was synthesized following procedures reported in the literature (B. Bosnich, C.K. Poon, M.L. Tobe, *Inorg Chem.* 1965, **4**, 1102.) Two different methods were employed to synthesize $Co^{III}(cyclam)X/TiO_2$. In the reflux method, 200 mg TiO₂ were dispersed in a solution of 40 mL acetonitrile, to which 20 mg (0.055 mmol) [Co(cyclam)Cl₂]Cl and 120 µL (0.86 mmol) triethylamine were added. The suspension was refluxed under aerobic atmospheric conditions for 24 h. The resulting brownish precipitate was recovered by centrifugation and washing 2 times with chloroform and 2 times with ethanol. After drying at room temperature, $Co^{III}(cyclam)X/TiO_2$ was obtained as a brownish powder.

In the microwave method, 100 mg TiO₂ in 15 ml acetonitrile were mixed with 10 mg [Co(cyclam)Cl₂]Cl (0.028 mmol) and 65 μ L triethylamine (0.46 mmol). The mixture in a capped reaction vessel was placed in a CEM Discover single-mode microwave reactor and underwent reaction for 120 min at 80 °C. After the microwave reaction, the resulting brownish precipitate was recovered by centrifugation, and washed 2 times with chloroform and 2 times with ethanol. After drying at room temperature, Co^{III}(cyclam)X/TiO₂ was obtained as a light brownish powder.

Following the same methods, $Co^{III}(cyclam)X/Silica$ samples were synthesized in the presence of Silica, and $Co^{III}(cyclam)X$ was synthesized in the absence of TiO₂ or Silica nanoparticles.

1.3. Materials Characterization

Elemental analysis of Co in $Co^{III}(cyclam)X/TiO_2$ and $Co^{III}(cyclam)X/Silica$ was conducted by acid digestion of the powder sample, followed by quantification using a Varian Vista AX induced coupled plasma atomic emission spectrometer. SEM images were taken on an Amray 3300FE field emission SEM with PGT Imix-PC microanalysis system. XPS spectra were collected on a Kratos Axis HS XPS system. NMR spectra were collected on a Varian Mercury 400 MHz NMR spectrometer. UV-visible spectra were obtained on a Cary 50 Bio spectrophotometer. A Barrelino diffuse reflectance probe was used to collect UV-visible spectra of powder samples using $BaSO_4$ as a standard. Transmission FTIR spectra were collected on a Thermo Nicolet iS10 FTIR spectrometer. DRIFT spectra were collected on a Thermo Nicolet 6700 FTIR spectrometer equipped with a Harrick Praying Mantis diffuse reflectance accessory.

Electrochemical studies were carried out using a PAR model VersaSTAT 4 potentiostat using a single compartment cell. Cyclic voltammograms of $[Co(cyclam)Cl_2]Cl$ and $Co^{III}(cyclam)X$ were collected using a glassy carbon working electrode in DMF; cyclic voltammograms of P25 and $Co^{III}(cyclam)X/P25$ deposited on FTO electrodes were collected in acetonitrile. The electrochemical studies were done using 0.1 M TBAH as the supporting electrolyte, a Pt counter electrode, and a non-aqueous Ag/AgNO₃ reference electrode (BASi) at a scan rate of 100 mV s⁻¹. Argon was bubbled for 20 min through the electrochemical cell before every scan.

1.4. Photocatalytic Testing

In CO₂ reduction, a specific amount (~1 mg) of catalyst was dispersed in a 4.0-mL acetonitrile solution containing TEOA and methanol (acetonitrile : TEOA : methanol = 4:1:1 v/v) or just TEOA (acetonitrile : TEOA = 3:1 v/v) in a Pyrex test tube. Prior to photocatalytic testing, the reaction solution was bubbled with CO₂ (99.999%, Airgas) in the dark for 20 min. The reaction solution was then irradiated with a 200-W mercury lamp equipped with a water filter. In some tests, an AM 1.5 filter or a long-pass ($\lambda > 420$ nm) filter was used with the mercury lamp to provide simulated solar irradiation or visible light, respectively. Light intensity on the reaction solution was fixed at 100 mW/cm². The head space above the reaction solution was sampled with a gas-tight syringe at different time intervals for product analysis using an Agilent 7820 GC equipped with a TCD detector and a 60/80 Carboxen-1000 packed column (Supelco). Production of formic acid in reaction solutions was monitored by NMR.

The photodegradation of methylene blue was carried out in a 100-mL beaker, in which 10 mg of TiO_2 materials were mixed with a 50-mL solution of 5 mg/L methylene blue. The suspension was stirred in the dark for 15 min prior to UV irradiation provided by the mercury lamp. During photocatalysis, the reaction solution was sampled every 2 min and TiO_2 nanoparticles were separated from the solution by centrifugation. The absorbance of methylene blue remained in the reaction solution was used to construct the kinetics plot (Fig. S10).

2. Supplementary Figures



Fig. S1. (a) An SEM image of $Co^{III}(cyclam)X$, (b) a TEM image of $Co^{III}(cyclam)X$, and (c) a TEM image of $Co^{III}(cyclam)X/P25$ synthesized by the reflux method. Scale bars are 1 µm for (a) and 50 nm for (b) and (c). The TEM image of $Co^{III}(cyclam)X/P25$ shown in (c) suggests that $Co^{III}(cyclam)X$ may exist as a thin layer on the surface of P25 nanoparticles.



Fig. S2. Optical spectra of (a) Silica and (d) Co^{III}(cyclam)X/Silica in the powder form. The spectra were collected using a diffuse reflectance accessory.



Fig. S3. ¹H NMR spectra of (a) $[Co(cyclam)Cl_2]Cl$ and (b) $Co^{III}(cyclam)X$ in D_2O .



Fig. S4. ¹³C NMR spectra of (a) $[Co(cyclam)Cl_2]Cl$ and (b) $Co^{III}(cyclam)X$ in D_2O .



Fig. S5. Transmission FTIR spectra of (a) $[Co(cyclam)Cl_2]Cl$ and (b) $Co^{III}(cyclam)X$ pressed in KBr pellets. The peak at 1630 cm⁻¹ is associated with surface adsorbed water. The absorptions at 904, 890 and 815 cm⁻¹ in the spectra indicate that the cobalt complexes exist in the *trans* configuration (see C.K. Poon, *Inorg. Chim. Acta* **1971**, *5*, 322.) The absorption at 668 cm⁻¹ in (b) is associated with Co-O bonds in Co^{III}(cyclam)X.



Fig. S6. XPS survey spectra of (a) $[Co(cyclam)Cl_2]Cl$, (b) $Co^{III}(cyclam)X$, and (c) $Co^{III}(cyclam)X/P25$ synthesized by the reflux method. Major differences between the spectra of $[Co(cyclam)Cl_2]Cl$ and $Co^{III}(cyclam)X$ are highlighted with boxes. The spectrum of $Co^{III}(cyclam)X$ contains a peak at 529.5 eV characteristic of oxygen atoms bound to metals (trace b).



Fig. S7. Cyclic voltammograms of (a) $[Co(cyclam)Cl_2]Cl$ and (b) $Co^{III}(cyclam)X$ in dimethylformamide under argon. A reversible Co^{III}/Co^{II} couple at $E_{1/2} = -0.21$ V is seen for both samples. An irreversible Co^{II}/Co^{I} couple at -1.39 V is observed for $[Co(cyclam)Cl_2]Cl$, while an irreversible redox couple at -0.93 V is observed for $Co^{III}(cyclam)X$.



Fig. S8. Production of CO upon photocatalytic CO₂ reduction using Co^{III}(cyclam)X/P25 synthesized by the reflux method. The reaction solutions contain both TEOA and methanol. Light sources: (a) visible light ($\lambda > 420$ nm), (b) simulated sunlight (Hg lamp + AM1.5 filter), and (c) UV light (Hg lamp without any filter). The dotted line describes production of H₂ using Co^{III}(cyclam)X/P25 under UV light.



Fig. S9. Cyclic voltammograms of (a) P25 TiO_2 and (b) $\text{Co}^{\text{III}}(\text{cyclam})X/\text{P25}$ TiO_2 deposited on FTO electrodes in acetonitrile under argon.



Fig. S10. Photocatalytic degradation of methylene blue using (a) P25, (b) Rutile, and (c) Anatase. Specific surface areas of the TiO₂ materials are (a) 57 m²/g, (b) 20 m²/g, and (c) 56 m²/g, respectively.