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Molecular deposition of a macrocyclic cobalt catalyst on TiO_2 nanoparticles

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ABSTRACT

Hybrid photocatalysts consisting of molecular catalysts and solid-state surfaces have demonstrated great potential as robust and efficient systems in solar fuel production. Based on our prior work, we synthesized hybrid photocatalysts by depositing a macrocyclic Co(III) complex on three different TiO_2 nanomaterials via a microwave method. The hybrid photocatalysts were tested in CO_2 reduction and were thoroughly characterized with spectroscopic (UV–vis, FTIR and EPR) and microscopic (TEM) techniques. The presence of terminal OH groups on TiO_2 surfaces was essential for the molecular deposition of catalytically active Co(III) sites. On a TiO_2 material without such terminal OH groups, the Co(III) complex formed amorphous aggregates, which hindered interfacial electron transfer from photoactivated TiO_2 to the surface molecular complex. EPR studies further revealed important information regarding the coordination geometry and interaction with CO_2 of surface cobalt sites in the hybrid photocatalysts.

1. Introduction

Photocatalysis is a promising approach to harvest, convert, and store solar energy. For example, in photocatalytic CO_2 reduction, solar energy can be converted into chemical energy and stored in the form of chemical bonds [1,2]. Currently known photocatalysts for CO_2 reduction include molecular and supramolecular complexes [3–5] as well as inorganic semiconductors [6,7]. A key challenge for solar fuel production by CO_2 reduction is the lack of photocatalytic systems that are both highly efficient and robust under photochemical conditions. In recent years, hybrid photocatalysts combining molecular catalysts with solid-state surfaces have attracted extensive interests from researchers in the field of solar fuels [8–10]. Such hybrid photocatalysts generally demonstrate enhanced solar conversion efficiency and improved photostability. In this report, we investigate a rare example of hybrid photocatalysts featuring photo-induced electron transfer from titanium dioxide (TiO_2) to a surface molecular catalyst.

In hybrid systems for solar CO_2 reduction, molecular catalysts are covalently attached to solid-state surfaces [9–12], incorporated in frameworks/porous environment [13–16] or confined to surfaces by polymerization [17,18]. Typical solid-state surfaces for molecular CO_2-reduction catalysts include periodic mesoporous organosilicas, metal-organic frameworks, and inorganic semiconductors. For example, Takeda and co-workers prepared a hybrid photocatalyst by covalently attaching a tricarbonyl Re(I) complex on a light-absorbing mesoporous organosilica [16]. Enhanced CO_2-to-CO conversion was achieved upon UV light activation of the organosilica and subsequent resonance energy transfer to the Re(I) catalytic centers. In addition, the mesoporous structure protected the molecular Re(I) complex against photochemical decomposition [16]. Similar effects of catalyst heterogenization were observed in photocatalytic CO_2 reduction using a Re(I) catalyst incorporated in a light-absorbing metal-organic framework [19].

Inorganic semiconductors such as TiO_2 have been utilized as the solid-state support for several molecular CO_2-reduction catalysts [20–26]. Windle and co-workers synthesized a hybrid Re(I) photocatalyst by grafting a molecular Re(I) complex onto TiO_2 through phosphate groups [24]. The surface immobilization significantly improved photocatalytic activity of the Re(I) complex in CO_2 reduction under visible-light irradiation, which activates the Re(I) complex but not the TiO_2 support. The researchers utilized transient absorption spectroscopy to demonstrate increased lifetime of a reduced Re(I) intermediate on the TiO_2 surface. It was suggested that the longer-lived anionic Re(I) species on TiO_2 has a

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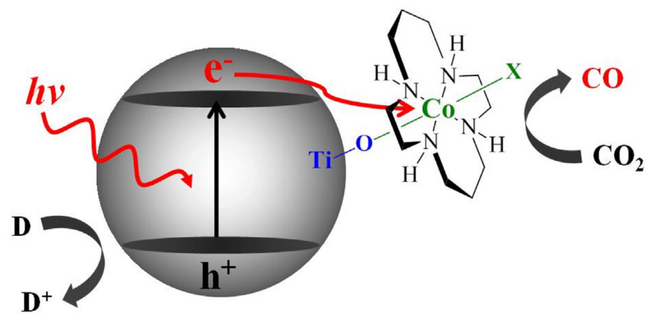

Fig. 1. Schematic of the hybrid Co(III) photocatalyst. D is an electron donor. X = OH or Cl.

greater probability of reacting with CO_2 and undergoing the second reduction required for the production of CO [24].

Recently, we prepared a hybrid photocatalyst by depositing a molecular Co(III) complex, [Co(cyclam)Cl_2]Cl where cyclam is 1,4,8,11-tetraazacyclotetradecane, onto TiO_2 (Fig. 1) [21]. The hybrid photocatalyst was photoactive in CO_2 reduction in the presence of sacrificial electron donors. The molecular Co(III) complex was also grafted onto a mesoporous silica for use in photocatalytic CO_2 reduction in the presence of a molecular photosensitizer [27]. The best catalytic activity was achieved when the surface Co(III) complex formed a monolayer in the silica mesopores.

In this work, we build on prior work to demonstrate the importance of molecular deposition in achieving photo-induced electron transfer from TiO_2 to the molecular catalyst for CO_2 reduction in the presence of an electron donor. We synthesize three hybrid photocatalysts using different TiO_2 nanomaterials via a microwave method. We further investigate the hybrid photocatalysts using spectroscopic and microscopic techniques, including UV–vis, Fourier Transform infrared (FTIR) and electron paramagnetic resonance (EPR) spectroscopies, and transmission electron microscopy (TEM). Through these studies, we identify surface characteristics that are key to the molecular deposition of the molecular catalyst, and further investigate coordination geometry of the surface metal sites and their interaction with CO_2.

2. Experimental section

2.1. Materials

Triethylamine (TEA, ≥99%), triethanolamine (TEOA, ≥99%), acetonitrile (99.999%), hydrochloric acid (37%), and 1,4,8,11-tetraazacyclotetradecane (cyclam, 98%) 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 TiO_2 (specific surface area 57 m^2/g, phase composition ∼80% Anatase and ∼20% Rutile, see Fig. S1 in Electronic Supplementary information) was obtained from Evonik and used as received. Anatase TiO_2 nanopowder (99.7% trace metal basis, specific surface area 56 m^2/g) and Rutile TiO_2 nanopowder (99.5% trace metal basis, specific surface area 20 m^2/g) were obtained from Sigma-Aldrich and used as received.

2.2. Catalyst synthesis

Hybrid photocatalysts were synthesized by a microwave method (Fig. 2). In a typical synthesis, 100 mg TiO_2 was mixed with 10 mg [Co(cyclam)Cl_2]Cl and 65 μl triethylamine in 15 ml acetonitrile. The presence of triethylamine was found to be essential for the successful deposition of the Co(III) catalyst on TiO_2 via reacting with surface Ti—OH groups. 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 twice with chloroform and twice with ethanol. After drying at room temperature, the hybrid photocatalyst was obtained as a light brownish powder. Our previous results [21] clearly indicated that the molecular structure of Co^{III}(cyclam) was retained upon deposition on TiO_2 surfaces, with some of the Cl ligands replaced by OH groups (Fig. 2).

Following this microwave synthesis, three hybrid photocatalysts were prepared in the presence of P25, Anatase and Rutile TiO_2 nanomaterials. The three hybrid photocatalysts are denoted as Co^{III}(cyclam)X/P25, Co^{III}(cyclam)X/Anatase, and Co^{III}(cyclam)X/Rutile. Catalyst loadings were determined by elemental analysis to be 59, 63, and 88 μmol Co per gram of Co^{III}(cyclam)X/P25, Co^{III}(cyclam)X/Anatase, and Co^{III}(cyclam)X/Rutile, respectively. The loadings were used to calculate turnover numbers (TONs) in photocatalysis.

2.3. Catalyst characterization

Elemental analysis was conducted by acid digestion of powder samples, followed by quantification using a Varian Vista AX induced coupled plasma atomic emission spectrometer. Transmission electron microscopy images were taken on a Zeiss/LEO 922 Omega system. UV–vis spectra were obtained on a Cary 50 Bio spectrophotometer. A Barrelino diffuse reflectance probe was used to collect UV–vis spectra of powder samples using $BaSO_4$ as a standard. FTIR spectra were collected on a Thermo Nicolet 6700 FTIR spectrometer using a Harrick Praying Mantis diffuse reflectance accessory (for powder samples) or a transmission cell (for gaseous samples). EPR spectra were collected on a Bruker ELEXSYS E580 spectrometer operating in the X-band (9.4 GHz) mode and equipped with an Oxford CF935 helium flow cryostat. Spectra of powder samples were collected under N_2 at liquid He temperature. For the studies of CO_2 adsorption, the samples were purged with CO_2 at room temperature, cooled to liquid He temperature, and illuminated in the EPR cavity using a 300 W Xe lamp (PerkinElmer) with 400 nm long-pass and water as IR cutoff filters.

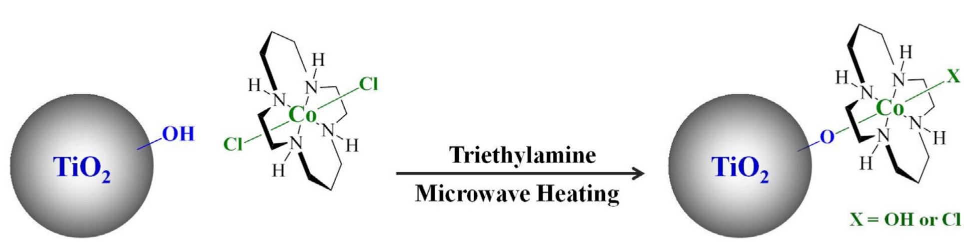

Fig. 2. Synthesis of the hybrid photocatalyst in the presence of triethylamine (TEA).