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Communication

# Photocatalytic CO<sub>2</sub> Reduction using a Molecular Cobalt Complex Deposited on TiO<sub>2</sub> Nanoparticles

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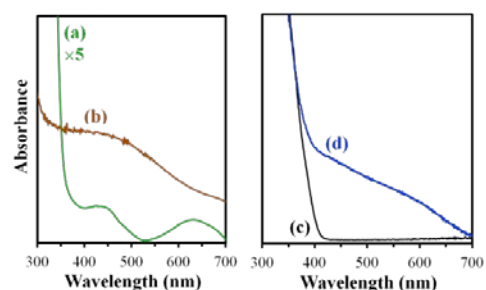
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Hybrid photocatalysts were prepared by depositing a macrocyclic cobalt complex on TiO<sub>2</sub> surfaces. Upon UV light irradiation, photoexcited electrons in TiO<sub>2</sub> nanoparticles were transferred to the surface cobalt catalyst for CO<sub>2</sub> reduction.

Photocatalysis is a promising long-term solution to sustainable CO<sub>2</sub> utilization.<sup>1</sup> Molecular catalysts based on metal-ligand complexes have demonstrated excellent activity in photocatalytic CO<sub>2</sub> reduction.<sup>2-4</sup> However, these molecular catalysts are usually not stable enough to achieve high turnover numbers, and we still lack simple methods to effectively couple molecular catalysts with photosensitizers. Hybrid photocatalysts, particularly those consisting of molecular catalysts coupled with nanostructures, have been investigated to address issues associated with molecular catalysts.<sup>5</sup> In this study, we prepared hybrid photocatalysts by simple solution-phase deposition which led to effective coupling of a cobalt catalyst with TiO<sub>2</sub> nanoparticles.

We employed a commercially available TiO<sub>2</sub> material, P25, which consists of ~80% anatase and ~20% rutile.<sup>6</sup> In our synthesis, P25 TiO<sub>2</sub> nanoparticles and [Co(cyclam)Cl<sub>2</sub>]Cl, where cyclam is 1,4,8,11-tetraazacyclotetradecane, were refluxed in a solution of acetonitrile containing a small amount of triethylamine under aerobic atmospheric conditions. A brownish powder, denoted “Co<sup>III</sup>(cyclam)X/P25”, was collected from the resulting mixture. The same procedure was used to synthesize Co<sup>III</sup>(cyclam)X/Silica and Co<sup>III</sup>(cyclam)X in the presence of Silica and in the absence of P25 or Silica, respectively. The ligand X in Co<sup>III</sup>(cyclam)X could be Cl and OH, as will be discussed later. Microscopic studies indicate that Co<sup>III</sup>(cyclam)X is amorphous and may be uniformly deposited on the surface of P25 nanoparticles (see Fig. S1, ESI<sup>†</sup>).

Unlike [Co(cyclam)Cl<sub>2</sub>]Cl, Co<sup>III</sup>(cyclam)X is not soluble in methanol. However, Co<sup>III</sup>(cyclam)X is well dispersed in water, allowing structural characterization using conventional UV-visible, NMR and electrochemistry. The optical spectrum of [Co(cyclam)Cl<sub>2</sub>]Cl contains two peaks around 430 and 630 nm characteristic of the *trans* isomer (Fig. 1a).<sup>7</sup> In comparison, the spectrum of Co<sup>III</sup>(cyclam)X in water is poorly resolved without the presence of distinguishable peaks (Fig. 1b). A similar broad absorption is seen in the optical spectra of Co<sup>III</sup>(cyclam)X/P25 (Fig. 1d) and Co<sup>III</sup>(cyclam)X/Silica (Fig. S2). The non-zero absorption of Co<sup>III</sup>(cyclam)X at 700 nm (Fig. 1b) suggests strong light scattering by Co<sup>III</sup>(cyclam)X in H<sub>2</sub>O.



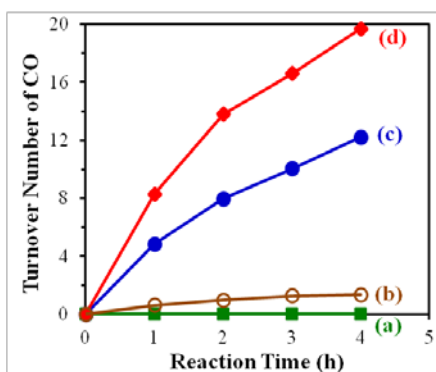
**Fig. 1** Optical spectra of (a) 0.5 mg [Co(cyclam)Cl<sub>2</sub>]Cl in 1 ml H<sub>2</sub>O, (b) 0.5 mg Co<sup>III</sup>(cyclam)X in 1 ml H<sub>2</sub>O, (c) P25 and (d) Co<sup>III</sup>(cyclam)X/P25 in the powder form. The spectra of P25 and Co<sup>III</sup>(cyclam)X/P25 were collected using a diffuse reflectance accessory.

The synthesized catalysts were further characterized with NMR, FTIR, XPS and electrochemistry. The NMR and FTIR spectra of Co<sup>III</sup>(cyclam)X are almost identical to those of [Co(cyclam)Cl<sub>2</sub>]Cl, suggesting Co<sup>III</sup>(cyclam)X has a macrocyclic structure (Figs. S3-S5). Close examination of the FTIR spectra indicates that both [Co(cyclam)Cl<sub>2</sub>]Cl and Co<sup>III</sup>(cyclam)X are in the *trans* configuration, and that Co-O bonds are present in Co<sup>III</sup>(cyclam)X (Fig. S5). The presence of Co-O bonds in Co<sup>III</sup>(cyclam)X is confirmed by XPS results (Fig. S6). Electrochemical studies suggest that the coordination environment of the Co center in Co<sup>III</sup>(cyclam)X is similar to that in [Co(cyclam)Cl<sub>2</sub>]Cl (Fig. S7). Likely, the majority of Cl ligands in [Co(cyclam)Cl<sub>2</sub>]Cl were replaced by O-containing ligands, possibly OH, during the synthesis of Co<sup>III</sup>(cyclam)X.

In this study, Co<sup>III</sup>(cyclam)X/P25 was tested in photocatalytic CO<sub>2</sub> reduction using triethanolamine (TEOA) as an electron donor. Since Co<sup>III</sup>(cyclam)X/P25 was compared against [Co(cyclam)Cl<sub>2</sub>]Cl, in some experiments methanol was added to reaction solutions to completely dissolve [Co(cyclam)Cl<sub>2</sub>]Cl. It should be noted that methanol can also function as an electron donor and a proton/hydrogen atom source in CO<sub>2</sub> reduction using TiO<sub>2</sub>-based photocatalysts. In photocatalytic CO<sub>2</sub> reduction using Co<sup>III</sup>(cyclam)X/P25, CO and H<sub>2</sub> were found to be major products (CO-to-H<sub>2</sub> ratio ~1, see Fig. S8); no significant production of formic acid was observed. Under the same conditions, a significant amount of H<sub>2</sub> was produced by bare P25. Both P25 and Co<sup>III</sup>(cyclam)X likely contributed to the production of H<sub>2</sub> in photocatalysis using Co<sup>III</sup>(cyclam)X/P25 since Co cyclams are known to produce H<sub>2</sub> under photochemical conditions.<sup>8-9</sup>

Turnover numbers (TONs) of CO, defined as ratios between the amounts of CO produced and the amounts of Co present in reaction solutions, were calculated to compare different catalysts. [Co(cyclam)Cl<sub>2</sub>]Cl is a highly active CO<sub>2</sub>-reduction catalyst when coupled with molecular photosensitizers.<sup>8-10</sup> In a prior study by others, a TON of 54 for CO production was reported after CO<sub>2</sub> reduction for 1 h using [Co(cyclam)Cl<sub>2</sub>]Cl as the catalyst and *p*-terphenyl as a UV photosensitizer.<sup>8</sup> Under similar conditions, we obtained TONs of 64 and 55 using [Co(cyclam)Cl<sub>2</sub>]Cl and Co<sup>III</sup>(cyclam)X catalysts, respectively.

In this study, we focused on using TiO<sub>2</sub> nanoparticles as the photosensitizer. No CO was detected in the head space above a mixture of [Co(cyclam)Cl<sub>2</sub>]Cl and P25 nanoparticles under UV irradiation (Fig. 2a). This can be explained by the fact that photoexcited electrons in the TiO<sub>2</sub> conduction band are not energetically sufficient to reduce [Co(cyclam)Cl<sub>2</sub>]Cl into its active states, such as Co<sup>I</sup> species,<sup>2-3, 10</sup> for CO<sub>2</sub> reduction. A small amount of CO (TON ~1.3 after 4 h) was generated by a mixture of Co<sup>III</sup>(cyclam)X and P25, and a TON of 12.2 was obtained after 4 h using Co<sup>III</sup>(cyclam)X/P25 (Fig. 2, b and c).

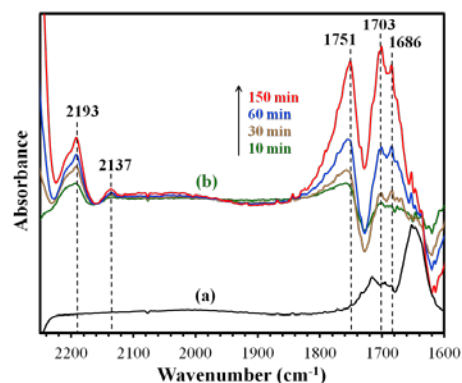


**Fig. 2** CO production in photocatalytic CO<sub>2</sub> reduction using (a) 1 mg P25 + [Co(cyclam)Cl<sub>2</sub>]Cl, (b) 1 mg P25 + Co<sup>III</sup>(cyclam)X, (c) 1 mg Co<sup>III</sup>(cyclam)X/P25 prepared by the reflux method, and (d) 1 mg Co<sup>III</sup>(cyclam)X/P25 prepared by the microwave method. The reaction solutions contain both TEOA and methanol.

A microwave synthesis was also employed to prepare hybrid photocatalysts. The microwave synthesis was conducted at 80 °C and significantly shortened the time, from 24 h to 2 h, needed for depositing Co<sup>III</sup>(cyclam)X on TiO<sub>2</sub> surfaces. After photocatalysis for 4 h, a TON of 19.7 was obtained for Co<sup>III</sup>(cyclam)X/P25 prepared by the microwave method (Fig. 2d). This enhancement in photocatalytic activity is partly associated with the loading of Co<sup>III</sup>(cyclam)X on TiO<sub>2</sub> surfaces, as will be discussed later.

In the presence of CO<sub>2</sub> and TEOA, no CO was produced by P25 under UV irradiation, or by Co<sup>III</sup>(cyclam)X/P25 under visible-light irradiation ( $\lambda > 420$  nm) which cannot activate P25 (Fig. S8). Our electrochemical studies using P25 TiO<sub>2</sub> electrodes suggest that electrons can be transferred from P25 nanoparticles to Co<sup>III</sup>(cyclam)X deposited on P25 surface (Fig. S9). Although the exact mechanism for CO<sub>2</sub> reduction on Co<sup>III</sup>(cyclam)X/P25 is still unclear, these results clearly indicate that Co<sup>III</sup>(cyclam)X is the active CO<sub>2</sub>-reduction catalyst in Co<sup>III</sup>(cyclam)X/P25 while P25 function as the photosensitizer for light harvesting and electron transfer to Co<sup>III</sup>(cyclam)X. We are currently investigating electron transfer from photoactivated TiO<sub>2</sub> nanoparticles to Co<sup>III</sup>(cyclam)X using EPR spectroscopy.

We further studied the hybrid photocatalysts with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), in which Co<sup>III</sup>(cyclam)X/P25 or P25 in powder form was placed in a three-window photoreactor equipped with *in situ* infrared detection.<sup>11</sup> The photocatalyst was purged with argon and then exposed to CO<sub>2</sub> prior to UV irradiation. Infrared spectra were collected before and after the light irradiation. In order to show changes in absorption features associated with photochemical events at the gas-surface interface, difference DRIFTS spectra were obtained by subtracting spectra collected in dark from corresponding spectra after UV irradiation. We observed the formation of surface adsorbed carbonate species (1751, 1703 and 1686 cm<sup>-1</sup>) and CO adsorbed on Co<sup>3+</sup> (2193 cm<sup>-1</sup>) and Co<sup>2+</sup> (2137 cm<sup>-1</sup>)<sup>12</sup> in the difference spectra of Co<sup>III</sup>(cyclam)X/P25 upon UV irradiation (Fig. 3b). This observation suggests that CO<sub>2</sub> reduction on Co<sup>III</sup>(cyclam)X/P25 might proceed via a formate-bridged dimer.<sup>2</sup> No significant formation of surface adsorbed CO was observed on bare P25 after UV irradiation (Fig. 3a). This comparison confirms that Co<sup>III</sup>(cyclam)X is the active CO<sub>2</sub>-reduction catalyst in Co<sup>III</sup>(cyclam)X/P25. A possible electron donor for CO<sub>2</sub> reduction shown in Fig. 3a is triethylamine that was used in the synthesis of Co<sup>III</sup>(cyclam)X/P25.



**Fig. 3** Difference DRIFTS spectra of (a) P25 TiO<sub>2</sub> after UV irradiation for 150 min, and (b) Co<sup>III</sup>(cyclam)X/P25 after UV irradiation for 10, 30, 60 and 150 min (from bottom to up). The reaction was carried out at the gas-surface interface. No solvent or TEOA was used in this study.

Hybrid photocatalysts were also synthesized using other TiO<sub>2</sub> materials, including commercially available Anatase and Rutile. The same amounts of [Co(cyclam)Cl<sub>2</sub>]Cl and TiO<sub>2</sub> nanoparticles were always used in each synthesis. Table 1 summarizes the performance of different hybrid photocatalysts in CO<sub>2</sub> reduction. For each synthesis method, the amount of Co<sup>III</sup>(cyclam)X deposited on Anatase is about the same as on P25, possibly due to the fact that the two materials have similar particle sizes and surface areas. The photocatalytic activity of Co<sup>III</sup>(cyclam)X/P25 is slightly better than Co<sup>III</sup>(cyclam)X/Anatase. Results in Table 1 also show that more Co<sup>III</sup>(cyclam)X was deposited on P25 and Anatase by the reflux method than the microwave method. The microwave synthesis at higher temperatures (100 and 120 °C) led to higher loadings of Co<sup>III</sup>(cyclam)X. In general, hybrid photocatalysts with lower Co<sup>III</sup>(cyclam)X loadings gave greater TONs in CO<sub>2</sub> reduction. In our study, the same amount of TEOA was always used in photocatalysis, resulting in lower TEOA-to-Co ratios (and lower activities) at higher Co<sup>III</sup>(cyclam)X loadings. No significant CO production was observed in the presence of

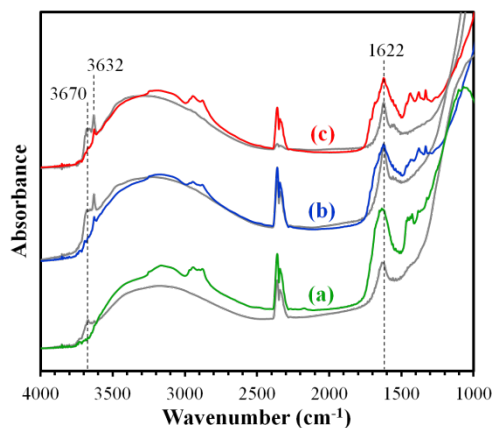
Co<sup>III</sup>(cyclam)X/Silica under UV irradiation (Table 1), further confirming the role of P25 and Anatase nanoparticles as photosensitizers for Co<sup>III</sup>(cyclam)X in CO<sub>2</sub> reduction.

**Table 1** TONs of CO after CO<sub>2</sub> reduction for 4 h using 1 mg hybrid photocatalysts and TEOA as the sole electron donor.

Photocatalysts	Reflux Method		Microwave Method	
	[Co] <sup>a</sup>	TON	[Co] <sup>a</sup>	TON
Co <sup>III</sup> (cyclam)X/P25 <sup>b</sup>	0.11	<b>7.7</b>	0.06	<b>11.2</b>
Co <sup>III</sup> (cyclam)X/Anatase	0.13	<b>6.4</b>	0.06	<b>10.4</b>
Co <sup>III</sup> (cyclam)X/Rutile	0.05	<b>0.5</b>	0.09	<b>0.3</b>
Co <sup>III</sup> (cyclam)X/Silica	0.16	<b>0</b>	0.12	<b>0</b>
Co <sup>III</sup> (cyclam)X/P25-100C <sup>c</sup>			0.15	<b>4.5</b>
Co <sup>III</sup> (cyclam)X/P25-120C <sup>c</sup>			0.20	<b>2.5</b>

<sup>a</sup> Concentration of Co<sup>III</sup>(cyclam)X in μmol/mg; <sup>b</sup> P25 consists of ~80% anatase and ~20% rutile; <sup>c</sup> Co<sup>III</sup>(cyclam)X/P25 synthesized by the microwave method at elevated temperatures (100 or 120 °C).

Interestingly, Co<sup>III</sup>(cyclam)X/Rutile showed negligible activity in CO<sub>2</sub> reduction although the Rutile sample demonstrated higher activity than Anatase in degradation of methylene blue (Fig. S10). One possible reason for the poor reactivity of Co<sup>III</sup>(cyclam)X/Rutile might be associated with its surface characteristics. Fig. 4 shows the DRIFTS spectra of the three TiO<sub>2</sub> materials before and after deposition of Co<sup>III</sup>(cyclam)X by the microwave method. The spectra of the hybrid photocatalysts contain several absorptions around 3000 cm<sup>-1</sup> and between 1500-1300 cm<sup>-1</sup> (not labeled) characteristic of cyclam ligands, as well as a broad peak assigned to surface adsorbed water (1622 cm<sup>-1</sup>) in comparison to the spectra of bare TiO<sub>2</sub> materials. We note that there are at least two types of surface hydroxyl groups, corresponding to a broad band around 3670 cm<sup>-1</sup> and a sharp peak at 3632 cm<sup>-1</sup>, in the spectra of P25 and Anatase (Fig. 4, b and c). In contrast, only the band around 3670 cm<sup>-1</sup> is present in the spectrum of Rutile (Fig. 4a).



**Fig. 4** DRIFTS spectra of (a) Co<sup>III</sup>(cyclam)X/Rutile, (b) Co<sup>III</sup>(cyclam)X/Anatase, and (c) Co<sup>III</sup>(cyclam)X/P25. Spectra of corresponding TiO<sub>2</sub> materials prior to deposition of Co<sup>III</sup>(cyclam)X are also plotted (gray).

The two bands around 3670 at 3632 cm<sup>-1</sup> have been assigned to bridging and tightly bound hydroxyl groups on TiO<sub>2</sub> surfaces, respectively.<sup>13</sup> Upon deposition of Co<sup>III</sup>(cyclam)X, the surface hydroxyl groups in the DRIFTS spectra disappeared or significantly decreased in intensity (Fig. 4). Therefore, the deposition of Co<sup>III</sup>(cyclam)X on TiO<sub>2</sub> surfaces might occur via

the replacement of the surface hydroxyl groups with Co<sup>III</sup>(cyclam)X. The comparison shown in Fig. 4 suggests that the presence of tightly bound hydroxyl groups is important for the deposition of Co<sup>III</sup>(cyclam)X that could effectively couple with photoactivated TiO<sub>2</sub> for CO<sub>2</sub> reduction.

TiO<sub>2</sub> nanomaterials have been extensively investigated in solar energy conversion,<sup>14</sup> in which the n-type TiO<sub>2</sub> is often utilized to collect photogenerated electrons from surface molecular complexes.<sup>15</sup> Our hybrid photocatalysts are among the few systems featuring electron transfer from TiO<sub>2</sub> to surface molecular catalysts.<sup>16-17</sup> One limitation of TiO<sub>2</sub> photocatalysis is the lack of photoresponse in the visible light region. Molecular photosensitizers, particularly Ru(bpy)<sub>3</sub><sup>2+</sup> complexes where bpy = 2,2'-bipyridine, were used in combination with enzyme-modified TiO<sub>2</sub> nanoparticles for CO<sub>2</sub> reduction under visible light.<sup>16</sup> Other semiconductors with narrow bandgaps, including CdS, were employed to harvest visible light in CO<sub>2</sub> reduction.<sup>18</sup> In our study, a TON of 35 for CO production was obtained using a mixture of Co<sup>III</sup>(cyclam)X/P25 and Ru(bpy)<sub>3</sub><sup>2+</sup> under visible-light (λ > 420 nm) irradiation. However, the use of Ru(bpy)<sub>3</sub><sup>2+</sup> in our system dramatically lowered the selectivity to CO formation (CO-to-H<sub>2</sub> ratio ~0.2). Deposition of Co<sup>III</sup>(cyclam)X on CdS was unsuccessful, suggesting the importance of surface hydroxyl groups in the formation of Co<sup>III</sup>(cyclam)X on surfaces.

In summary, we have prepared hybrid photocatalysts by simply depositing a molecular Co complex on TiO<sub>2</sub> nanoparticles. In the presence of an electron donor, photogenerated electrons in TiO<sub>2</sub> were transferred to the surface Co catalyst for CO<sub>2</sub> reduction. Further studies are in progress to obtain more structural information of the surface Co catalyst and to understand electron transfer across the TiO<sub>2</sub>/Co catalyst interface which is essential to CO<sub>2</sub> reduction on the hybrid photocatalysts.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: experimental details and supplementary figures, including electron micrographs of Co<sup>III</sup>(cyclam)X and Co<sup>III</sup>(cyclam)X/P25; optical spectra of Silica and Co<sup>III</sup>(cyclam)X/Silica; NMR and FTIR spectra of [Co(cyclam)Cl<sub>2</sub>]Cl and Co<sup>III</sup>(cyclam)X; XPS spectra of [Co(cyclam)Cl<sub>2</sub>]Cl, Co<sup>III</sup>(cyclam)X and Co<sup>III</sup>(cyclam)X/P25; cyclic voltammograms of [Co(cyclam)Cl<sub>2</sub>]Cl and Co<sup>III</sup>(cyclam)X; photocatalytic CO<sub>2</sub> reduction using Co<sup>III</sup>(cyclam)X/P25 under different light conditions; cyclic voltammograms of P25 and Co<sup>III</sup>(cyclam)X/P25 electrodes; and degradation of methylene blue using different TiO<sub>2</sub> materials. See DOI: 10.1039/b000000x/

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