Visible light assisted reduction of CO$_2$ into formaldehyde by heteroleptic ruthenium metal complex-TiO$_2$ hybrid in aqueous medium

Alok Kumar, a Rajakumar Ananthakrishnan*  

*aDepartment of Chemistry, Environmental Materials & Analytical Chemistry Laboratory, Indian Institute of Technology, Kharagpur 721302, India

Contents

Scheme S1. Synthetic route of ligands and metal complexes……………………………………3

Scheme S2 Repetative synthesis Scheme of TiO$_2$ nano particles…………………………4

Fig. S1-S10 Proton and $^{13}$C NMR, MALDI-TOFMS and FTIR…………………………5-9

Fig. S11 UV-Vis and fluorescence spectra……………………………………………………10

Fig. S12 UV-Vis diffuse reflectance spectra (DFigure S15 TGA profile)…………….10

Fig. S13 (a)Fluorescence lifetime and Photoluminescence…………………………11

Fig. S14 Cyclic voltammogram……………………………………………………………..12

Fig. S15 Nyquist plots……………………………………………………………..12

Fig. S16 Raman spectra……………………………………………………………………13

Fig. 17 HRTEM and FESEM images………………………………………………………14

Fig. S18 UV-Vis spectra of MV$^2$…………………………………………………………14

Fig. 19 UV-Vis spectra of reaction mixture in water………………………………………..15

Fig. S20-S27 GCMS spectra analysis of 4-aminobenzoic acid and aniline………………16-20

Fig. S28-S29 LCMS of paraquat (Methyl viologen, MV$^{2+}$)…………………………..20-21

Fig. S30-31 FTIR and LCMS spectra ho homogeneous catalysis………………………21-22

Fig. S32 Trace GC chromatogram of TCD3………………………………………………22

Fig. S33 DRS spectra of reused catalyst…………………………………………………..23

Fig. S34-35 XPS profile of hybrid photocatalyst…………………………………………23-24

Fig. S36 EDX profile of hybrid photocatalyst………………………………………………24
Table S3. Summary previously reported photocatalytic CO₂ reduction..........................25-26

Fig. 37 UV-Vis of metal complex at pH medium....................................................... 27

Experimental section

Materials: The entire chemical were taken by the commercial sources and used without further purification. 2,2-bypyridine, 1, 10-Phenanthroline (phen), and RuCl₃·xH₂O were purchased form Merck India. Ammonium acetate, KBr, 4-formylbenzoic acid, and 4-nitro benzaldehyde were taken from Spectrochem. All the solvents were GR grade.

Synthesis of 1

The ligands were synthesized from previously adapted method.¹ For the typical synthesis, 1, 10-Phenanthroline (5.0g), was dissolved in concentrated sulphuric acid (30 ml) in 100 ml round bottom flask. Than 2.5 g KBr was added followed by 15 ml HNO₃ at 4-5 °C. The mixtures were allowed for reflux for 2h. After cooling down at room temperature 500 ml ice cold deionised water was added. The mixture was carefully neutralized by using the sodium hydroxide. Than the solvents extraction were done in dichloromethane (DCM) and water to afford the yield 95% for compound 1. ¹H NMR (400 MHz, DMSO-d₆, δ ppm): 9.08 (2H, m), 8.48 (2H, m), 7.58 (2H, m).

Synthesis of L1OH

0.42 g (2 mmol) of 1 and 0.34g (2.2 mmol) of 4-formylbenzoic acid were taken in round bottom flask. 30 ml glacial acetic acid was added followed by addition of 2.31 g (30 mmol) ammonium acetate. The mixture was allowed to reflux for 3.5 h. At room temperature deionised water was added and yellow colour precipitate was obtained (yield, 86%). The compound was characterised by ¹H NMR before further used. ¹H NMR (400 MHz, DMSO-d₆, δ ppm): 12.67 (1H, s), 7.76 (2H, d), 7.64 (2H, d), 7.11 (2H, d), 6.91 (2H, d), 6.57 (2H, m). ¹³C-NMR (400 MHz, DMSO-d₆, δ ppm) δ 167.71 (COOH), 150.15-124.12 (ArC). Calculated mass for C₂₀H₁₂N₄O₂ (M = 340.33) and found (MALDI Tof MS): m/z = 341.5 [M + H]⁺.

Synthesis of L2NO

All the procedure was followed as for L1OH synthesis, however, 4- nitrobenzaldehyde was used instead of 4-formylbenzoic acid. ¹H NMR (400 MHz, DMSO-d₆, δ ppm): 7.84 (2H, d),
Synthesis of metal complexes

Firstly, [Ru(bpy)₂Cl₂] metal precursor was prepared from previous report.² 0.3 g (0.619 mmol) of metal precursor and 0.21 g (0.619) of L1OH was refluxed in ethanol under nitrogen atmosphere. The crude product was collected using rotary evaporator and minimum amount of cold methanol was added. The unreacted ligand was obtained as precipitate and a red orange color solution was evaporated to afford crystalline metal complex product. ^1H NMR (400 MHz, DMSO-\(d_6\), δ ppm): ^1H NMR (DMSO-\(d_6\)): δ 7.31 (t, \(J = 6.6, 2\)H, bpy), 7.56–7.63 (m, 4H, bpy), 7.83 (d, \(J = 5.2, 2\)H, bpy), 7.98 (m, 2H, phen), 8.02–8.15 (m, 4H, bpy), 8.18–8.21 (m, 4H, bpy, \(C_6H_4\)), 8.45 (d, \(J = 8.2, 2\)H, \(C_6H_4\)), 8.82–8.88 (m, 4H, phen, bpy), 9.1–9.2 (m, 2H, phen), 13.8 (s, 1H, COOH). Calculated mass for \(C_{40}H_{28}N_8O_2Ru\) (\(M = 754\)) and found (MALDI Tof MS): \(m/z = 755.07\) [M + H]⁺.

Scheme S1. Synthetic route of ligands and metal complexes
Synthesis of TiO$_2$ nano particles and catalyst

Scheme S2 (1) Repetative synthesis Scheme of TiO$_2$ nano particles. (2) immobilization process, for example, 1000 mg of TiO$_2$ powder and 2.5 µM of metal complexes (RuL1OH, RuL2NO) were stirred in CH$_3$CN solvent for 12 h (a). The solution was centrifuged to separate TiO$_2$ powder (b, d). TiO$_2$ was washed 5 times using mother solvents and water (c,d). The dried powder is shown above in both the solvents (CH$_3$CN and DMF).
Fig. S1. $^1$H NMR spectra of ligand recorded at room temperature in DMSO-d$_6$

Fig. S2. $^{13}$C NMR spectra of ligand recorded at room temperature in DMSO-d$_6$
Fig. S3. $^1$H NMR spectra of ligand (L1) recorded at room temperature in DMSO-d$_6$.

Fig. S4. $^{13}$C NMR spectra of Ligand (L1) recorded at room temperature in DMSO-d$_6$. 
**Fig. S5.** $^1$H NMR spectra of ligand (L2) recorded at room temperature in DMSO-$d_6$.

**Fig. S6.** MALDI ToF MS of ligand L1 (2,4 DHB used as matrix).
Fig. S7. MALDI Tof MS of ligand L2 (2,4 DHB used as matrix).

Fig. S8. MALDI Tof MS of ligand [RuL1(bpy)2]^{2+} (2,4 DHB used as matrix).
Fig. S9. MALDI ToF MS of ligand [RuL2(bpy)2]^{2+} (2,4 DHB used as matrix).

Fig. S10 (a) ART-FTIR spectra of metal complex [RuL1(bpy)_2]^{2+} and [RuL2(bpy)_2]^2
Fig. S11 (a) UV-Vis and fluorescence spectra of metal complexes [RuL1(bpy)$_2$]$^{2+}$, and (b) [RuL2(bpy)$_2$]$^{2+}$ measured in MeCN at pH 7.

Fig. S12 UV-Vis diffuse reflectance spectra (DRS) of pure metal complexes, TiO$_2$ and TiO$_2$ hybrids. (i) RuL1OH. (ii) RuL2NO. (iii) TiO$_2$/RuL1OH. (iv) TiO$_2$/RuL2NO. (v) TiO$_2$. 
Table S1. Photophysical properties of synthesized metal complex.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\lambda_{\text{abs}}$ a(nm) (ε (1x 10^3 M^-1 cm^-1))</th>
<th>$\lambda_{\text{em}}$ b(nm)</th>
<th>$&lt;\tau&gt;$ c(µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuL1OH</td>
<td>246 (28), 286 (78), 457 (15)</td>
<td>618</td>
<td>0.165</td>
</tr>
<tr>
<td>RuL2NO</td>
<td>244 (29), 287 (89), 353 (21), 460 (18)</td>
<td>636</td>
<td>0.064</td>
</tr>
<tr>
<td>[Ru(bpy)_3]^{2+}</td>
<td>244(25), 287(84), 451(14)</td>
<td>621</td>
<td>0.855</td>
</tr>
</tbody>
</table>

*aAbsorption maxima (molar extinction coefficient).  bEmission maxima.  cAverage life time.

Fig. S13 (a) Fluorescence life time of metal complexes [RuL1(bpy)_3](PF6)_2 and [RuL2(bpy)_3]^{2+}. (b) Solid state fluorescence of hybrid photo catalyst along with TiO_2.
Fig. S14 Cyclic voltammogram of [RuL1(bpy)_2](PF6)_2 in MeCN with AgCl as reference electrode. (a) Scan at negative direction. (b) Scan 0 to 1.6 V. (c) Full scan of [RuL2(bpy)_2](PF6)_2.

Fig. S15 Nyquist plots of TiO_2/RuL1OH and TiO_2/RuL2NO measured at 0.70 V bias under dark and light.
**Fig. S16** Raman spectra of TiO$_2$ and hybrid photocatalyst (TiO$_2$/RuL1OH, TiO$_2$/RuL2NO) with excitation wavelength at 514 nm.

**Table S2** Gaussian Fit of the wavenumber and the corresponding FWHM of E$_g$ (140) phonon (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>FWHM (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>140.0</td>
<td>8.7</td>
</tr>
<tr>
<td>TiO$_2$/RuL1OH</td>
<td>140.5</td>
<td>10.2</td>
</tr>
<tr>
<td>TiO$_2$/RuL2NO</td>
<td>142.5</td>
<td>13.6</td>
</tr>
</tbody>
</table>
**Fig. 17** (a) TEM images of as prepare hybrid catalyst TiO$_2$/RuL1OH. (b) HRTEM lattice fringes pattern. (c) FESEM images. SEAD images of hybrid.

**Fig. S18** (a) UV-Vis spectra of freshly prepared MV$^{2+}$ and after light reaction in H$_2$O. (b) Corresponding fluorescence spectra was measured at excited wavelength 360 nm in H$_2$O.
**Fig. S19 (a)** TGA of hybrid photocatalyst and TiO$_2$. The weight loss of metal complex is indicated by slope. (b) UV-Vis spectra of reaction mixture in water.

**Immobilization of metal complexes over the TiO$_2$**

\[
\frac{A(\text{initial}) - A(\text{final}) \times C}{A(\text{initial}) \times 0.05g} \times \frac{\text{mol}}{L} \times 0.025 L
\]

The amounts of meal complexes adsorbed over the TiO$_2$ surface were determined by UV-Vis spectroscopy. 50 mg of TiO$_2$ nanoparticle dried in vacuum at 50 °C for 6 h and the same was dispersed in DMF (25 ml) solution. The amount of metal complex was added to achieve the concentration 8.0 µM. The mixtures were stirred at room temperature in dark for 12 h. the solid particles were isolated and absorbance of the solutions were recorded. The adsorbed amount of the complexes was estimated by using the following equation.
For a typical example, Initial and final absorption of metal complex (RuL1OH) were obtained as 0.45 and 0.062 respectively. The initial stock solution was 10 µM. Therefore the adsorbed metal complex over the TiO$_2$ surface was 4.3 nM/g of the TiO$_2$.

**Fig.20** Represnetative GC chromatogram of pure aniline.
Fig. 21 Mass spectrum of pure aniline at corresponding retention time 5.43-5.53 min.
Fig. S23 Mass spectrum of aniline after in situ reaction with formaldehyde. The corresponding m/z value at retention time 3.04 min.
**Fig. S24** Mass spectrum of aniline after *in situ* reaction with formaldehyde. The corresponding m/z value at retention time 16.87 min.

**Fig. S25.** GC-MS spectra of standard 4-aminobenzoic acid recorded in H$_2$O.
Fig. S26. GC-MS spectra of 4-aminobenzoic acid after reaction recorded in H$_2$O.

Fig. S27. GC-MS spectra of 4-aminobenzoic acid after reaction recorded in H$_2$O.
**Fig. S28.** LC-MS chromatogram and corresponding ESI-MS of standard paraquat (MV$^{2+}$) recorded in H$_2$O

![LC-MS chromatogram and corresponding ESI-MS of standard paraquat (MV$^{2+}$) recorded in H$_2$O](image1)

**Fig. S29.** LC-MS chromatogram and corresponding ESI-MS of paraquat (MV$^{2+}$) after 2.5 h irradiation in presence of catalyst (TiO$_2$/RuL1OH, $\lambda > 400$ nm) recorded in H$_2$O

![LC-MS chromatogram and corresponding ESI-MS of paraquat (MV$^{2+}$) after 2.5 h irradiation in presence of catalyst (TiO$_2$/RuL1OH, $\lambda > 400$ nm) recorded in H$_2$O](image2)
**Fig. S30** FTIR spectra of pure 4-aminobenzoic acid (a) and after reaction in homogeneous medium under CO$_2$ pressure (b).

![FTIR spectra of pure 4-aminobenzoic acid and after reaction](image)

**Fig S31** LCMS of aniline after reaction in homogenous medium

![LCMS of aniline](image)

**Fig. S32.** GC-Trace chromatogram of TCD3 and the peak at retention time 2.93 is corresponding to hydrogen as per the standard.

![GC-Trace chromatogram of TCD3](image)
**Fig. S33.** DRS spectra of hybrid catalyst (TiO$_2$/RuL1OH) after catalysis. The sample was first dried after catalysis (5$^{th}$ and 8$^{th}$ recycle) then DRS spectra were recorded.

**XPS spectra of before and after catalysis**
**Fig. S34.** XPS survey of hybrid photocatalyst (TiO$_2$/RuL1OH).

**Fig. S35.** XPS survey of hybrid photocatalyst (TiO$_2$/RuL1OH) after 3 time catalytic reaction in water.
Table S3: Summary of Ruthenium metal complex based photocatalytic CO\(_2\) reduction.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Reaction conditions</th>
<th>Products [µmol] (TON)</th>
<th>Selectivity (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-loaded TiO(_2)–SiO(_2)</td>
<td>1000 W Hg-lamp (365 nm), CO(_2) saturated aqueous solution containing 1 M 2-propanol</td>
<td>CH(_3)OH [210 mmol g(^{-1})] for 6 h; CH(_4) [40 mmol g(^{-1})] for 6 h over 0.5% Ru–TiO(_2)/SiO(_2)</td>
<td>Not defined Depende on Ru doped TiO(_2) loading</td>
<td>4</td>
</tr>
<tr>
<td>Pd-loaded TiO(_2)</td>
<td>500 W Hg-lamp ((\lambda) &gt; 350 mg catalyst in 1.5 mL CO(_2) saturated solution</td>
<td>CO and CH(_4) [1.1]</td>
<td>Not defined CO is major products</td>
<td>5</td>
</tr>
<tr>
<td>Ru/TiO(_2) hybrid nanocomposite</td>
<td>20 W white cold LED, water and a DMF system</td>
<td>CH(_3)OH [1876 g(^{-1})]</td>
<td>Not defined Single product reported</td>
<td>6</td>
</tr>
<tr>
<td>TiO(_2) film sensitised by ruthenium N719.</td>
<td>A 300 W Xe lamp (L25, (\lambda)(_{\text{max}}) = 500 nm)</td>
<td>HCOOH [8.35], HCHO [120] and CH(_3)OH [17] cm(^{-2})</td>
<td>Not defined Three products reported</td>
<td>7</td>
</tr>
<tr>
<td>Mononuclear C(_5)H(_5)-RuH complex oxo-bridged TiO(_2) hybrid</td>
<td>visible light ((\lambda) &gt; 420 nm) irradiation 300w Xe lamp</td>
<td>CH(_4) (44.0 µL g(^{-1}) h(^{-1})) at 0.6 wt% Ru content in water medium</td>
<td>Almost 100 % reported</td>
<td>8</td>
</tr>
<tr>
<td>Method</td>
<td>Reactants</td>
<td>Products</td>
<td>Notes</td>
<td></td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>-------------------</td>
<td>---------------------------</td>
<td>--------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Adsorbed onto Ag-loaded TaON (Ag/TaON)</td>
<td>Methanol</td>
<td>Formic acid as product and formaldehyde as the oxidized product of methanol.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>500 W Hg lamp</td>
<td>HCOOH [0.956] (41)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂ [0.678]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CO [0.068] (2.8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>λ &gt; 400 nm with a high-pressure Hg lamp. Aqueous solutions</td>
<td>HCOOH [7.0] (600)</td>
<td>CO[0.3] (28)</td>
<td>37 %</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂[11.4] (978)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Visible light (λ &gt; 420 nm) irradiation</td>
<td>CO [2050] g⁻¹ cat.</td>
<td>50% selectivity for CO the loading amount of 7.8 μmol g⁻¹.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MECN DMA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorinated Anatase TiO₂ Nanosheets, Exposed {001} Facets</td>
<td>UV illumination</td>
<td>Methane [1.23]</td>
<td>Not defined</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methanol [1.09]</td>
<td>Mixture of products</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Formaldehyde [0.38]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂ sensitization</td>
<td>250-watt tungsten lamp (λ &gt; 420 nm) combined with NaNO₂ aqueous solution filter</td>
<td>HCHO [90] (720) CO [17] 136 CH₄ [8 ] 64</td>
<td>65 % selective for HCHO This work</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. S37 (a) UV-visible spectra of complex (RuL1OH) in acidic (Perchloric acid) medium (pH 5) recorded in MeCN. (b) UV-visible spectra in basic medium (pH 8). Tetrabutylammonium hydroxide was used as the base.

References
