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Introduction

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Visible light assisted reduction of CO₂ into formaldehyde by heteroleptic ruthenium metal complex-TiO₂ hybrid in aqueous medium

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Photocatalytic reduction of CO₂ and its simultaneous functionalization is a profound journey to achieve in an ambient condition. In the current research, precedent exists for the formation of HCHO, HCOOH, CO, CH₄, and CH₃OH after reduction of CO₂ under provided suitable conditions. In this progression, HCHO is considered a very reactive molecule; therefore, it remains to be observed in the photocatalytic process. Herein, we report CO2 reduction to formaldehyde via heterogeneous photocatalysis in aqueous medium at pH 7. Synthesized hybrid photocatalyst capable of active under visible light (λ > 420 nm) by utilizing the heteroleptic ruthenium metal complex over the TiO₂ nanoparticles through covalent interaction. The major reaction product was identified as formaldehyde, a trace amount of CO and CH₄ were detected in the presence of triethanolamine (TEOA) as a sacrificial donor. The maximum turnover number (720) for HCHO was obtained based on the metal complex used over the surface after 5 h visible-light irradiation. Furthermore, formaldehyde (in situ) was utilized for reaction with primary amine (aniline, 4-aminobenzoic acid) into the corresponding imine under the visible light. Directed by mechanistic studies, the results demonstrate for the first time that C_1 reduced product of CO₂ in a heterogeneous medium can be utilized for useful products.

> under UV light.^{7, 8} In additions, the reduced bandgap heterostructures were well explored by utilizing noble metals and graphene to improve the properties under the visible light.^{9, 10} However, the primary constraints are related to non-aqueous solvents, mixed solvents, and complication in product selectivity in a confined medium. On the other hand, CO₂ reduction in H₂O is dominated by competitive hydrogen evaluation reaction (HER) on the catalyst surface. Therefore, it has become a challenge to control over the thermodynamics and kinetics of reaction in a water medium; however, and the progression has not been limited in current research.^{11, 12}

> A molecular catalyst (homogeneous) such as ruthenium, osmium, iridium, and cobalt complexes are known to give the selectivity as well as good quantum yield for CO₂ reduction in a reliable and suitable system.^{13, 14, 15} Frederick et al. had used an aqueous homogeneous medium to produce methanol and formate from CO₂ by Ru(II) chromophore.¹⁶ Hamers¹⁷ and Einaga et al. had shown the electrocatalytic reduction of aqueous CO₂ to formaldehyde over the boron-doped diamond (BDD) electrode,¹⁸ and other groups had demonstrated direct formaldehyde synthesis using polyhydride ruthenium complex.¹⁹ The method described by Gratzel for dye-sensitized solar cells has paid attention to utilizing a wide band gap semiconductor under visible light.²⁰ Among the family of semiconductor, TiO₂ is well known non-toxic, bio-friendly, readily available semiconductor which extensively being

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The visible light assisted photocatalytic reduction of CO₂ to

useful products has become considerable interest due to

the sustainable development of the environment and fossil

fuels scarcity. Imitating from nature (photosynthesis), there

were enormous efforts been continuously attempted to

utilize the sunlight in the presence of H_2O and CO_2 in the

laboratory scale.¹⁻⁴ Both H₂O and CO₂ are stable molecules,

consequently strenuous to oxidized and reduced at normal

conditions. The significant challenges for CO₂ reduction are

product selectivity as well as conversion efficiency at the

provided system. This is due to the presence of highest

oxidations sate of carbon atoms (CO₂) that follows a multi-

electron and proton pathways to reduce the products such

as HCOOH, CO, CH₃OH, HCHO, etc.^{5, 6} Therefore, increased

selectivity, convenient methods for catalysis, and high yield

of product are immensely desirable in today research. For

this purpose, various wide-bandgap semiconductors like

TiO₂, ZnO, and others were introduced for CO₂ conversion



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[†] Footnotes relating to the title and/or authors should appear here.

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studied.^{7, 21-23} There were various anchor groups explored over the TiO₂ surface to increase the efficiency and stability of photocatalytic activities in the past.²⁴ Scheme 1a represented the catalytic reactions of CO₂ in aqueous medium using dye-sensitized (N719) TiO₂ film resulting mixture of products.²³



Schemes 1 (a) CO_2 reductions over the TiO_2 film using N719 dye give mixture of product. (b) Represent the CO_2 reduction by synthesized ruthenium complex (RuL1) immobilized TiO_2 hybrid (This work).

Our group had reported the utilization of Ru(II)-complex as homogeneous and heterogeneous conditions for the photocatalytic organic transformation and environmental applications.^{25, 26} Notably, here we aimed to introduced benzimidazole containing ruthenium metal complexes with two different functionality (-COOH, -NO₂) for TiO₂ sensitizations (Scheme 2). A few numbers of literature associated with both functional group (-COOH and -NO₂) have been introduced to understand the sensitization process of semiconductor.^{27, 28} The prominent advantage of using benzimidazole spacer in the complexes, which enhances the better electron-donating capability hence, electronic (ground state) properties of ruthenium metal complex can be tuned. The strategy behind for choosing this phenanthroline chelate site linked via benzimidazole spacer with a different terminal functional group (-COOH, -NO₂) are as follows. (a) Metal complex exhibits enhanced lifetime in aqueous and protic solvents, which has useful advantages in photocatalysis to overcome the recombination processes, and (b) Metal complex is photostable over classical [Ru(bpy₃)]²⁺ in aqueous media.



Scheme 2 TiO_2 Hybrid photocatalyst of ruthenium (II) heteroleptic metal complex anchored on surface. Two functional groups namely, a carboxylic acid group and nitro group respectively. Excited state ruthenium (II) injects the electron into conduction band of TiO_2 . The conduction band is actively participating for CO_2 reduction.

(c) The free NH rich surface could modulate the CO_2 adsorption over the heterogeneous surface which may lead to increase the rate of CO_2 reduction. Interestingly, the hybrid catalyst has shown the excellent photocatalytic activity towards the CO_2 reduction yielding the selective product (HCHO) after 5 h irradiation in aqueous medium (Scheme 1b). Furthermore, in situ formaldehyde was allowed to react with amine (aniline, 4-aminobenzoic acid) resulting into imine formation. The mechanistic pathways of the nature of active species during the catalytic process are discussed. We demonstrate the use of CO_2 reduced product as C_1 can further be used in heterogeneous photocatalytic system under visible light by green approach.

Results and discussion

Ligands L1, L2 (abbreviated L1OH, L2NO) and metal complexes were synthesized by adapting from previous literature with slight modification (Scheme S1⁺).^{29, 30} L1 and L2 gives significant yield 86% and 93% respectively. The metal complexes were synthesized in ethanol medium. [Ru(bpy)₂]Cl₂ was used as a precursor for the synthesis of complex [RuL1(bpy)₂]²⁺ and [RuL2(bpy)₂]²⁺ abbreviated as a RuL1OH and RuL2NO respectively. The details of synthetic procedure have been discussed in supporting information. All the ligands and metal complexes were well characterized by Proton NMR, ¹³CNMR, FTIR, Maldi-TOF MS as described in supporting information (SI⁺, Fig. S1-S10). The electronic photophysical properties of the metal complexes were characterized by UV-Vis and fluorescence spectroscopy in CH₃CN solvents whereas stated otherwise. Complex (RuL1OH) is very sensitive to the pH, soluble in polar solvents and has an excellent hydrogen bonding site. The details photophysical properties concerning the pH of metal complex RuL1OH have been described elsewhere.30 However, RuL2NO has preferably only one side (NH-proton) of hydrogen bonding. Lifetime measurements were carried out using time-correlated single photon counting (TCSPC) in CH₃CN at pH 7. Complexes RuL1OH and RuL2NO revealed the fluorescence lifetime 164 ns and 64 ns respectively (Table S1[†]). Both the metal complexes were immobilized on synthesized TiO₂ nanoparticle in suitable solvent (CH₃CN or DMF) at room temperature. Though both the solvents gave same result, the DMF solvent had been used to estimate the amount of incorporated metal complex into the TiO₂ surface to avoid any concentration error. Detailed synthesis of TiO₂ nanoparticles are mentioned in SI⁺ (Scheme S2⁺). The loaded amount of metal complex over the surface was estimated by UV-Vis spectroscopy. The results gave 0.125 μ M/g of RuL1OH and 0.093 μ M/g of RuL2NO over the TiO₂, respectively. Hence, it is clear that metal complexes were successfully anchored on the TiO₂ surface. Binding of metal complexes with TiO₂ was studied by ATR-FTIR, diffuse reflectance spectroscopy (DRS), cyclic voltammetry, and Raman spectroscopy.

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Photophysical and Electrochemical Properties

The UV-Vis spectra of the metal complexes RuL1OH and RuL2NO shows the two transition band at 288 nm and 457 nm which correspond to π to π^* (transition) and metal to ligand charge transfer (MLCT) of ruthenium center (Fig. 1).³¹ On the other hand, the MLCT band was significantly redshifted for RuL2NO which is presumably because of electron-withdrawing substituents (NO₂) as shown in Fig S11[†]. Diffuse reflectance spectra of the hybrid catalyst (TiO₂/RuL1OH, TiO₂/RuL2NO) showed MLCT transition band and can significantly be perceived at 463 nm which is due to ruthenium complexes (Fig. 1). In addition, similar effect was attributed to solid-state of pure metal complex (RuL2NO), which revealed bathochromic shift in important MLCT transition as compared to RuL1OH complex. The more electronegative ligand (electron-withdrawing at terminal site) will lead to attract electron from the metal center. Therefore, electron density will be delocalized.32 Consequently, delocalization prefers larger effective conjugation, which results in bathochromic shift of MLCT transition.



Fig. 1 (a) UV-Vis absorptions spectra of the metal complex (RuL1OH) measured in CH₃CN (dotted line, ii). (i) Solid-state DRS of TiO₂ nanoparticles. (iv, iii) For hybrids TiO₂/RuL1OH, TiO₂/RuL1NO, respectively. Tauc plot for TiO₂/RuL1OH (inset).

However, a small red-shift in the hybrid $TiO_2/RuL1OH$ indicates the strong interaction through carboxyl group of metal complex (Fig S12†). This effect is consistent with a

decrease in energy of the ligand π^* orbital due to electron. withdrawing properties of carboxylate¹³³⁰BOTH The hybrid catalysts are capable of adsorbing visible light up to 600 nm. The corresponding band gap energy shifted from 3.2 eV to 2.5 eV as obtained from Kubelka–Munk (K-M method) equation (Fig 1, inset).³⁴ Furthermore, Similar effect observed in the fluorescence spectra of the complex [RuL2NO] which is slightly red-shifted on contrary to RuL1OH (Fig.S11[†]). Besides, the presences of benzimidazole free proton in complexes and acid proton that could show flexible properties with respect to the pH of medium under investigation. Hence, we restricted our photocatalytic studies at a neutral aqueous medium. Metal complex Immobilized TiO₂ nanoparticle can be preferably photoexcited under the irradiation of a wavelength greater than 400 nm. Both the complexes are presented MLCT transition band over TiO₂ surface. However, despite the several reports the stability and accountability of NO2 over the TiO₂ surface have not been fully understood in reaction medium.^{27, 28} The various binding mechanism of -COOH group over the TiO₂ surface was proposed previously.³⁵ The room temperature photoluminescence spectrum of nanocrystalline TiO₂ and hybrid catalyst are shown in Fig. S13b⁺. The TiO₂ photoluminescence exhibits Fabry-Perot fringes due to interference between backscattered and forward-scattered PL light. The emission wavelength of TiO₂ is almost 535 nm which reflects partial oxygen vacancy.³⁶ Moreover, after immobilization an additional emission intensity was observed to red region (630 nm) in hybrid due to the intact ruthenium complexes. In addition, Ruthenium complex is well known for its variable oxidation state (Ru²⁺/Ru³⁺). Hence, the electrochemical properties of the complexes and hybrid catalysts were examined in purified acetonitrile by cyclic voltammetry (CV). The typical CV scan of the metal complexes revealed quasi reversible nature with distinct anodic (oxidation) and cathodic (reduction) peak (Fig.S14[†]). The results are depicted in Table 1. A positive potential, vs. Ag/AgCl, RuL1OH shows couple (Ru^{3+}/Ru^{2+}) at 1.01 V with a peak separation of 70 mV. However, the classical [Ru(bpy)₃]²⁺ couple (Ru³⁺/Ru²⁺) was reported vs. Ag/AgCl as 1.25 V.³⁷ On contrary to [Ru(bpy)₃]²⁺ nearly 0.24 V less positive potential was observed for RuL1OH, suggesting that L1 is moderately donor than 2,2'bipyridine (bpy) ligand.

Table 1 Electrochemical data and respective energy.								
Samplo	ae . ox [\/]	ac red [\/]			د [۵۷]	dE [1/]	ee [\/]	
Sample	L _{1/2} [V]	$E_{1/2}$ [V]			E ⁰⁻⁰ [ev]	L _{red} [V]	E _{ox} [V]	
RuL1OH	1.01	-1.26	-5.43	-3.16	2.10	0.84	-1.09	
RuL2N	0.97	-1.31	-5.39	-3.11	1.99	0.68	-1.02	
Ru[(bpy) ₃] ²⁺	1.25	-1.34	-5.67	-3.08	2.14 ^g	0.80	-0.89	

 ${}^{a}E_{pa}$ = anodic peak potential, E_{pc} = cathodic peak potential, and $E_{1/2}$ = (E_{pc} + E_{pa})/2 versus AgCl. ^cHOMO and LUMO levels were determined using equations^f: E_{HOMO} (eV) = -e($E_{1/2}^{cx}$ + 4.42), and E_{LUMO} (eV) = -e($E_{1/2}^{red}$ + 4.42). ^c E_{0-0} from the fluorescence data. ^dExcited-state reduction potential estimated using E_{red}^* = $E_{1/2}^{red}$ + E_{0-0} . ^eExcited-state oxidation potential estimated using E_{ox}^* = $E_{1/2}^{cx}$ - E_{0-0} . ^gReference 37.

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Fig. 2 Cyclic voltammogram for hybrid catalyst recorded in MeCN 0.2 mM of $\mathsf{TBABF}_{\mathsf{6}}$

Moreover, the hybrid TiO₂ presents the (Ru³⁺/Ru²⁺) couple at 1.12 V with same peak separation. A negative potential reduction peak of the complexes and hybrid catalyst shows at -1.26 V and -0.715 V respectively (Fig. 2). The hybrid catalyst was almost 0.11 V more positive value than RuL1OH strongly suggesting that metal complex immobilized over the TiO₂ surface. Furthermore, the corresponding HOMO and LUMO energy level of complexes and hybrid catalyst were calculated (Table 1). The LUMO energy level (-3.16 V) of the complex is higher than the conduction band of TiO₂ (-4.2 eV vs NHE).³⁵ Therefore, the possibility of photoexcited electron into the conduction band of TiO₂ is thermodynamically more reliable in both complexes even without any applied bias.

To understand the photo efficacy of the prepared hybrid catalysts, photo response was measured by shining light from a xenon lamp (model no. 66902; Newport Corp. USA) over the Indium Tin Oxide (ITO) electrode. The current was measured between two contacts (sandwiched between ITO electrode, 3 mm distance apart) using a Keighley sources meter (Model 2400). Fig. 3a shows the dark-current-voltage (I-V) plot in both positive and negative bias which is almost Ohmic in nature for all the hybrid catalyst. We have identified that hybrid photocatalyst shows law dark current (0.005 nA) at 0.5 V, and reveals a good photocurrent response after illuminations of Xenon light source. It can be noticed that 8 times (0.04 nA) increase in the current was found apparently at the same potential bias. However, the half less than increase current (0.02 nA) was observed for TiO₂/RuL2NO hybrid catalyst. The increase in conductivity is and evidence for the presence of immobilized ruthenium complexes over the TiO₂ surface.



Fig. 3 (a) Dark and photocurrent behaviour of hybrid photocatalysts measured on ITO glass (*I-V* curves). (b) Transient photoresponse of hybrid photocatalyst at on/off condition.

Furthermore, electrochemical impedance spectroscopy (EIS) for the hybrid catalysts (TiO₂/RuL1OH, and TiO₂/RuL2NO) were carried out to investigate the charge transfer efficiency of the hybrid. The impedance was measured with the bias of -0.7 V under dark and light. The Nyquist plots are shown in Fig. S15⁺. The experimental data are shown with symbols while solid line represents fit obtained using Nova 2.1 software. Nyquist plot showed two semicircles. However, such semicircle was not identified in TiO₂/RuL1OH hybrid. In the dark both the hybrid presented high impedance may be related to large resistance for TiO₂. However, in light the impedance has been significantly reduced. The electron lifetime (τ_n) was calculated to investigate the backward electron transfer from TiO_2 conduction band to electrolyte.38 The values were 28.94 and 25.23 ms for RuL1OH and RuL2NO, respectively. The higher τ_n manifests low recombination at the electrolyte interface.39

FTIR and Surface morphology studies

Furthermore, ATR-FTIR of the pure metal complexes shows the major IR characteristic peak at 1704 cm⁻¹ for C=O stretching mode whereas 1624 cm⁻¹ and 1380 cm⁻¹, indicate asymmetric and symmetric vibrations of -COO⁻ group.²² The peak at 1406, 1431, 1550 cm⁻¹ is signature of bipyridyl ligand vibration. Hence, FTIR spectra indicated the successful binding of complex over the TiO₂ surface with bidentate covalent attachment mode (Fig. 4a). To further confirm the complexes over the TiO₂ surface the Raman scattering spectra were recorded at excitations wavelength 514 nm. Spectra exhibits the Raman active mode for TiO₂ 140 cm⁻¹ (E_g), 397 cm⁻¹ (B_{1g}), 515 cm⁻¹ (A_{1g}), and 640 cm⁻¹ (Eg) respectively (Fig. 4b). All these lines are characteristic of anatase TiO₂ nanoparticles.⁴⁰ The band at 640 cm⁻¹ is due to symmetric Ti-O vibrations form A_{1g} symmetric modes, whereas as other two bands (397 cm⁻¹, 515 cm⁻¹) corresponds to the degenerates modes of TiO₆ octahedra.⁴¹ Moreover, at higher wavenumber in the ranges of 1000-2200 cm⁻¹ the characteristic weak line of ruthenium metal complexes appears in hybrid TiO₂ (Fig. S16d⁺). The shoulder peak appears in the range of 1250-1360 due to C-C ring and C-O stretching modes whereas 1380 cm⁻¹ reveals for symmetric COO⁻ stretching.⁴² The fact that no sign of C=O vibrations is visible. However, the presence of COOstrongly suggests the coordination of metal complex over the TiO₂ nanoparticles via bidentate bridging. It is worthwhile noticing that the relative Raman intensity got increased after adsorption of complexes.43 However, there is no change in energy was observed for RuL1OH (Fig S16b[†]). In addition, the wavenumber of hybrid (RuL2NO) slightly shifted towards lower region whereas Raman intensity remains almost constant (Fig S16c[†]).

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The full widths at half-maximum (FMWH) were calculated with respect to E_g (140) phonon mode (table S2⁺). The hybrid (TiO₂/RuL2NO) shows significant change in FWHM as compare to pure TiO₂. This change is due to phonon confinement effect.⁴⁴ The surface morphology of the hybrid was obtained by using the field emission scanning electron microscope (FESEM) and high-resolution transmission electron microscope (HRTEM) as shown in Fig. S17⁺. The SEM images of the hybrid show spherical particles with average diameter of 75 nm (Fig.S17c†). TEM analysis of the hybrid provides the details views of surface morphology which further confirm 75 nm spherical particles size. It is important to note that there are no changes in morphology of the particles perceived with the attached metal complex. HRTEM lattice image gives the 0.35 nm d spacing which corresponds to thermodynamically stable 101 facets of anatase TiO₂ nanoparticles.⁴⁵ In addition HRTEM images of pure TiO₂ and immobilised TiO₂ hybrid (TiO₂/RuL1OH) were compared as shown in Fig.5a-d. The lattice fringes and SEAD pattern confirm the particles are highly crystalline as synthesized. The HRTEM image of pure TiO₂ shows clear fringes pattern and there is no trace of core (amorphous) was found on contrary to complex (RuL1OH) immobilized TiO₂ (Fig. 5c). Lattice fringes of TiO₂/RuL1OH demonstrate a thin core layer where the fringes are not crystalline this indicates that presence of metal complex (RuL1OH) over surface, and amorphous nature is due to ligand (Fig.5d). In addition, the amorphous core is not visible for TiO₂/RuL2NO complex. RuL2NO contains NO₂ functional group that lead to weak interaction through TiO₂. Therefore, it can be anticipated that metal complex has been successfully incorporated on oxide surface. The active functional group (-COOH) capable of covalent interaction over the TiO₂ surface whereas NO₂ prefer non-covalent interaction (electrostatic). Moreover, for further confirmation of the elemental compositions of the particles, we have performed STEM-EDS elemental mapping. Fig. 5e-m shows the TEM images of individual hybrid TiO₂ NPs and a corresponding STEM mapping of different elements that are present in the sample. The mapping nicely executes element present and their uniform distribution in the hybrid TiO₂ NPs. We can quickly identify the ruthenium metal, carbon, and more importantly nitrogen coming from the ligands (EDX, Fig. S36†). In addition, the pure ${\rm TiO_2}$ STEM-EDS elemental mapping has been compared as shown in Fig.5e-g. Hence, evidence from the result,

suggested that the metal complex uniformly binds to the surface of anatase TiO_2 NPs. DOI: 10.1039/C9GC03549D





Surface Composition, Chemical State, and Surface area

Understanding the chemical state of the element presents in the sample, the X-Ray photoelectron spectroscopy (XPS) has been carried out at room temperature. The typical XPS spectra of the hybrid are shown in Fig. S34[†]. The doublet binding energy peaks (458.2 eV and 464.3 eV) for Ti⁴⁺ (2p_{3/2}) and Ti⁴⁺ (2p_{1/2}) are agreement with the TiO₂ nanoparticles.⁴⁶ Fig. 6 shows the deconvoluted XPS of hybrid for elements present. The binding energy peak at 530.5 eV and 531.6 eV are attributed to O⁻ and Ti-OH from TiO₂ surface. However, a peak at 531.6 eV has also some contributions for C=O

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group of the metal complex. Furthermore, C1s show the two characteristic peaks of binding energy at 284 eV and 285.8 eV respectively. The former is designated for pyridine, whereas later peak is contributed by C=O, C-C, and C-O groups. Small peaks at approximately 280.3 eV demonstrate the presence of Ru²⁺ species (Ru3d_{3/2}).⁴⁷ Moreover, it should be noted that there is a substantial overlap between C1s and Ru3d_{3/2} binding energy; hence it is not well resolved.



Furthermore, in a heterogeneous system, all the reactions will take place over the surface when we deal with the solid powder catalyst. Therefore, this is a considerable interest to explore the surface area with adsorption and desorption properties of the catalyst under investigations. Based on the N₂-adsorption isotherm the TiO₂ particles and their hybrid (TiO₂/RuL1OH, TiO₂/RuL2NO) show (Brunauer–Emmett–Teller) BET surface area at 25 m²/g (TiO₂), 63.8 m²/g (TiO₂/RuL1OH), and 52 m²/g (TiO₂/RuL2NO) respectively. The increased surface area of the material is possibly due to attached ruthenium metal complex. The amine functional group have widely been used for CO₂ trap in industries due to formation of carbamate later gives carbonate upon hydrolysis.



Fig. 7 (a) CO_2 adsorption isotherm of TiO_2 and hybrid photocatalyst measured at 298 K. (b) Powder XRD pattern of TiO_2 , simulated and hybrid photocatalyst (TiO2/RuL1OH).

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Besides, some efforts have been made to introduce aminefunctionalized solid-materials to enhance16023adsorption948 As conspicuous from FTIR and Raman spectra, the metal complexes are covalently attached over the surface. Hence, advantage of this metal complex has free NH group which may promote CO₂ adsorption on catalyst surface. These finding motivated us, to perform CO₂ adsorption experiment at 298.0 K. The results showed nearly 4.5 times higher (17.23 cm3/g) uptake of CO_2 than pure TiO2 (3.32 cm3/g). Interestingly, at low CO₂ pressure, the TiO₂/RuL1OH increased stiffly, whereas TiO₂ and TiO₂/RuL2N showed linear adsorption as depicted in Fig. 7a. Furthermore, the crystallographic structure information of TiO₂ and hybrid was obtained by XRD. All these characteristic peaks matched with the standard anatase TiO₂ Pattern (JCPDS File Card No. 21-1272). The crystallinity of the TiO₂ remains intact after immobilization result no change in 20 values. However, the intensity got increased in case of hybrid photocatalyst.

Photocatalytic activity

There are enormous efforts have been attempted by utilising ruthenium metal complex sensitised nanoparticles, pd-doped TiO₂, and ruthenium doped TiO₂. We found that the reduced product of CO₂ specially depends on supplied environments (solvents, pH), experimental condition and loading amount of noble metals (Table S3⁺). The synthesized hybrid catalyst was employed for CO₂ reduction $(\lambda > 420 \text{ nm}, 250 \text{ W lamp})$ in aqueous medium at pH 7. For a typical run, a powder of hybrid catalyst (RuL1OH, 1 g/L) was dispersed thoroughly in aqueous medium (10 ml), and 0.8 mM of triethanoloamine was added. The solution was allowed for visible light irradiations ($\lambda > 420$ nm) under CO₂ atmosphere. The temperature was maintained at 25 °C through water circulation in glass jacket reactor. After 5 h continuous irradiation the liquid sample was analysed by UV-Vis spectroscopy. The spectra show the significant transitions at almost 286 nm which is characteristic of carbonyl group (C=O, n to π^*) transition (Fig.S19b⁺). Therefore, liquid product was analyzed in HPLC by using the different standards such as HCOOH, HCHO, and CH₃OH. The major product was identified as formaldehyde.





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However, there was no additional peak observed for formate and methanol. We further extended the analysis to determine any gaseous products formed using gas analyzer (Thermo Fisher Scientific GC-Trace 1110) equipped with FID detector.

The result shows CO and CH₄ were produced (trace amount) with a turnover number (TON) 17 µmol (136), and 8 µmol respectively (Fig. 8). Hence, we continued (64) formaldehyde as a standard for quantitative analysis of reduced products. Firstly, known concentrations of formaldehyde were prepared in deionized water49 and calibrated with HPLC. The linear regression line was obtained R² (0.997 %) close to unity. Fig. 9a shows the HPLC chromatograms of reaction mixture which had been taken at different interval of time after irradiations. The product (HCHO) was quantitated by following reported method.⁵⁰ The reaction product yield 90 µmol of a catalyst with TON (720) was estimated which is very significant in terms of selectivity for CO₂ reduction. In additions, the conventional method is used to detect the formaldehyde by using 2,4dinitrophenylhydrazine (DNPH) which gives 2.4dinitrophenylhydrazone after reaction with formaldehyde.⁵¹ Fig. 9b presents the HPLC of DNPH and formaldehyde. These results further confirmed the CO2 reduced product in our experimental condition.



Fig. 9 (a) HPLC chromatogram kinetics of reaction mixture measures H_2O : CH₃CN (60:40), and (b) 2,4 DNPH treated reaction mixture.

Moreover, the same experiment was repeated with the hybrid catalyst (RuL2NO, 1 g/L) at the aforementioned conditions. Surprisingly, we found a few products with the hybrid catalyst (RuL2NO, 1.0 g/L). We end up with the mixture of products (HCHO, CO, CH₄) under the identical condition which is difficult to quantify. The stability of the metal complex over the surface is less due to electrostatic interaction with NO₂ group. Consequently, an MLCT transition band can be perceived in liquid reaction mixture after catalysis. The result suggesting that NO₂ groups are not adequate for the sensitization process hence, the efficiency of catalyst in visible light is less. In order to understand the photo-assisted reduced product selectivity as well as to identify the origin of formaldehyde, we performed in situ reaction with amine. Sabo-Etienne et al. has first demonstrated the borane reduction CO₂ catalyzed by polyhydride ruthenium complex to formaldehyde and trapped in situ condition by aromatic amine.¹⁹ This method is fascinating to provide reliable information about the

reduced C₁ building block. Fundamentally this <u>weatcheore</u> known as Mannich reaction. Generally <u>coordensation</u> and <u>a</u> amine with aldehyde is indeed common technique to generate the imine.⁵² The formaldehyde and aniline reaction in acidic medium has been reported in the literature and essential for industrial application.⁵³ Therefore, two primary amines (aniline and 4-aminobenzoic acid) were used in our system for *in situ* photocatalytic processes. The idea of taking 4-aminobenzoic acid is could provide the conceptual mechanistic insight into catalytic system.

Table 2 Photocatalytic reaction for 8 h using hybrid catalyst under CO2 atmosphere ^a
and <i>in situ</i> reaction with amine ^b

		Product/µmol (TON)					
Entry	Photocatalyst	НСНО	со	CH ₄	Con		
1	, TiO₂/RuL1OH	90(720)	17 (136)	8 (64)	(%) 65		
2	TiO ₂ /RuL2NO	0.8(12)	< 0.2	N.D	28		
3	TiO ₂ /Ru(bpy) ₃	N.D	N.D.	N.D.	N.D		
4	TiO ₂ /RuN179	80 (N.D) ^R	N.D	N.D	N.C		

^aConditions: hybrid photocatalyst 1 g/L in aqueous solution, 0.8 mmol of TEOA, CO₂ pressure, visible light irradiation (λ > 420 nm), ^bDetermined by GC using bromobenzene as an internal standard. Aniline and 4-aminobenzoic acid were taken as amine sources. R = Reference 23.

After 8 h irradiation (λ > 420 nm) of reaction in H₂O with (0.05 mmol) distilled aniline GC-MS spectra were analyzed (Fig. S20-S24[†]). Interestingly, we identified a 4-(4aminobenzyl) aniline with m/z (198) and methylene-aniline (Intermediate) as new species. Furthermore, respective conversion (%) and selectivity were determined by using bromobenzene as internal standard in GCMS. Similarly, the possible identified intermediate for 4-aminobenzoic acid is shown in Fig. S25-S27[†]. Our studies categorically provide the stepwise reaction of CO₂ reduced product and insights direct observation of formaldehyde in a visible light assisted heterogeneous catalytic system. Furthermore, for the efficacy of electron transfer mechanism in catalytic process, we were intrigued by the idea of paraquat (Methyl viologen, MV2+) one-electron reduction process. The MV2+ is employed as suitable electron acceptor as well as pHindependent reversible redox potential (0.45 V vs NHE).54 Furthermore, it can be readily identified (MV^{+.}) by their unique characteristic blue color upon anaerobic irradiation to light in the presence of a suitable catalyst or donor (EDTA, Cl⁻, etc). However, upon aerobic exposure, the it forms MV^{+.} which gives green fluorescence by formation of 1',2'-dihydro-1,1-dimethyl-2'-oxo-4,4-bipyridylium cation.55, ⁵⁶ In general, the freshly prepared aqueous solution of MV²⁺ is not fluorescence in aqueous medium. Hence, we preferred to investigate the electron transfer process by using MV^{2+} . The freshly prepared solution in D_2O of MV^{2+} was irradiated under the visible light (aerobic condition) in the presence of catalyst without allowing any donor. ¹HNMR were recorded systematically concerning time. The kinetic of MV²⁺ after irradiation is shown in Fig.10. We found that the chemical shift is deshielded at around 0.016

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ppm in 180 min. The deshielding is attributed to increases electron densities at carbon center. In addition, the UV-Vis spectra show bathochromic shift after catalysis and emit at around 528 nm (Fig. S18†). The characteristic emission of green fluorescence in D₂O at $\lambda \leq 365$ nm is shown in Fig. 10. We further confirmed the products in LC-MS (Fig. S28-S29†). The results strongly support the efficiency of catalyst performance in aqueous medium.



Fig. 10 1 H NMR kinetic of MV²⁺ in D₂O measures after visible light catalysis in the absence of donor (TEOA).

Moreover, to further confirm the existence of Ti³⁺, low temperature EPR spectra of TiO₂ and hybrids (TiO₂/RuL1OH, TiO₂/RuL2NO) were recorded at 100 K. The solid samples were irradiated in in visible light ($\lambda > 420$ nm) for 2 h. Fig. 11 significantly showed the EPR signal of Ti³⁺ (paramagnetic), while pure TiO₂ is inactive. The observed g value (1.953, 1.968) was calculated which corresponds to paramagnetic Ti³⁺ center.



Fig. 11 (a) EPR spectra of TiO_2 , $TiO_2/RuL1OH$. (b) $TiO_2/RuL2NO$. All measurements were carried out at 100K after visible light illumination (2 h).

Surprisingly, we have noticed one additional peak having gvalue is close to 2.0 appears for hybrid TiO₂/RuL1OH. The origin of this peak is due to ruthenium metal complex which was generated during photo excitation in visible light.⁵⁷ The Ti³⁺ has also been observed for hybrid (TiO₂/RuL2NO). However, there is no ruthenium signal was identified perhaps due to low concentration. In addition, the intensity was relatively lower in both the sample analysis. Characteristic EPR signals of TiO₂ and hybrids attributed to Ti^{3+} ions in the g < 2 were observed on anatase TiO_2 after excitation of solid in visible light.5% The results strongly corroborate the activity of catalyst in visible light. The process of CO₂ reduction mechanism in the aqueous medium has been proposed previously.59, 60 Therefore, based on data obtained by performing CO₂ reduction with hybrid catalyst in heterogeneous medium, we introduced the mechanism for catalytic process in our experimental condition (Scheme 3). First, surfaced ruthenium complex was excited in visible light and transfer an electron to the conduction band of TiO₂. TiO₂ nanoparticles are capable of adsorbing CO₂ on the surface and activated through conduction band electrons. The sources of H⁺ occurred from water in our system. Initially formic acid was formed. However, the formic acid was converted to formaldehyde after 5 h continuous CO₂ pressure and irradiation. The concentration of formic acid was decreased for time and applied CO₂ pressure as a result, not detectable by analytical technique. Besides, amine (aniline) was reacted with formaldehyde to form N-hydroxymethyl aniline activated by H⁺ which is coming from water splitting at initial stage. Additionally, this attained equilibrium with Nmethylideneanilinium (1).



Scheme 3 Proposed mechanism of reaction based on identified compounds in GCMS.

Finally, it gives the N-(p-aminobenzyl) aniline (2) after reaction with aniline. Interestingly, we have recognized a defined m/z (107.02) for 4-aminobenzylium ion. This is the crucial step for the formation of 4,4'-methylene diphenyldiamine after rearrangement and industrially important reaction.⁶¹ Our results are evident to support for direct capturing of formaldehyde from CO_2 reduction.

Moreover, the control experiments were repeated by adapting the same procedure (I) in the dark, (II) nitrogen atmosphere, and (III) blank (without catalyst). None of three conditions gained a single species of CO_2 reduced products in both UV-Vis and HPLC characterization. Again

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the reaction was analyzed in acetonitrile provided the identical conditions. Fig. 12 shows ATR-FTIR kinetics of reaction mixture after irradiation. The donor is completely consumed suggesting the potential activation of catalyst under visible light. The hybrid catalysts (TiO₂/RuL1OH, TiO₂/RuL2NO were isolated after catalysis and characterized by DRS. The DRS spectra show the significant MLCT transition for ruthenium complex (RuL1OH). The blank reaction (without CO2, catalyst) was performed to further conformed the stability of metal complex in course of catalytic process. Catalyst (1 g/L) in CH₃OH solvents was irradiated (λ > 420 nm). Aliquot did not show signatures of complexes apparently in FTIR spectra. However, solid catalyst showed significant stretching frequency of metal complex.



Furthermore, the recyclability experiments of catalytic reaction were carried out upto eight cycles (Fig.13b). After each cycle, the catalyst was washed with H_2O and then reused. We notice that even after fifth subsequent catalytic cycle, the yield of formaldehyde remains almost the same. A slight decrease of product (10-15%) occurred after sixth cycle, it could be due to very minor loss of catalyst (fine particle) during the washing and recycling steps. The metal complex can also be reduced over the TiO₂ surface after repeated treatment (long run, say after eighth recycle) as observed from DRS spectra (Fig S33⁺). The recyclability test confirmed that metal complex is robust, stable and capable of used for several catalytic cycles without significant loss of their catalytic activity. The post characterization of catalyst was analysed after the dried. XPS survey revealed the presence of ruthenium over the TiO₂ surface (Fig.S35⁺). Furthermore, the turnover number of each product vs irradiation time was plotted (Fig.13a). We observed the formaldehyde formation increases with respect to time. In addition, further experiments were carried out in an aqueous medium to understand the role of the ruthenium metal complex alone. We have systematically investigated



Fig. 13. (a) The time courses of HCHO, CO, and CHQIfdGMiltGMiGQGSMDEHght irradiation ($\lambda > 420$ nm) under CO₂ atmosphere. (b) Recyclability of hybrid catalyst TiO₂/RuL1OH for HCHO formation in aqueous medium.

the reaction by using different concentration (5-10 mmol) of the ruthenium metal complex. We found that the formaldehyde formation was not reliable after 10-15 h irradiation. However, the usage of 10 mmol of RuL1OH, we end up with 15 μ M of formaldehyde (in 20 h). Furthermore, we had tried to capture formaldehyde (in situ) using the aniline and 4-aminobenzoic acid. The 4-aminobenzoic acid solid products were isolated after the reaction. We identified that a new C-H stretching frequency appeared around 2900-3000 cm⁻¹. Moreover, the characteristic of N-H for IR absorption frequency decreases relatively (Fig S30[†]). The liquid aniline was difficult to isolate from a homogeneous medium. However, we performed the preparatory TLC in a mixture of DCM (2%) and hexane by adding 0.01% of triethylamine. The LCMS spectra of the samples were recorded and then m/z at 107 were interpreted as shown in Fig. S31[†]. The results suggest that using the 10 mmol of the ruthenium metal complex the conversion of CO₂ to formaldehyde is slow. Furthermore, the *in situ* traps by using the amine are also low almost < 50 % conversion. The RuL1NO had not yielded any products even after 24h irradiation. Moreover, the hybrid catalysts were tested in the acidic medium. The reaction is dominated by hydrogen evolution at pH \leq 5.5. We have further characterized the product in Trace GC-Trace 1110 equipped with FID, TCD2 and TCD3. We identified around 10 μ mol H₂ is produced at per gram of catalyst (Fig. S32⁺). However, we could not get any C₁ reduced product in the liquid reaction mixture (in HPLC). Further, the TiO₂/RuL1OH and TiO₂/RuL1NO could not give any product in the basic alkaline medium.

Experiments

Materials and Methods

The entire chemicals were taken by the commercial sources and used without further purification. 2,2-bipyridyl, 1, 10-Phenanthroline (phen), aniline, D₂O, and RuCl₃.xH₂O had purchased from Merck. Aniline was used after distillation. Ammonium acetate, KBr, 4-formylbenzoic acid, and 4-nitro benzaldehyde were taken from Spectrochem. GC grade solvents were used for reactions and HPLC grade solvent was used for HPLC analysis. UV-Vis, DRS, and fluorescence spectra were recorded with Shimadzu (Model UV-2450) spectrophotometer, a Varian Cary 500 UV-vis-NIR (BaSO₄ background) spectrophotometer, and a Hitachi (Model F-7000) spectrofluorimeter, respectively. ¹H and ¹³C (400 MHz) were measured using Bruker Lambda spectrometer in DMSO-d₆, D₂O, and CDCl₃. MALDI-TOF MS Studies were performed by using BrukerUltrafleXtreme instrument in which DHB (2,5-dihydroxy benzoic acid) used as matrix. Solid and liquid sate cyclic voltammetry was studied using a BASi Epsilon electrochemical work station in MeCN and AgCl used as a reference electrode. The XPS spectrum of

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the hybrid photocatalyst, acquired using a PHI 5000 VersaProbe II instrument. The emission profiles of metal complexes were analyzed using the time-correlated singlephoton counting (TCSPC) picosecond spectrophotometer in CH₃CN at pH 7. FT-IR spectra were recorded using Perkin-Elmer Spectrum II. Powder XRD of TiO₂ and hybrid catalyst were obtained using a Bruker Apex-2 X-ray diffractometer with CuK α radiation (λ = 1.5418 Å) and scan rate 0.5 cm. FESEM, HRTEM, and STEM, images of TiO_2 and hybrid catalyst were recorded using a Supra 40 scanning electron microscope (Carl Zeiss Pvt. Ltd), and JEOL JEM2010 transmission electron microscope over carbon-copper grids. Raman spectra of the synthesized sample were measured using a Renishaw Raman microscope equipped with a diode laser excitation source at 532 nm. BET surface area of hybrid catalyst and N_2 sorption isotherms (77 K) were obtained using a QuantachromeAutosorb-iQ instrument. CO2 adsorptions studies were performed at 298 K, and all the samples were degassed for overnight before analysis. EPR experiments were carried out using Bruker ELEXSYS 580 X-band EPR spectrometer at 100K after visible-light irradiation ($\lambda > 420$ nm).

Photocatalytic reaction

A suspension of photocatalyst (1 g/L) in a reaction solution (10 ml H₂O) was taken in a quartz tube (50 ml). The solution was evacuated first, and CO₂ purged continuously. 0.8 mmol of Triethanolamine was added to the mixture. Suspensions were irradiated using 250 W tungsten lamp (λ > 420 nm) combined with $NaNO_2$ aqueous solution filter. The temperature of solution was maintained at 298 ± 3 K through continuous flow of water chiller. Formaldehyde (HCHO) was in the liquid phase was analyzed by UHPLC equipped with diode array detection (Thermo Fisher Dionex UltiMate 3000 SD). Standard formalin solution containing 37 wt% in H₂O (10-15 % MeOH stabilizer) was used. The gaseous reaction products, such as CO and CH4 were analyzed using Thermo Fisher Scientific Trace-GC 1110 equipped with an FID detector (molecular sieve 5Å packed column). For the direct observations of formaldehyde initially 0.05mmol of aniline was introduced to the reaction mixture. In this condition the reaction time was increased 3h (Total 8 h) for reaction between formaldehyde and aniline. The liquid product was directly analyzed in GC-MS (Thermo Scientific Trace 1300 gas chromatography and ISQ Single Quadrupole MS) using FID detector. The same steps were repeated for 4-aminobenzoic acid reaction. We estimated the photocatalytic activity of hybrid catalyst after each photocatalytic reaction using turnover no (TON) and selectivity (equations 1 and 2).

ГОN =	Product (mol)	1	1
	Used metal complexes (mol)	1	

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Selectivity =
$$\frac{CO_2 \text{ reduced product}}{\text{Reduction products Particle Online}}$$
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The experiments were repeated twice to calculate the mol and average TON has been reported.

Conclusions

We have successfully developed an efficient and reliable hybrid photocatalyst for CO₂ reduction in the aqueous medium. Metal complexes are used as sensitizer over the surface of TiO₂ (average size: 70 nm). The NO₂ group is found to be insufficient to provide the electron over the TiO₂ (CB) due to weak interaction. It may bind to the surface employing electrostatic interaction rather than -COOH which is covalently linked. Formaldehyde is a C1 reduced product of CO₂ and challenging to identify in an aqueous medium. We have described the stepwise reduction of CO₂ yielding formaldehyde including CO and CH₄ was minor products. The product is almost 68% selective. We have first time used the aniline to identify the formaldehyde in situ reaction during the heterogeneous photocatalytic process. The mechanistic investigations are well supported through GC-MS, HPLC, Trace GC, and LC-MS. In additions, by using Benzimidazole spacer provided the long-live time of excited-state electron which brings faster and selective reduced products. Moreover, it can also help to adsorb the CO₂ on surface due to free NH group in the ring. The reusability of catalyst (TiO₂/RuL1OH) revealed that it can be used for more than eight cycles effectively without significant loss. This work contributes to the utilization of CO₂ into useful products under the visible light irradiation by a green approach, which will be extended for many future applications.

Conflicts of interest

The authors declare no conflict of interest.

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Outline: CO_2 reduction was carried out in aqueous medium at neutral pH 7.0. We identified the 68 % selective products as formaldehyde after 5 h under visible light ($\lambda > 420$ nm) irradiation. Furthermore, formaldehyde has been used to react with aniline in situ condition under visible light. The source of hydrogen is coming from water, which provided the reliable environment to react with amine. The mechanism of reaction is well investigated and supported by GC-MS., HPLC, and Trace GC with multiple detectors.