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Visible light assisted photocatalytic reduction of CO₂ using a graphene oxide supported heteroleptic ruthenium complex†

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A new heteroleptic ruthenium complex containing 2-thiophenyl benzimidazole ligands was synthesized using a microwave technique and was immobilized to graphene oxide *via* covalent attachment. The synthesized catalyst was used for the photoreduction of carbon dioxide under visible light irradiation without using a sacrificial agent, which gave 2050 μmol g⁻¹ cat methanol after 24 h of irradiation

Finding cleaner energy sources to satisfy the world's growing demand is one of society's foremost challenges for the next half-century. Utilization of solar energy through the generation of hydrogen from water splitting¹ and/or through the photocatalytic reduction of carbon dioxide² to fuels (CO, CH₃OH, and CH₄) has been widely accepted to be a realistic solution to fulfill the energy demands. The subject has been recently reviewed in a number of critical reviews,³ and a significant number of patents⁴⁻⁹ have been granted in last few decades showing considerable progress towards practical utility of photogeneration of hydrogen from water or from fuels, such as carbon monoxide, methanol, and/or methane from the photo-induced reduction of carbon dioxide. Despite various known heterogeneous photocatalysts, such as metal oxides, metal doped oxides, mixed metal oxides and composites,¹⁰⁻¹⁶ transition metal complexes, such as rhenium(i) bipyridine, ruthenium(ii) complexes, cobalt(ii) trisbipyridine, cobalt(iii) macrocycles, metalloporphyrins and nickel tetra-aza macrocycles (cyclams) have also been reported in the literature to carry out the photocatalytic reduction of CO₂ to valuable C1 building blocks.¹⁷ However, the homogeneous nature of these catalysts makes the process unviable from economic as well as environmental viewpoints.¹⁸ This problem can be solved by anchoring such homogeneous complexes to a photoactive support, which provides facile recovery of the catalyst, whereas the photoactive support and complexes may work synergistically to provide better electron transfer to CO₂.¹⁹

Chemically derived graphene oxide (GO), owing to the presence of ample oxygen functionalities and higher surface area, has come out to be an outstanding support matrix for immobilizing homogeneous metal complexes.²⁰ By using graphene oxide as photocatalyst, Hsu *et al.* reported 0.172 μmol g⁻¹ cat h⁻¹ methanol as photoreduction product of carbon dioxide.²¹ The yield can further be increased by anchoring a visible light absorbing molecule to the support of the graphene oxide. Recently, we have reported graphene oxide immobilized cobalt phthalocyanine for the photoreduction of CO₂ under visible light irradiation. The yield of methanol after 48 hours of reaction was found to be 3781.8881 μmol g⁻¹ cat.^{22a} Subsequently, we reported graphene oxide immobilized ruthenium trinuclear complexes for the photoreduction of CO₂, and the yield of methanol after 48 h illumination was found to be 3977.57 ± 5.60 μmol g⁻¹ cat.^{22b} The methanol yield using these immobilized catalysts was found to be much higher as compared to the graphene oxide alone; however, the need of triethylamine as sacrificial donor makes the developed methods less practical in utility. In continuation of our ongoing research, herein, we present a novel approach for synthesizing a heteroleptic ruthenium complex and its immobilization to graphene oxide by covalent bonding. Activation of the synthesized graphene oxide immobilized ruthenium catalyst under visible light in the absence of a sacrificial donor led to the reduction of CO₂ into methanol and afforded methanol in a yield of 2050 μmol g⁻¹ cat after 24 h of irradiation.

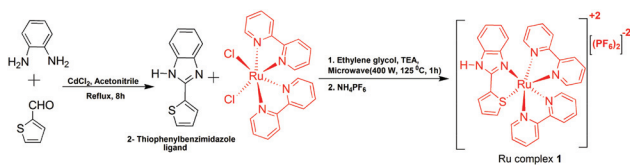
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†Electronic supplementary information (ESI) available: Detailed experimental procedures and characterization of catalyst as well as reaction products are given in ESI. See DOI: 10.1039/c4gc01400f

Synthesis and characterization of the catalyst

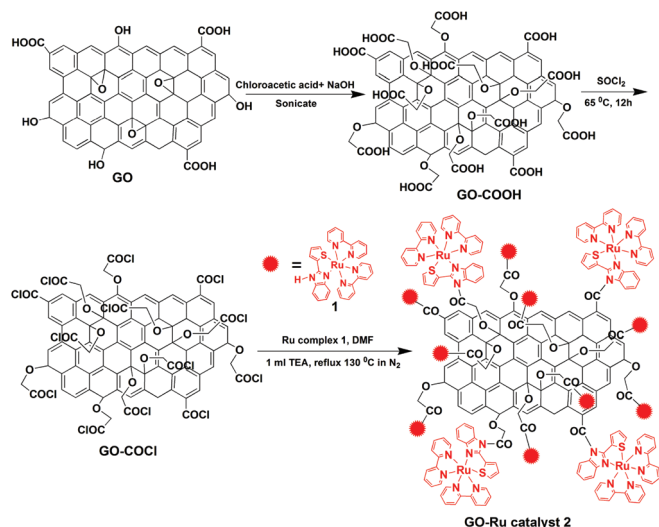
At first, the 2-thiophenyl benzimidazole ligand was synthesized from the reaction of *o*-phenylene diamine and thiophene 2-carboxaldehyde in the presence of cadmium



Scheme 1 Synthesis of 2-thiophenylbenzimidazole ligand and heteroleptic ruthenium(II) complex 1.

chloride.²³ As-prepared sulphur containing ligand was used for the synthesis of corresponding ruthenium complex²⁴ by reacting the ligand with $\text{Ru}(\text{bpy})_2\text{Cl}_2$ under microwave irradiation as shown in Scheme 1. The synthesized homogeneous heteroleptic ruthenium complex was subsequently immobilized to a graphene oxide support *via* covalent attachment. For this purpose, graphene oxide was obtained from the oxidation of graphite with KMnO_4 and H_2SO_4 according to Hummers method.²⁵ Occurrence of many oxygen containing functionalities in the form of free $-\text{OH}$, $-\text{COOH}$ and epoxide groups and a high specific surface area made graphene oxide an ideal material for the grafting of homogeneous complexes. In most of the literature reports, the oxygen containing functional groups presented at the edges of the GO were used for immobilization and therefore a low loading of catalyst was obtained.²⁶ Here, we have also targeted the epoxide groups located on the basal plane of the sheets for the attachment of the metal complex. Thus, we have treated the GO with chloroacetic acid to convert $-\text{OH}$ and epoxide groups to $-\text{COOH}$ groups. The obtained COOH functionalized graphene oxide was readily converted to $-\text{COCl}$ functionalized GO by treating it with thionyl chloride. The obtained chemically functionalized COCl -GO support was treated with ruthenium complex 1 to give the graphene oxide immobilized ruthenium catalyst 2 as shown in Scheme 2.

The loading of the ruthenium complex on the GO support was found to be 0.51 mmol g^{-1} as determined by ICP-AES



Scheme 2 Synthesis of GO-Ru catalyst 2.

analysis. The complete characterization of the catalyst including surface properties, XRD, FTIR, SEM, TEM, UV-Vis and TGA are given in the ESI of the manuscript (see ESI file†).

The photocatalytic activation of CO_2

The photocatalytic activities of the synthesized GO and GO-Ru catalyst 2 were tested for the photoreduction of CO_2 in water and a DMF system saturated with CO_2 without using a sacrificial agent under visible light irradiation. After various periods of irradiation, a $1 \mu\text{l}$ sample was withdrawn and analyzed in a GC/FID equipped with a 30 m long Stabilwax® w/Integra-Guard® column. To maintain the accuracy of measurements, the sample was injected with the help of an autosampler. The peak area was correlated to a standard calibration curve for the quantitative determination of methanol. The methanol yield was used to evaluate the performance of the catalysts as it was the major reduction product. To determine the gaseous products, $20 \mu\text{L}$ of sample was injected in the GC-RGA (TCD-FID). The gas phase analysis did not show the presence of any possible by-product, such as CO , CH_4 *etc.* The absence of peaks in the GC-FID and the GC-MS for any other possible liquid product, and in the GC-RGA (TCD-FID) for any possible gaseous product inferred the high selectivity (catalytic selectivity = 1) of the catalyst 2 for methanol formation. As methanol was the major photoreduction product, its formation rate, R_{MeOH} ($\mu\text{mol g}^{-1} \text{ cat}$), as a function of reaction time was calculated and plotted in Fig. 1. It can be clearly seen that after 24 hours of illumination, the methanol yield for catalyst 2 was found to be $2050 \mu\text{mol g}^{-1} \text{ cat}$ in the absence of a sacrificial agent. However, the use of graphene oxide as a photocatalyst provided only $482 \mu\text{mol g}^{-1} \text{ cat}$ yield of methanol under otherwise identical experimental conditions. The quantum yield (ϕ) for methanol formation was estimated to be 0.180 for GO-Ru catalyst 2 and 0.044 for GO. Further, to evaluate the effect of the ruthenium complex units attached to GO, we conducted CO_2 reduction experiments by using GO-COOH, 5% RuCl_3/GO , and equimolar homogeneous complex 1 as presented in GO-Ru 2. The methanol yield using these catalysts was found to be 320, 739 and $1048 \mu\text{mol g}^{-1} \text{ cat}$, respectively, and the

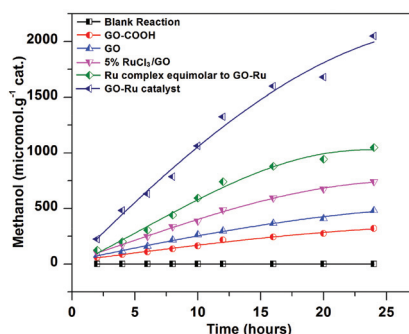


Fig. 1 CO_2 to methanol formation rate (a) blank reaction (b) using GO-COOH (c) GO (d) 5% RuCl_3/GO (e) Ru complex equimolar amount to GO-Ru catalyst 2 and (c) GO-Ru catalyst 2.

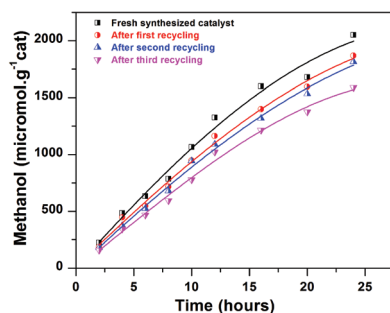


Fig. 2 Reuse experiments for catalyst 2.

corresponding quantum yield (ϕ) was 0.029, 0.067 and 0.09, respectively. These results suggested that the incorporation of ruthenium complex **1** units to the GO sheet enhanced the photocatalytic activity of the GO significantly, which is most likely due to the better inflow of electrons to the conduction band of the GO.

Three blank experiments, *i.e.* (i) visible light irradiation without catalyst **2**; (ii) under dark with catalyst **2**; and (iii) purging with N_2 instead of CO_2 were also performed. There was practically no photoreduction product found in all the above mentioned blank experiments even after a long period of illumination.

After the photocatalytic reaction, the catalyst was easily recovered by centrifugation and reused for recycling experiments. It can be seen from Fig. 2 that the recovered catalyst exhibited almost similar activity for the photoreduction of CO_2 as the fresh one. There was no leaching of metal/ligand observed, which was further ascertained by ICP-AES analysis of recovered catalyst. The recovered catalyst after three runs gave ruthenium content of 5.07%, which was nearly similar to the fresh one (5.15%) considering the experimental error.

Isotopic tracer experiments

To establish the origin of methanol from CO_2 , instead of organic matter presented in the reaction media or catalyst, we performed an isotopic tracer experiment by using $^{13}CO_2$ in place of $^{12}CO_2$ while all other conditions were kept identical. After illumination of the photoreaction mixture, the product was analyzed by GC-MS, giving $^{13}CH_3OH$ at m/z 33 instead of $^{12}CH_3OH$ at m/z 32 (Fig. S19†).

To explain the better photoactivity of the catalyst, optical band gap values were calculated. A Tauc plot of ruthenium complex **1** Fig. 3a gave the optical band gap value of 1.90 eV to 2.29 eV, which was a strong indication of the visible light active nature of complex **1**.²⁷ For GO in Fig. 3b, instead of a sharp optical band gap, a range of a band gap (2.9–3.7 eV) was obtained that was due to the uneven oxidation of the sheets. This value was in good agreement with the reported literature value.^{21,28} While in the case of GO-Ru catalyst **2**, the values of band gaps was found to be 1.15 eV and 2.9 eV, respectively. The value of band gap at 1.15 eV suggested that the attachment

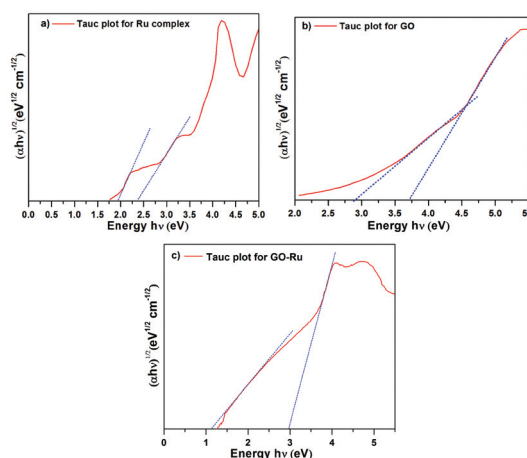


Fig. 3 Tauc plots for calculating band gap of (a) ruthenium complex **1** (b) GO (c) GO-Ru catalyst **2**.

of ruthenium complex **1** to the GO support enhanced the photoactivity of the material significantly. Another band gap value at 2.9 eV, corresponding to the conjugated aromatic ring system, was observed most likely due to the participation of oxygen containing groups in bond formation with Ru complex **1**, and therefore numerous aromatic domains were evolved on the sheets of catalyst **2**.

Further experimental data of cyclic voltammetry gave the difference in the HOMO–LUMO (half wave potential, $E_{1/2}$). The value of 1.915 eV (Fig. 4, Table S1†) was in good agreement with the optical band gap, as determined by Tauc's plot.²⁹ This value was well below the value for better visible light mediated transitions.

Based on the band gap values, a plausible mechanism for the photoreduction of CO_2 to methanol is shown in Scheme 3.

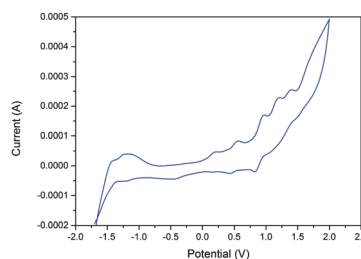
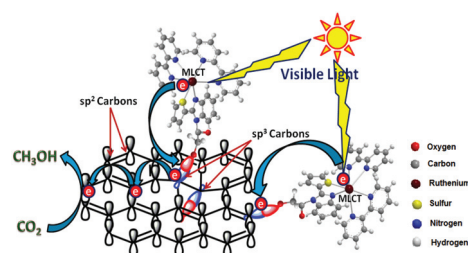
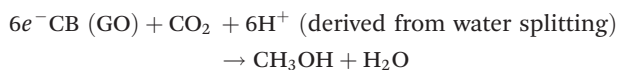
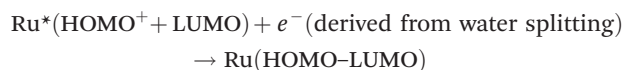
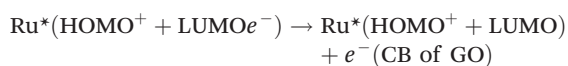
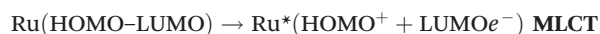


Fig. 4 Cyclic voltammetry curve of homogeneous Ru complex **1**.



Scheme 3 Plausible mechanism of photoreaction.

Oxygen containing functionalities in the GO converts aromatic sp^2 carbon into sp^3 carbons such that a 2D network of sp^2 and sp^3 domain is created on the GO's surface. Aromatic sp^2 hybridized carbon containing domains behave like conduction bands from which electrons can freely move with minimum resistance. Sp^3 carbon containing domains have tightly held electrons and behave as valence band. Thus, a number of semiconductor zones evolve on the surface of the graphene oxide.³⁰ As shown in the Tauc plot of GO, the large band gap prevents the transition of electrons from the valence band to the conduction band in visible light. Because of the small difference in the HOMO–LUMO, the synthesized ruthenium complex can absorb strongly in visible region. Thus, it can easily get excited after absorbing visible light and transfer electrons to the conduction band of GO. Finally, these electrons are used for the reduction of CO_2 adsorbed on the surface of GO to methanol.^{22,31}



Conclusions

We have successfully developed and demonstrated a novel heteroleptic ruthenium(II) complex immobilized to graphene oxide as an efficient heterogeneous photocatalyst for the photocatalytic reduction of CO_2 to methanol without using a sacrificial agent and under visible light irradiation. After the photoreduction, the catalyst was easily recovered by centrifugation and reused for subsequent runs. The recovered catalyst showed almost similar activity and provided similar yield of methanol in all cases, which is a significant finding considering that immobilization of such photoactive complexes on a suitable support is one of the major challenges for their practical exploitation. Importantly, the developed catalyst also does not require any sacrificial agent for the photoreduction of CO_2 , which makes the developed protocol more promising from both environmental and industrial viewpoints.

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