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Metal-organic hybrid: Photoreduction of CO_2 using graphitic carbon nitride supported heteroleptic iridium complex under visible light irradiation

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ABSTRACT

A novel heteroleptic iridium complex supported on graphitic carbon nitride was synthesized and used for photoreduction of carbon dioxide under visible light irradiation. The methanol yield obtained after 24 h irradiation was 9934 μmol g^{-1}cat (TON 1241 with respect to Ir) by using triethylamine (TEA) as a sacrificial donor, which was significantly higher as compared to the semiconductor carbon nitride 145 μmol g^{-1}cat under identical conditions. The presence of triethylamine was found to be vital for the higher methanol yield. After the reaction, the photocatalyst could easily be recovered and reused for subsequent six runs without significant loss in photo activity.

1. Introduction

Photoreduction of carbon dioxide to energy rich chemicals using solar energy is an area of tremendous importance in view of providing alternative energy source as well as to mitigate concentration of CO_2 in atmosphere [1,2]. Photocatalytic CO_2 reduction using a semiconductor based photocatalyst under mild reaction conditions has been appeared to be a potential approach for CO_2 conversion due to its simplicity and potential scalability for practical applications [3]. However, most of the semiconductors requires ultra-violet light due to large band gap and provide poor efficiency and conversion to the desired product. For the efficient utilization of solar light which comprises 5% UV and 45% visible light, a photocatalyst that is able to harvest visible light is desired [4,5]. Due to large band gap, most of the semiconductor photocatalysis suffers from the drawback of poor visible light absorption and faster electron-hole recombination which resulted to the poor conversion efficiency and selectivity [6]. Unlike to these semiconductor photocatalysts, molecular complexes of transition metals such as Ir, Ru(II) or Re(II) bipyridyl complexes possess good visible light absorbance and long lived excited states; hence they provide better electron transfer which resulted to the more efficient reduction of CO_2 [7–9]. In addition, in metal complexes, metal centre can bind with CO_2, which in turn provide higher CO_2 concentration and higher conversion efficiency [10,11].

Despite of several advantages, molecular complexes suffer from the inherent disadvantages of homogeneous catalysis of difficult recovery and non-recyclability. Thus, combining a visible light responsive semiconductor with molecular photocatalyst to make the system heterogeneous seems to be a straight forward approach for carrying out the CO_2 reduction. In this regard, recently our group has developed a number of CO_2 reduction systems by using organic semiconductors such as graphene oxide/reduced graphene oxide in combination of transition metal complexes for carrying out CO_2 reduction under visible light irradiation [12–15]. A significant improvement due to the better charge separation efficiency was observed in hybrid photocatalysts and they provided higher conversion/yield of methanol than the individual components with the added benefits of facile recovery and recyclability for several runs

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with nearly consistent activity.

Recently, nanoporous graphitic carbon nitride (npg-C_3N_4) an organic semiconductor owing to its easy accessibility from low cost raw materials, higher stability and visible light responsiveness, has been extensively used for various applications including as electrochemical electrode, photocatalyst and gas sensors [16,17]. It contains sp^2 hybridized carbon and nitrogen atoms-forming conjugated graphitic planes and exhibit higher photoconductivity, better separation and transport of photo-induced carriers [18]. In the recent years a number of photocatalysts has been developed by combining the semiconductors with npg-C_3N_4 for various applications such as dye degradation, hydrogen evolution and waste water treatment [19]. However, the use of npg-C_3N_4 as metal free semiconductor [20,21] for photocatalytic reduction of CO_2 is relatively less explored. In this regard, recently, Kuriki et al. reported a Z-scheme photocatalytic system comprising of npg-C_3N_4 and ruthenium (II) binuclear complex for the conversion of CO_2 to formic acid with higher TON (33,000) and selectivity (87–99% for formic acid) under visible light [3].

In the present work, we describe an efficient metal-organic hybrid photocatalyst i.e. nanoporous graphitic carbon nitride (npg-C_3N_4) grafted iridium heteroleptic complex (npg-C_3N_4/Ir-T) [22,23] for photoreduction of CO_2 to give methanol selectively in significantly higher yield (9.93 mmol g^{-1} cat) by using triethylamine (TEA) as a sacrificial donor under visible light irradiation (Scheme 1). This value is much greater than those reported for molecular complexes, semiconductors and semiconductor-metal complex hybrid photocatalysts for CO_2 reduction. Furthermore, formation of methanol as selective product is beneficial as it is useful liquid fuel which contains higher energy density and can be transport easily [24].

2. Experimental

2.1. Materials

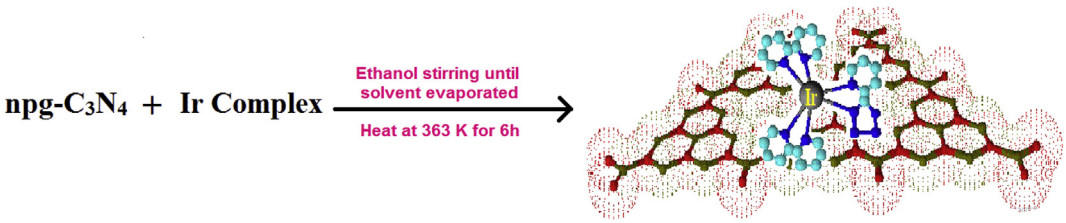
2,2′-Bipyridine (99%), dicyandiamide (99%), thiourea (≥99%), sodium azide (≥99.99%), iridium chloride hydrate (99.8%), copper (II) sulfate pentahydrate (98%) and 2-cyanopyridine purchased from Sigma-Aldrich were of analytical grade and used without further purification. Solvents like dimethylsulfoxide (DMSO), ethanol, chloroform, hydrogen peroxide (30%) and water were of HPLC grade and procured from Alfa Aesar. All other chemicals were of analytical grade and used without further purification.

2.2. Techniques used

The surface morphology of the synthesized material was determined with the help of field emission scanning electron microscopy (FE-SEM) by using Jeol Model JSM-6340F. Ultrafine structure of material was determined by high resolution transmission electron microscopy (HR-TEM) using FEI-TecnaiG^2 Twin TEM operating at an acceleration voltage of 200 kV. Dilute aqueous suspension of material was deposited on carbon coated copper grid for the preparation of sample. FTIR spectra of the compounds were collected on Perkin–Elmer spectrum RX-1 IR spectrophotometer containing potassium bromide window. X-ray diffraction pattern for determining the phase purity and crystallinity of the material was carried out at Bruker D8 Advance diffractometer at 40 kV and 40 mA with Cu Kα radiation (λ = 0.15418 nm). Sample for XRD was prepared on glass slide by adding well dispersed catalyst in slot and drying properly. Absorption spectra of iridium complex in acetonitrile and solid UV of oxidized carbon nitride supported iridium complex was collected on Perkin Elmer lambda-19 UV-VIS-NIR spectrophotometer using a 10 mm quartz cell, using $BaSO_4$ as reference. The Surface properties like BET surface area (S_{BET}), BJH porosity, mean pore diameter of samples were examined by N_2 adsorption-desorption isotherm at 77 K by using VP; Micromeritics ASAP2010. Thermogravimetric analyses (TGA) of Ir complex and C_3N_4 grafted Ir complex for comparing the thermal stability was carried out using a thermal analyzer TA-SDT Q-600. Analysis was carried out in the temperature range of 40–800 °C under nitrogen flow with heating rate 10 °C min^{-1}. Iridium content of catalyst was determined by ICP-AES analysis which was carried out through inductively coupled plasma atomic emission spectrometer (ICP-AES, DRE, PS-3000UV, Leeman Labs Inc, USA). Sample for ICP-AES were made by digesting a particular amount of sample with nitric acid followed by filtration and dilution it up to 10 ml volume by adding distilled water. ESI-High Resolution Mass spectra of iridium complex was performed on (Thermo Exactive Orbitrap system in HESI mode). Electrochemical studies were performed by using an Electrochemical Workstation Bioanalytical Systems (BASi) Epsilon potentiostat and three-electrode, single chamber cell. Solutions were made in 0.1 M tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6) in spectrophotometric grade acetonitrile (Himedia). The working electrode was a Pt disk, the auxiliary electrode was a glassy carbon Pt wire and potentials were measured against either a Ag/AgCl (3 M NaCl) reference electrode or Ag wire quasi-reference electrode (QRE), each calibrated against a $FeCp_2^{0/+}$ internal standard (0.46 V vs Ag/AgCl). The scan rate was 100 Mv/s and the initial concentration of analyte was changed 50 mg to 200 mg for getting better response.

2.3. Synthesis of 2-(1H-tetrazol-5-yl)pyridine ligand [22]

In a typical synthesis, sodium azide (0.0650 g, 1 mmol) and 2-cyanopyridine (0.104 g, 1 mmol) were refluxed in DMSO (2 ml) at 140 °C for 3 h in the presence of copper (II) sulfate pentahydrate (0.0050 g, 2 mol%) as catalyst. The progress of the reaction was checked with TLC. After completion of reaction, the reaction mixture was cooled at room temperature and 10 mL HCl (4 mol l^{-1}) was added to it and then with 10 mL ethyl acetate. The organic layer was separated, washed with 20 mL distilled water, dried over anhydrous sodium sulfate, and concentrated to give the crude solid



Scheme 1. Synthesis of npg-C_3N_4/Ir-T photocatalyst.