Applied Catalysis A: General 499 (2015) 32–38

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Octahedral rhenium $K_4[Re_6S_8(CN)_6]$ and $Cu(OH)_2$ cluster modified TiO_2 for the photoreduction of CO_2 under visible light irradiation

Pawan Kumar[a], Nikolay G. Naumov[b], Rabah Boukherroub[c,**], Suman L. Jain[a,*]

[a] Chemical Sciences Division, CSIR-Indian Institute of Petroleum, Dehradun 248005, India
[b] Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, 3, Acad. Lavrentiev Ave., Novosibirsk, 630090, Russia
[c] Institut de Recherche Interdisciplinaire (IRI, USR 3078 CNRS), Université Lille 1, Parc de la Haute Borne, 50 Avenue de Halley, BP 70478, 59658 Villeneuve d'Ascq, France

ARTICLE INFO

Article history:
Received 14 November 2014
Received in revised form 11 February 2015
Accepted 2 April 2015
Available online 9 April 2015

Keywords:
Rhenium cluster
Modified titania
Photocatalysis
Carbon dioxide
Methanol

ABSTRACT

Octahedral hexacyano rhenium $K_4[Re_6S_8(CN)_6]$ cluster complexes were grafted onto photoactive $Cu(OH)_2$ cluster modified TiO_2 $\{Cu(OH)_2/TiO_2\}$ support. The rhenium and copper cluster modified TiO_2 photocatalyst combines the advantages of heterogeneous catalyst (facile recovery, recycling ability of the catalyst) with the reactivity, selectivity of the soluble molecular catalyst. The synthesized heterogeneous catalyst was found to be highly efficient photoredox catalyst for the reduction of CO_2 under visible light irradiation. Methanol was found to be the major liquid product with the formation of hydrogen as a by product as determined with GC-FID and GC-TCD, respectively. The methanol yield after 24 h irradiation was found to be 149 μmol/0.1 g cat. for Re-cluster@$Cu(OH)_2/TiO_2$ photocatalyst that is much higher than 35 μmol/0.1 g cat. for $Cu(OH)_2/TiO_2$ and 75 μmol/0.1 g cat. for equimolar rhenium cluster in the presence of triethanolamine (TEOA) as a sacrificial donor. The quantum yields (ϕ_{MeOH}) of Re-cluster@$Cu(OH)_2/TiO_2$ and $Cu(OH)_2/TiO_2$ were found to be 0.018 and 0.004 mol einstein^{-1}, respectively. These values are much higher than those reported for other heterogeneous catalysts for six electron transfer reaction.

1. Introduction

Reduction of carbon dioxide (CO_2) to produce high value chemicals and fuels has attracted much attention due to the global warming problem and shortage of fossil fuels. In particular, the efficient photocatalytic reduction of CO_2 with H_2O is one of the most desirable and challenging goals in the realm of sustainable chemistry with CO_2 as C1 feedstock [1–4]. Among the various photocatalysts for CO_2 reduction such as soluble metal complexes and semiconductors, rhenium (I) type complexes have been recognized as being very efficient and selective catalysts [5–8]. Despite of their high reactivity and selectivity, homogeneous nature of such complexes hinders their widespread utilization for practical applications [9,10]. Thus, supporting a soluble metal complex onto an inorganic solid matrix is one of the promising approaches to combine the advantages of both homogeneous catalyst such as high reactivity, selectivity with heterogeneous one such ease of separation from products, lack of corrosiveness, and robustness for operation at high temperatures [11–14]. Furthermore, the use of photoactive supports such as TiO_2 for immobilizing transition metal complexes is a step forward in this direction. Recently, Yamashita et al. reported that addition of copper (II) onto TiO_2 matrix could improve the efficiency and selectivity for photocatalytic reduction of CO_2 to produce methanol [15]. Furthermore, Tseng et al. also found that the formation of methanol was much more effective on Cu-titania catalysts [16].

The chemistry of octahedral rhenium cluster complexes with cluster core $[Re_6Q_8]^{2+}$ (Q = S, Se, Te) is gaining considerable interest in recent years [17–22]. A large number of reports have appeared within the last few years on the synthesis of molecular cluster complexes of the $Re_6Q_8L_6$ type where L = Cl, Br, I, or different organic ligands [23–25]. However, studies on their use as catalysts for various applications are rarely been explored in the literature. One of the goals of our research is to develop efficient visible light active metallic cluster photocatalysts for the reduction of CO_2. Recently, we have demonstrated the high efficiency of hexanuclear molybdenum $[Mo_6Br_{14}]^{2-}$ cluster complexes for the photoreduction of CO_2 to methanol under visible light irradiation [26]. In the present paper, we report for the first time on the synthesis and

---

* Corresponding author. Tel.: +91 135 2525788; fax: +91 135 2660202.
** Corresponding author.
E-mail addresses: suman@iip.res.in, sumanjain@hotmail.com (S.L. Jain).

http://dx.doi.org/10.1016/j.apcata.2015.04.001
0926-860X/

application of hexanuclear rhenium cluster supported on copper-modified TiO_2 as efficient and reusable photocatalyst for the photoreduction of CO_2 under visible light irradiation.

2. Experimental

2.1. Catalyst preparation

Degussa P25 TiO_2, copper nitrate (99%) and solvents were purchased from Sigma–Aldrich and used without further purification.

2.1.1. Synthesis of copper doped TiO_2 support [27]

The TiO_2 Degussa-P25 powder was used as a reference catalyst. Copper-doped TiO_2 catalyst was prepared by impregnating Degussa-P25 with copper nitrate solution by following the literature procedure. Briefly, in a 250 ml of 0.25 M NaOH solution, P25 TiO_2 (4 g) was dispersed and then added 100 ml of 0.0077 M $Cu(NO_3)_2$ drop-wise with vigorous stirring. The resulting mixture was stirred for additional 6 h. The resulting solid was washed with distilled water, ethanol for five times and then dried at 80 °C for 12 h. The copper content in the synthesized material was found to be 1.68 wt% as determined by ICP-AES analysis.

2.1.2. Synthesis of rhenium cluster supported on $Cu(OH)_2/TiO_2$ (Re-cluster@$Cu(OH)_2/TiO_2$)

A mixture containing $Cu(OH)_2/TiO_2$ (1 g) and rhenium cluster complex $K_4[Re_6S_8(CN)_6]$ (200 mg) was refluxed in 25 ml DMF for 24 h under nitrogen atmosphere. The resulting solid was separated by filtration, washed with ethanol for five times and then dried at 80 °C under vacuum for 12 h. The rhenium content in the solid was found to be 1.65 wt% as determined by ICP-AES analysis.

2.2. Catalyst characterization

Micro-porosity (rp), BET surface area, pore volume (Vp) and other surface properties of the synthesized materials were examined by N_2 adsorption–desorption isotherm at 77 K by using VP; Micromeritics ASAP2010. The crystalline phase of the synthesized samples was determined by X-ray powder diffraction pattern using a Bruker D8 Advance diffractometer at 40 kV and 40 mA with Cu K_α radiation ($\lambda = 0.15418$ nm). The sample was deposited on glass slide and inserted in slots before drying. The surface morphology of the synthesized $Cu(OH)_2/TiO_2$ and Re cluster supported $Cu(OH)_2/TiO_2$ was determined with scanning electron microscopy (SEM) by using FE-SEM (Jeol Model JSM-6340F). UV–vis absorption spectra of rhenium cluster complexes in water and solid state after immobilization onto $Cu(OH)_2/TiO_2$ support were collected on Perkin-Elmer lambda-19 UV–vis-NIR spectrophotometer using a 10 mm quartz cell, using $BaSO_4$ as reference. ICP-AES analysis was carried out by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, DRE, PS-3000UV, Leeman Labs Inc., USA). Samples for ICP-AES were prepared by leaching metal in conc. HNO_3 followed by volume make up to 10 ml. Elemental analysis was performed using CHN analyser. The photoreaction products were identified and quantified with GC–MS (Hewlett-Packard HP5890 equipped with an HP-INNOWAX column and a mass-selective detector) and GC-FID (Varian CP-3800 equipped with a 30 m long Stabilwax® w/Integra-Guard® column using the following parameters: flow rate = 0.5 ml/min, injector temperature = 250 °C, FID detector temperature = 275 °C).

2.3. Photocatalytic reduction of CO_2

For photocatalytic reduction experiment, initially a borosil cylindrical vessel (5 cm dia.) was charged with water (10 ml), triethanolamine (5 ml), and DMF (35 ml). The solution was degassed by purging with nitrogen for 30 min and then saturated with CO_2 by purging for 30 min. Then the synthesized heterogeneous rhenium cluster catalyst (100 mg) was loaded in the reactor followed by bubbling of CO_2 for additional 5 min. The vessel was illuminated under visible light by using 20 W LED (Model No.-HP-FL-20W-F-Hope LED Opto-Electric Co., Ltd., $\lambda > 400$ nm) with stirring. The distance between light source and vessel was 3 cm and intensity at the surface of vessel was estimated to be 75 W/m^2. For preventing external light interference, the vessel was placed in a box. After every 2 h intervals, the samples were collected with the help of a needle and analysed with GC-FID (Varian CP-3800) equipped with a 30 m long Stabilwax® w/Integra-Guard® column using the following parameters: flow rate = 0.5 ml/min, injector temperature = 250 °C, FID detector temperature = 275 °C. For accuracy purpose, an auto-sampler was used for injection. Quantification and linear response to different sample concentrations were confirmed by plotting a calibration curve.

For ensuring that methanol was produced as a result of CO_2 photoreduction instead of carbonaceous impurities, three blank reactions were carried out: (i) in the presence of catalyst and CO_2 in dark without illumination, (ii) visible light illumination of a CO_2 saturated solution in the absence of catalyst and (iii) visible light illumination of N_2 saturated mixture in the presence of catalyst. In all the above blank reactions, no product was detected. Gaseous products were analysed using GC-TCD and GC-FID (Agilent 7890A GC system) using capillary column (RGA, refinery gas analyser) at the flow rate (H_2: 35 ml/min, air: 350 ml/min, makeup flow: 27 ml/min, for TCD reference flow: 45 ml/min, Helium flow: 2 ml/min), injector temperature: 220 °C, TCD detector temperature and FID detector temperature: 220 °C.

2.4. $^{13}CO_2$-labelling experiment

To identify the carbon source of methanol, a $^{13}CO_2$ labelling experiment was conducted using ^{13}C 99 atom%, $^{18}O < 3$ atom% supplied by Sigma–Aldrich under the identical experimental conditions as described above. The photoreaction product was analysed by Hewlett-Packard HP5890 GC equipped with an HP-INNOWAX column and a mass-selective detector (HP 5972). The formation of $^{13}CH_3OH$ (m/z 33) confirmed that the methanol is generated from the photoreduction of CO_2 (Fig. S5).

3. Results and discussion

3.1. Synthesis and characterization of the catalyst

The synthesis and characterizations of $K_4[Re_6S_8(CN)_6]$ have been fully described in the literature [23]. The structure is based on $[Re_6Q^i_8L^a_6]$ cluster units as anionic building blocks and K^+ as counter cation (Fig. 1).

$K_4[Re_6S_8(CN)_6]$ **1** octahedral rhenium cluster complex was synthesized by the reaction of $Re_6Q_8Br_2$ (Q = S, Se, Te) with molten KCN at 650 °C. This salt is readily soluble in aqueous solution and stable toward decomposition and apical ligand exchange.

The main aim of the present work is to synthesize supported rhenium cluster complexes with the objective of obtaining a highly efficient and recyclable photoredox catalyst for CO_2 photoreduction under visible light irradiation. For this, we have targeted the hydroxyl groups on the $Cu(OH)_2$ cluster modified TiO_2 support which have high affinity towards metallic centres and therefore provided efficient and stable anchoring of the rhenium cluster complexes to the support. Cyanocomplexes $[Re_6Q_8(CN)_6]^{4-}$, Q = S, Se, Te with apical cyano-ligands are unique example due to their high stability in aqueous and organic media as well as basic and acidic solutions. The bidentate nature of cyano ligands affords the

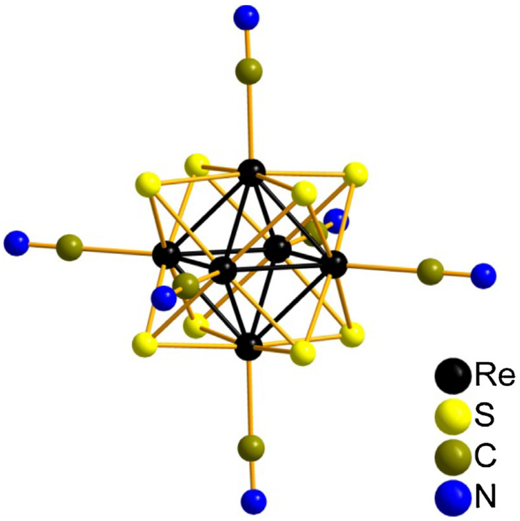

Fig. 1. Schematic representation of the $[Re_6S_8(CN)_6]^{4-}$ cluster unit **1**.

formation of coordination polymers in reactions of $[Re_6Q_8(CN)_6]^{4-}$ with cations 3d transition metals [28–32]. Interaction of $[Re_6Q_8(CN)_6]^{4-}$ with M^{2+} in aqueous solution leads to immediate precipitation of phases based on covalent Re-CN-M bridges. As Cu(II) is at the end of Irving–Williams Series, it forms less soluble phases. To crystallize $[Re_6Q_8(CN)_6]^{4-}$ with Cu^{2+} concurrent ligands (NH_3, en, 1,2,3,4-tetraaminobutane) were used [31,32].

The morphology of $Cu(OH)_2$ modified TiO_2 (**2**) and Re-cluster@$Cu(OH)_2/TiO_2$ (**3**) photocatalysts was determined by scanning electron microscopy (SEM). The SEM image of $Cu(OH)_2/TiO_2$ indicated that particles were almost spherical with a diameter of 100–250 nm (Fig. 2a). EDX analysis of the $Cu(OH)_2/TiO_2$ sample confirmed the copper loading on the TiO_2 substrate (Fig. 2c). Modification of $Cu(OH)_2/TiO_2$ support with the rhenium cluster **1** did not induce any apparent morphological changes of the particles (Fig. 2b). Furthermore, EDX analysis confirmed the presence of rhenium on the synthesized $Cu(OH)_2/TiO_2$ catalyst (Fig. 2d).

The EDX peaks corresponding to Cu and Re are quite weak, suggesting that the concentrations of both elements in the TiO_2 substrate are small. The results were corroborated by the concentration values of 1.68 and 1.65 wt% of Cu and Re, determined by ICP-AES analysis of the samples **2** and **3**, respectively. Further elemental mapping clearly indicated that the rhenium cluster is evenly distributed in the synthesized material (Fig. 3a and b).

The surface properties of $Cu(OH)_2/TiO_2$ **2** and Re-cluster@ $Cu(OH)_2/TiO_2$ **3** were examined with the help of nitrogen adsorption/desorption isotherm. A Type (IV) loop was observed for $Cu(OH)_2/TiO_2$ in agreement with the mesoporous nature of the sample (Fig. S1a). However, the Re-cluster@ $Cu(OH)_2/TiO_2$ catalyst showed a Type (II), suggesting a macroporous nature of the sample (Fig. S1b) [33]. This change in porous properties was due

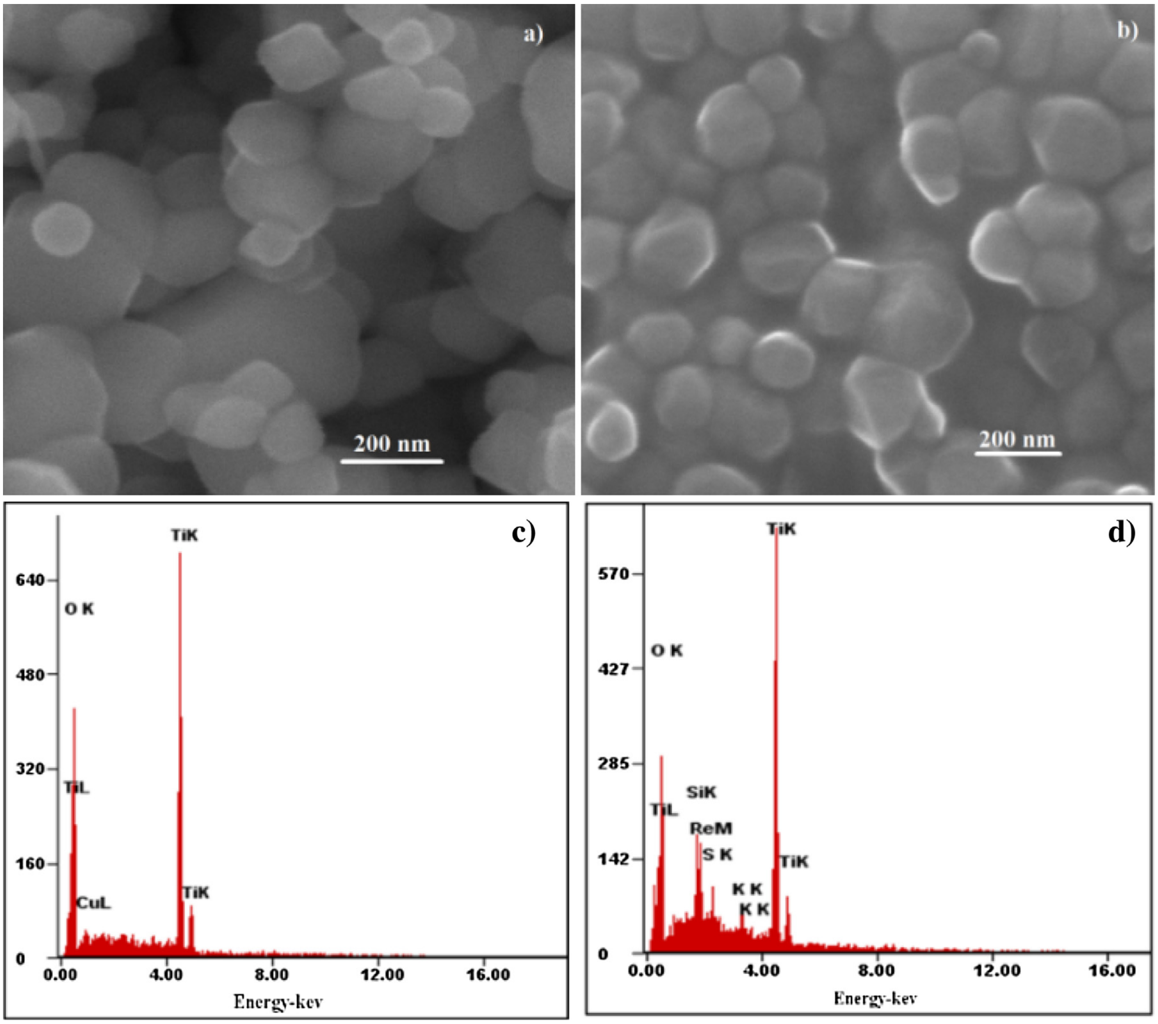

Fig. 2. SEM images of a) $Cu(OH)_2/TiO_2$, b) Re-cluster@$Cu(OH)_2/TiO_2$, and EDX spectra of c) $Cu(OH)_2/TiO_2$, d) Re-cluster@ $Cu(OH)_2/TiO_2$.

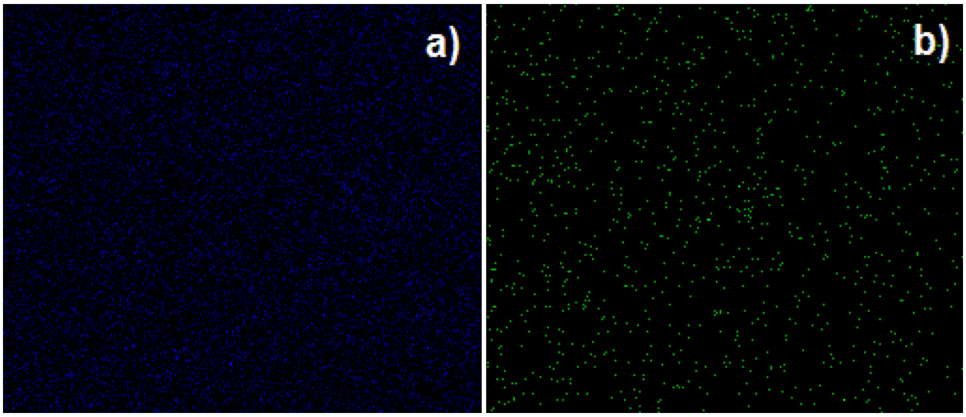

Fig. 3. Elemental mapping of Re-cluster@Cu$(OH)_2$/TiO_2 for a) Ti; b) Re.

to stacking of cluster on the surface so closing (or clogging) of the small pores (mesopores). The values of BET surface area, mean pore diameter and total pore volume were found to be 40.91 $m^2\,g^{-1}$, 11.87 nm and 0.1215 $cm^3\,g^{-1}$, respectively for Cu$(OH)_2$/TiO_2 (Fig. S1a) and 8.96 $m^2\,g^{-1}$, 83.51 nm, 0.1871 $cm^3\,g^{-1}$, respectively for Re-cluster@Cu$(OH)_2$/TiO_2 (Fig. S1b). This decrease in surface area and increase in mean pore diameter was attributed to the successful attachment of rhenium cluster complex units to the support.

The XRD diffraction patterns of the Degussa P25 TiO_2, Cu$(OH)_2$/TiO_2 and Re-cluster@Cu$(OH)_2$/TiO_2 are displayed in Fig. 4. The intense peak at $2\theta = 25.34°$ corresponds to the anatase phase of TiO_2 [27,34]. It can be seen, from Fig. 4, that for all the three samples i.e. TiO_2, Cu$(OH)_2$/TiO_2 and Re-cluster/Cu$(OH)_2$/TiO_2, only the characteristic peaks corresponding to TiO_2 were observed. The absence of the Cu peak ($2\theta = 35.6°$) in the copper modified TiO_2 samples is most likely due to the low content of the copper. In addition, the shape and relative intensity of the characteristic TiO_2 peaks remained unchanged, indicating that the crystalline form of the TiO_2 has not been altered neither by loading of Cu nor by grafting of Re cluster complex.

The thermal stability of the synthesized catalysts was evaluated using DT-TGA (Fig. 5). The DT-TGA curve of the rhenium cluster shows a weight loss of ~10% up to 150 °C, most likely due to the loss of water, while the second weight loss ~700 °C was attributed to the degradation of $K_4[Re_6S_8(CN)_6]\cdot 8H_2O$ cluster molecules. After attachment of rhenium cluster to Cu$(OH)_2$/TiO_2, a weight loss <3% was observed at ~700 °C due to the degradation of the Re cluser. In contrast, no obvious weight loss was observed for Cu$(OH)_2$/TiO_2 substrate in the temperature range investigated. The results indicate Re cluster attachment on the Cu$(OH)_2$/TiO_2 surface and corroborate the EDX analysis.

UV–vis absorption spectrum of the rhenium cluster complex salt i.e. $K_4[Re_6S_8(CN)_6]$ in water exhibited a strong broad peak between 200 and 400 nm and a weak shoulder at 465 nm (Fig. 6a), suggesting that the soluble cluster complex is visible light active. Absorption spectrum of Cu$(OH)_2$/TiO_2 showed a peak at 305 nm (Fig. 6c), while λ_{max} of P25 TiO_2 was observed at 287 nm, suggesting that doping with copper slightly red shifted the absorbance of TiO_2. Rhenium cluster immobilization on Cu$(OH)_2$/TiO_2 catalyst caused absorption spectra to shift to the visible region, in the range of 415–500 nm (Fig. 6b). This suggests that rhenium cluster immobilization on the Cu$(OH)_2$/TiO_2 enhances its absorption in the visible range.

The band gap of the $K_4[Re_6S_8(CN)_6]$, Cu$(OH)_2$/TiO_2 and Re-cluster@Cu$(OH)_2$/TiO_2 samples can be estimated by extrapolating the rising segment of the UV spectrum to the abscissa at zero absorption with the help of the Tauc plot [35]. The values of the band gap of the rhenium cluster complex were found to be 2.50 eV and 2.69 eV, respectively for different HOMO → LUMO transitions (Fig. 7a). These values were associated with 495.2 nm and 460 nm wavelengths of light, in accordance with the visible light

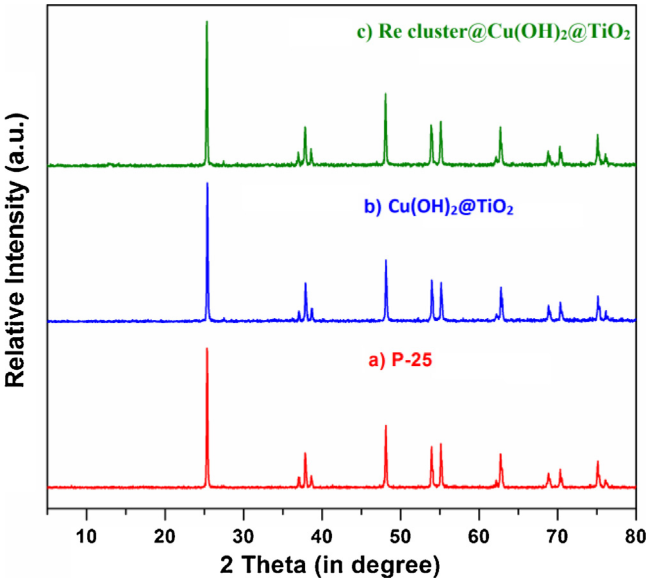

Fig. 4. XRD patterns of a) P-25 TiO_2, b) Cu$(OH)_2$/TiO_2 and c) Re-cluster@Cu$(OH)_2$/TiO_2.

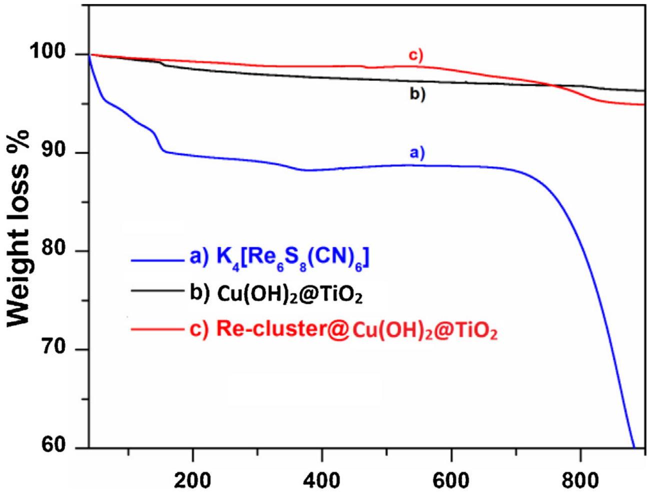

Fig. 5. TGA of a) $K_4[Re_6S_8(CN)_6]$, b) Cu$(OH)_2$/TiO_2 and c) Re-cluster/Cu$(OH)_2$/TiO_2.

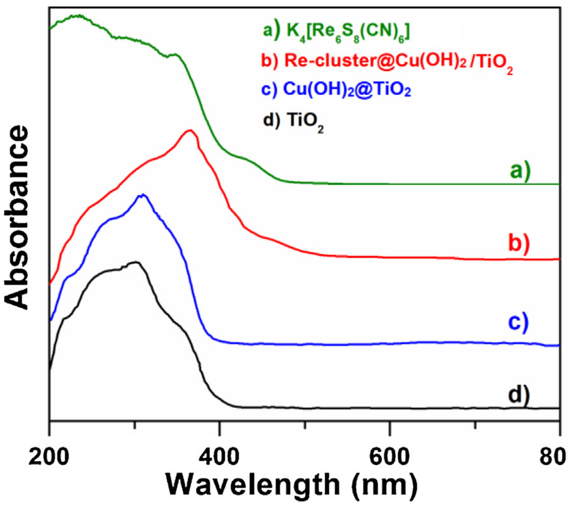

Fig. 6. UV/vis absorption spectra of a) $K_4[Re_6S_8(CN)_6]$, b) Re-cluster@$Cu(OH)_2/TiO_2$ and c) $Cu(OH)_2/TiO_2$ and d) TiO_2.

absorption by the cluster. For $Cu(OH)_2/TiO_2$, an optical band gap value of 3.11 eV was determined, which is high enough for preventing visible light driven transitions (Fig. 7b). After attachment of the rhenium cluster onto $Cu(OH)_2/TiO_2$, the value of the band gap decreased to 2.43 eV (λ = 509.5 nm), suggesting the high visible light activity of the synthesized heterogeneous catalyst (Fig. 7c).

3.2. The photocatalytic reduction of CO_2

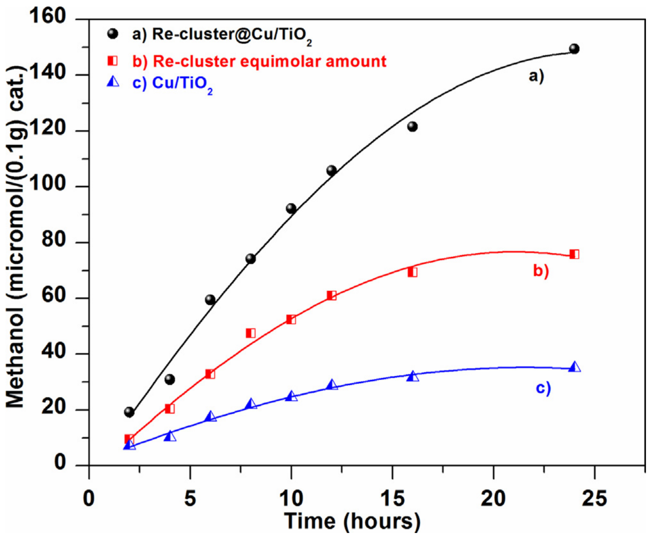

Fig. 8. CO_2 conversion to methanol using a) Re-cluster@$Cu(OH)_2/TiO_2$ **3**, b) Re complex **1** at same equimolar amount and c) $Cu(OH)_2/TiO_2$ **2**.

Photoreduction of CO_2 was carried out by using the soluble rhenium cluster complex **1**, $Cu(OH)_2/TiO_2$ **2** and Re-cluster@$Cu(OH)_2/TiO_2$ **3** in water/DMF mixture using triethanolamine as a sacrificial donor under illumination with 20 W white cold LED as a source of light (Fig. S2). After the photoreduction, 1 μL liquid sample was withdrawn and analysed using a GC/FID equipped with a 30 m long Stabilwax® w/Integra-Guard® column. Methanol yield was used to evaluate the performance of the catalysts as it was obtained as the major reduction product (Fig. S3). Methanol (MeOH) yield (μmol/0.1 g cat.), in the photocatalytic reduction of CO_2 by using soluble rhenium cluster **1**, $Cu(OH)_2/TiO_2$ **2** and Re-cluster@$Cu(OH)_2/TiO_2$ **3** photocatalysts was plotted as a function of reaction time (Fig. 8). The results showed that Re-cluster@$Cu(OH)_2/TiO_2$ exhibited higher photocatalytic activity and afforded higher yield of methanol as compared to the equimolar soluble rhenium cluster **1** and $Cu(OH)_2/TiO_2$ **2**. After 24 h illumination, the methanol yield was determined to be 35 μmol/0.1 g cat., 149 μmol/0.1 g cat. using $Cu(OH)_2/TiO_2$ and Re-cluster@$Cu(OH)_2/TiO_2$ catalysts, respectively. While for the same mol% of homogeneous rhenium cluster **1**, the methanol yield was found to be 75 μmol/0.1 g cat. The results suggested that after attachment of the rhenium cluster **1** to $Cu(OH)_2/TiO_2$, the photoactivity increased significantly. The turn over number for methanol formation by using $Cu(OH)_2/TiO_2$ and Re-cluster@$Cu(OH)_2/TiO_2$ catalysts was 0.004 mol einstein^{-1} and 0.018 mol einstein^{-1}, respectively. For the determination of the gaseous products, 20 μL of the sample was injected in GC-RGA (TCD-FID). The GC-RGA analysis of gaseous products gave CO_2 (99.24%, 1772.14 μmol), H_2 (0.68%, 12.14 μmol) and a small amount of CO (0.08%, 1.43 μmol). Blank reactions in the absence of catalyst under otherwise similar experimental condition did not produce any reduction product. Similarly, the reaction in dark using CO_2 showed that there was no organic product formed for long periods of exposure.

To establish the formation of methanol from the photocatalytic reduction of CO_2 and not deriving from DMF, we have performed the photoreduction of CO_2 in another polar aprotic solvent i.e. acetonitrile under otherwise identical experimental conditions. The yield of methanol in acetonitrile was found to be comparable to that obtained in DMF (Fig. S4a). Furthermore, we carried out the photoreaction by using acetonitrile and catalyst in the absence of CO_2 under identical reaction conditions (Fig. S4b). No methanol

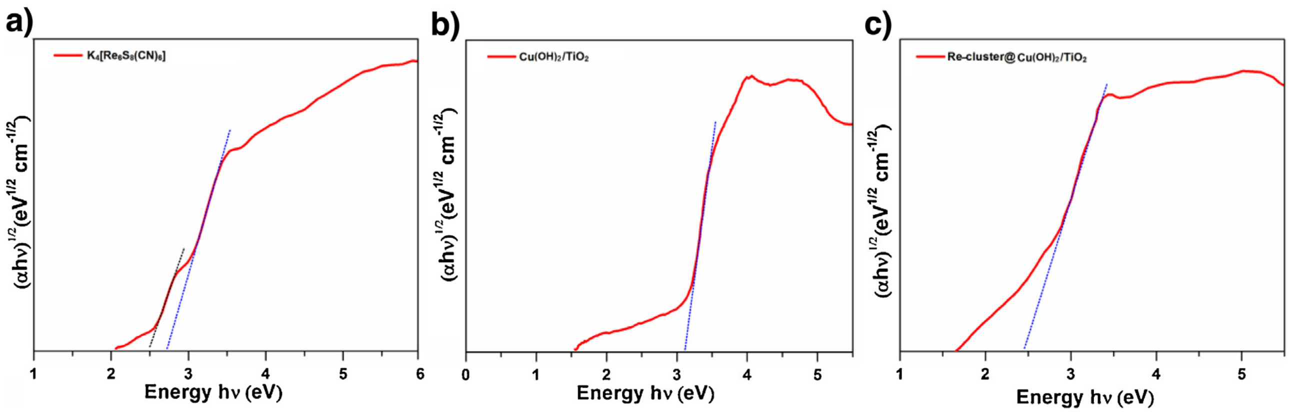

Fig. 7. Tauc plots for optical band gap determination of a) $K_4[Re_6S_8(CN)_6]$, b) $Cu(OH)_2/TiO_2$ and c) Re-cluster@ $Cu(OH)_2/TiO_2$.

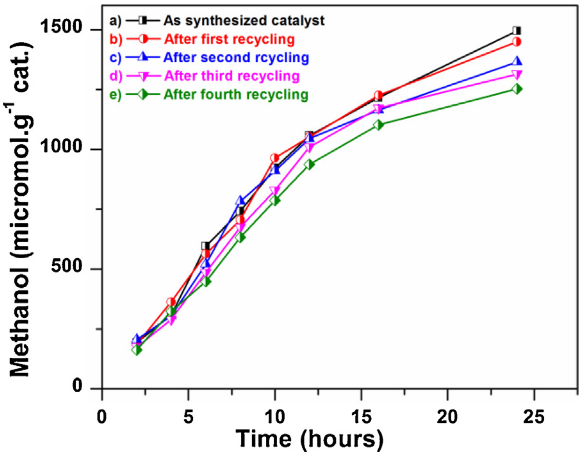

Fig. 9. Catalyst recycling experiment.

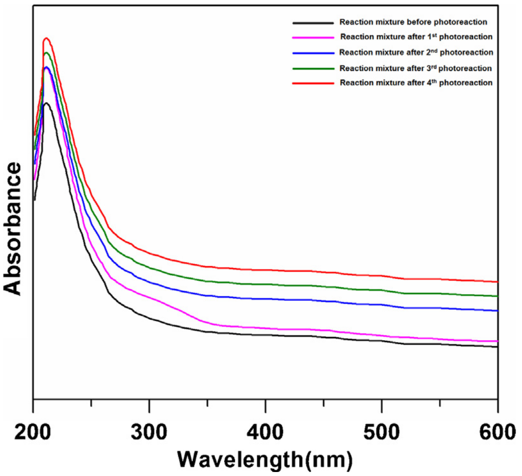

Fig. 10. UV–vis spectra of reaction mixtures of recycling experiments.

formation was observed, confirming that the methanol is being formed from the photoreduction of CO_2.

3.3. Isotopic tracer experiments with $^{13}CO_2$

To identify the carbon source of methanol, we performed the ^{13}carbon-labelling experiment by using $^{13}CO_2$ having purity (^{13}C 99 atom%, ^{18}O < 3 atom%) in place of $^{12}CO_2$ under identical experimental conditions. After the vis-illumination of reaction, the photoreaction product was analysed by GC–MS. The obtained methanol gave a sharp peak associated with $^{13}CH_3OH$ (m/z 33) instead of $^{12}CH_3OH$ (m/z 32) in GC–MS analysis (Fig. S5). The observed peak at m/z 33 clearly indicated that the methanol was produced directly from the photocatalytic reduction of CO_2 instead of any photo-dissociation of the carbon containing catalyst or solvent in the reaction mixture.

We have also performed recycling experiments for determining the robustness of the catalyst. After four catalytic cycles, no significant loss in activity was observed (Fig. 9) and rhenium content was found to be 1.61 wt% by ICP-AES, comparable to 1.65 wt% of the starting material. This is a good indication that the Re cluster does not leach off the $Cu(OH)_2/TiO_2$ support upon recycling the catalyst.

The colour change of reaction mixture after separating catalyst was monitored visually. There were no any detectable change was appeared after every recycling experiment. Further UV–vis spectra of reaction mixture before and after reaction was collected for confirming the leaching of metal cluster during the reaction (Fig. 10). No significant change in UV–vis absorption pattern was found which clearly indicated that the synthesized catalyst is quite stable and did not give any leaching during the reaction (Fig. 10).

To explain the high catalytic activity of the Re-cluster-@$Cu(OH)_2/TiO_2$ photocatalyst, we proposed a plausible mechanism on the basis of the band gap values. The commercial TiO_2 P25, which is mostly in anatase form, has a band gap of 3.20 eV that is enough for preventing any visible light mediated transition [27,36–38]. After modification with $Cu(OH)_2$ clusters, the calculated optical band gap of $Cu(OH)_2/TiO_2$ decreased slightly to 3.11 eV. As suggested in the literature, the reduction potential of $Cu(OH)_2/Cu$ is −0.634 V (vs NHE), which is higher than the reduction potentials of CO_2/CH_3OH (−0.38 V) and H^+/H_2 (−0.41 V), but slightly lower than the conduction band of TiO_2. So electrons can be easily transferred from the conduction band of TiO_2 to Cu cluster and used subsequently for the reduction of CO_2 and H^+. Because the reduction potential of H^+/H_2 is comparable to that of CO_2/CH_3OH so hydrogen is also observed as by product in this photocatalytic reaction. Still this transition requires high energy and can be performed in the UV region only [39–42]. Upon rhenium cluster immobilization onto $Cu(OH)_2/TiO_2$, there is an enhanced visible light absorption with a calculated optical band gap of 2.43 eV (λ = 509.5 nm). Upon visible light irradiation, an electron is promoted from the HUMO to the LUMO, which is in turn transferred to the conduction

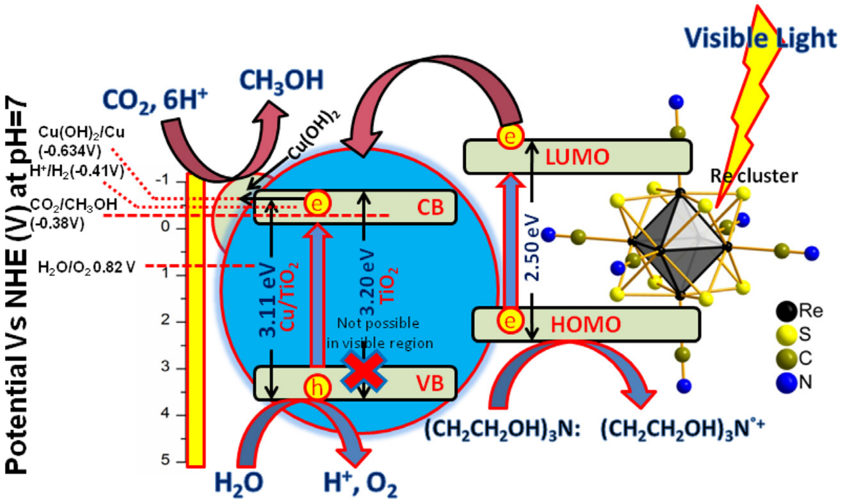

Fig. 11. Plausible mechanism of CO_2 reduction by Re-cluster@$Cu(OH)_2/TiO_2$ under visible light irradiation.

band of TiO_2. This electron, trapped by $Cu(OH)_2$, can finally be used for the reduction of CO_2 adsorbed on the catalyst surface (Fig. 11). Tiethanolamine acts as a sacrificial donor which provides electrons to oxidized rhenium cluster to continue the catalytic cycle.

4. Conclusion

We have developed a novel, highly efficient and reusable supported metallic cluster photocatalyst for the reduction of CO_2 under visible light irradiation. For this purpose, we have chosen copper cluster modified TiO_2 as photoactive solid support material for supporting water soluble hexanuclear rhenium cluster salt i.e. $K_4[Re_6S_8(CN)_6]$. Experimental results demonstrated that the grafting of the rhenium cluster onto $Cu(OH)_2$ cluster modified TiO_2 support provided significant enhancement in the photocatalytic activity for CO_2 photoreduction. Copper is an effective electron trapper able to prohibit the recombination of electron–hole pairs, hence significantly promoting the photo-efficiency. Furthermore, anchoring the rhenium clusters, which act as sensitizer to the copper modified support, resulted in the significant improvement of the photoreduction of CO_2 over TiO_2 matrix. High yield of methanol was achieved using the synthesized heterogeneous photocatalyst (149 μmol/0.1 g cat.) in comparison to the homogeneous rhenium cluster (75 μmol/0.1 g cat.) as well as copper cluster modified titania (34 μmol/0.1 g cat.) using visible light illumination under similar experimental conditions.

Acknowledgements

Authors would like to thanks Director IIP for granting permission to publish these results and analytical department for their moral support. PK is also thankful to CSIR, New Delhi for providing research fellowship under Emeritus Scientist Scheme No. 21(0888)/12/EMR-II. RB acknowledges financial support from the CNRS, the Université Lille1 and the Nord Pas de Calais region.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2015.04.001

References

[1] S.J. Davis, G.P. Peters, K. Caldeira, PNAS 108 (2011) 18554–18559.
[2] P.D. Tran, L.H. Wong, J. Barber, J.S.C. Loo, Energy Environ. Sci. 5 (2012) 5902–5918.
[3] S.N. Habisreutinger, L.S. Mende, J.K. Stolarczyk (Eds.), Angew. Chem. Int. 52 (2013) 7372–7408.
[4] J.-L. Wang, C. Wang, W. Lin, ACS Catal. 2 (2012) 2630–2640.
[5] J. Ettedgui, Y.D. Posner, L. Weiner, R. Neumann, J. Am. Chem. Soc. 133 (2011) 188–190.
[6] S. Sato, K. Koike, H. Inoue, O. Ishitani, Photochem. Photobiol. Sci. 6 (2007) 454–461.
[7] A.J. Morris, G.J. Meyer, E. Fujita, Acc. Chem. Res. 12 (2009) 1983–1994.
[8] Y. Tamaki, K. Watanabe, K. Koike, H. Inoue, T. Morimoto, O. Ishitani, Faraday Discuss. 155 (2012) 115–127.
[9] A. Inagaki, M. Akita, Coord. Chem. Rev. 254 (2010) 1220–1239.
[10] R. Reithmeier, C. Bruckmeier, B. Rieger, Catalysts 2 (2012) 544–571.
[11] T.M. Suzuki, H. Tanaka, T. Morikawa, M. Iwaki, S. Sato, S. Saeki, M. Inoue, T. Kajino, T. Motohiro, Chem. Commun. 47 (2011) 8673–8675.
[12] T.W. Woolerton, S. Sheard, E. Reisner, E.S.W. Ragsdale, F.A. Armstrong, J. Am. Chem. Soc. 132 (2010) 2132–2133.
[13] C.L. Anfuso, R.C. Snoeberger, A.M. Ricks, W. Liu, D. Xiao, V.S. Batista, T. Lian, J. Am. Chem. Soc. 133 (2011) 6922–6925.
[14] G. Qin, Y. Zhang, X. Ke, X. Tong, Z. Sun, M. Liang, S. Xue, Appl. Catal. B: Environ. 129 (2013) 599–605.
[15] H. Yamashita, H. Nishiguchi, N. Kamada, M. Anpo, Res. Chem. Intermed. 20 (1994) 815–823.
[16] I.-H. Tseng, W.-C. Chang, J.C.-S. Wu, Appl. Catal. B: Environ. 37 (2002) 37–48.
[17] J.C.P. Gabriel, K. Boubekeur, S. Uriel, P. Batail, Chem. Rev. 101 (2001) 2037.
[18] Z.P. Zheng, X.Y. Tu, CrystEngComm 11 (2009) 707.
[19] Y. Molard, A. Ledneva, M. Amela-Cortes, V. Circu, N.G. Naumov, C. Meriadec, F. Artzner, S. Cordier, Chem. Mater. 23 (2011) 5122.
[20] S. Cordier, B. Fabre, Y. Molard, A.B. Fadjie-Djomkam, N. Tournerie, A. Ledneva, N.G. Naumov, A. Moreac, P. Turban, S. Tricot, S. Ababou-Girard, C. Godet, J. Phys. Chem. C 114 (2010) 18622.
[21] T. Aubert, A.Y. Ledneva, F. Grasset, K. Kimoto, N.G. Naumov, Y. Molard, N. Saito, H. Haneda, S. Cordier, Langmuir 26 (2010) 18512.
[22] S.-J. Choi, K.A. Brylev, J.-Z. Xu, Y.V. Mironov, V.E. Fedorov, Y.S. Sohn, S.-J. Kim, J.-H. Choy, J. Inorg. Biochem. 102 (2008) 1991.
[23] T. Yoshimura, C. Suo, K. Tsuge, S. Ishizaka, K. Nozaki, Y. Sasaki, N. Kitamura, A. Shinohara, Inorg. Chem. 49 (2010) 531.
[24] T.G. Gray, C.M. Rudzinski, D.G. Nocera, R.H. Holm, Inorg. Chem. 38 (1999) 5932.
[25] M.W. Willer, J.R. Long, C.C. McLauchlan, R.H. Holm, Inorg. Chem. 37 (1998) 328.
[26] P. Kumar, S. Kumar, S. Cordier, S. Paofai, R. Boukherroub, S.L. Jain, RSC Adv. 4 (2014) 10420–10423.
[27] J. Yu, J. Ran, Eng. Environ. Sci. 4 (2011) 1364–1371.
[28] N.G. Naumov, A.V. Virovets, M.N. Sokolov, S.B. Artemkina, V.E. Fedorov (Eds.), Angew. Chem. Int. 37 (1998) 1943.
[29] L.G. Beauvais, M.P. Shores, J.R. Long, Chem. Mater. 10 (1998) 3783.
[30] N.G. Naumov, D.V. Soldatov, J.A. Ripmeester, S.B. Artemkina, V.E. Fedorov, Chem. Commun. (2001) 571.
[31] Y.V. Mironov, N.G. Naumov, K.A. Brylev, O.A. Efremova, V.E. Fedorov, K. Hegetschweiler (Eds.), Angew. Chem. Int. 43 (2004) 1297.
[32] N.G. Naumov, Y.V. Mironov, K.A. Brylev, V.E. Fedorov, J. Struct. Chem. 47 (2006) 771.
[33] IUPAC Recommendations, Pure Appl. Chem. 66 (1994) 1739–1758.
[34] J. Xu, L. Li, Y. Yan, H. Wang, X. Wang, X. Fu, G. Li, J. Colloid Interface Sci. 318 (2008) 29–34.
[35] J. Tauc, A. Menth, J. Non-Cryst. Solids 569 (1972) 8–10.
[36] K.M. Reddy, S.V. Manorama, A.R. Reddy, Mater. Chem. Phys. 78 (2002) 239–245.
[37] X. Chen, S.S. Mao, Chem. Rev. 107 (2007) 2891–2959.
[38] A.L. Linsebigler, G. Lu, J.T. Yates Jr., Chem. Rev. 95 (1995) 735–758.
[39] H.A. Schwarz, R.W. Dodson, J. Phys. Chem. 93 (1989) 409–414.
[40] T. Inoue, F. Akira, K. Satoshi, H. Kenichi, Nature 277 (1979) 637–638.
[41] G. Rothenberger, D. Fitzmaurice, M. Gratzel, J. Phys. Chem. 96 (1992) 5983–5986.
[42] E.E. Benson, C.P. Kubiak, A.J. Sathrum, J.M. Smieja, Chem. Soc. Rev. 38 (2009) 89–99.