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ARTICLE TYPE

Visible light assisted photocatalytic reduction of CO_2 using graphene oxide supported heteroleptic ruthenium complex

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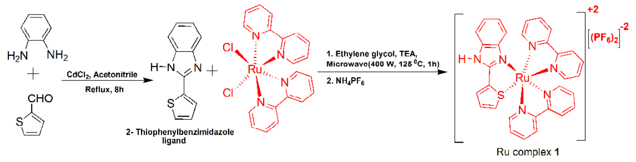
A new heteroleptic ruthenium complex containing 2-thiophenyl benzimidazole ligands was synthesized using microwave technique and immobilized to graphene oxide via covalent attachment. The synthesized catalyst was used for the photoreduction of carbon dioxide under visible light irradiation without using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

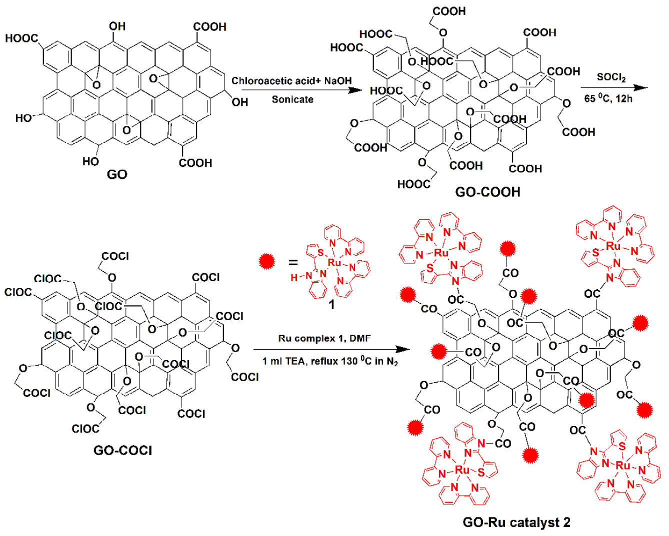
Finding cleaner energy sources to satisfy the world's growing demand is one of society's foremost challenges for the next half-century. Utilization of solar energy through the generation of hydrogen from water splitting[1] and/or through the photocatalytic reduction of carbon dioxide[2] to fuels (CO, CH_3OH, and CH_4) 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] as well as a significant number of patents[4-9] have been granted in last few decades showing the conisderable progress towards practical utility of photogeneration of hydrogen from water or of fuels, such as carbon monoxide, methanol and/or methane from the photoinduced reduction of carbon dioxide. Despite of 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 CO_2 to valuable C1 building blocks.[17] However, homogeneous nature of these catalysts makes the process unviable from economic as well as environmental viewpoints.[18] This problem can be solved by anchoring of such homogeneous complexes to photoactive support, which not only provide facile recovery of the catalyst, but also photoactive support and complexes may work synergistically to provide better electron transfer to CO_2.[19]
Chemically derived graphene oxide (GO) owing to the presence of ample oxygen functionalities and higher surface area, it 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 of visible light absorbing molecule to the support of graphene oxide. Recently we have reported graphene oxide immobilized cobalt phthalocyanine for the photoreduction of CO_2 under visible light irradiation. The yield of methanol after 48 hours of reaction was found to be 3781.8881µmol.g^{-1}-cat.[22a] Subsequently we reported graphene oxide immobilized ruthenium trinuclear complexes for the photoreduction of CO_2 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 hogher as compared to the graphene oxide alone, however the need of triethylamine as sacrificial donor makes the developed methods of less practical utility. In continuation to our ongoing research, herein we present a novel approach for synthesizing 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 sacrificial donor led to the reduction of CO_2 into methanol and afforded methanol yield 2050 µmol.g^{-1} cat after 24 h of irradiation.

Synthesis and characterization of the catalyst

At first 2-thiophenyl benzimidazole ligand was synthesized from the reaction of *o*-phenylene diamine and thiophene 2-carboxaldehyde in the presence of cadmium chloride.[23] As prepared sulphur containing ligand was used for the synthesis of corresponding ruthenium complex[24] by reacting it with $Ru(bpy)_2Cl_2$ under microwave irradiation as shown in Scheme 1. The synthesized homogeneous heteroleptic ruthenium complex was subsequently immobilized to graphene oxide support via covalent attachment. For this purpose, graphene oxide was obtained from oxidation of graphite with $KMnO_4$ and H_2SO_4 according to Hummer's method.[25] Occurrence of plenty oxygen containing functionalities in the form of free –OH, -COOH and epoxide groups and high specific surface area made graphene oxide an ideal material for grafting of homogeneous complexes. In most of the literature reports, the oxygen containing functional groups presented at edges of GO were used for immobilization and therefore low loading of catalyst was obtained.[26] Here, we have also targeted the epoxide groups located on the basal plane of sheets for the attachment of metal complex. Thus, we have treated the GO with chloroacetic acid to convert –OH and epoxide groups in to–COOH groups. Thus obtained COOH functionalized graphene oxide was readily converted to –COCl functionalized GO by treating it with thionyl chloride. The obtained chemically functionalized COCl-GO support was treated with ruthenium complex **1** to give graphene oxide immobilized ruthenium catalyst **2** as shown in Scheme 2.



Scheme 1: Synthesis of 2-thiophenylbenzimidazole ligand and heteroleptic Ruthenium (II) complex **1**



Scheme 2: Synthesis of GO-Ru catalyst **2**

The loading of ruthenium complex on GO support was found to be 0.51 mmol/g as determined by ICP-AES analysis. The complete characterization of the catalyst including surface properties, XRD, FTIR, SEM, TEM, UV-Vis and TGA are given in the supporting information of the manuscript (*See ESI file*).

The photocatalytic activation of CO_2

The photocatalytic activity of synthesized GO and GO-Ru catalyst **2** was tested for the photoreduction of CO_2 in water and DMF system saturated with CO_2 without using sacrificial agent under visible light irradiation. After various period of irradiation, 1μl sample was withdrawn and analyzed in a GC/FID equipped with a 30 m long Stabilwax® w/Integra-Guard® column. For maintaining the accuracy of measurements, the sample was injected with the help of autosampler. The obtained peak area was correlated with standard calibration curve for quantitative determination of methanol. Methanol yield was used to evaluate the performance of the catalysts as it was obtained as the major reduction product. To determine the gaseous products, 20 μL sample was injected in GC-RGA (TCD-FID). The gas phase analysis did not show the presence of any possible by-product like CO, CH_4 etc. The absence of peak in GC-FID and GC-MS for any other possible liquid product, and in 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} (μmol/g.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 μmol.g^{-1} cat in the absence of sacrificial agent. However, the use of graphene oxide as photocatalyst provided only 482 μmol.g^{-1}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 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 μmol/g.cat respectively and the corresponding quantum yield (ϕ) was obtained 0.029, 0.067 and 0.09 respectively. These results suggested that the incorporation of ruthenium complex **1** units to GO sheet enhanced the photocatalytic activity of GO significantly, which is most likely due to the better inflow of electrons to the conduction band of 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 the long period of illumination.

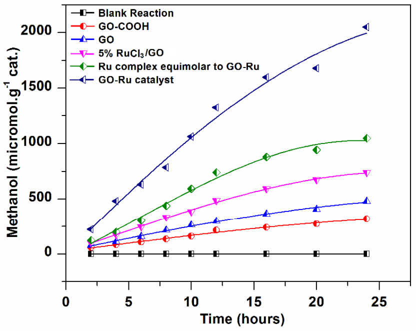


Fig. 1: CO_2 to methanol formation rate a) blank reaction b) using GO-COOH c) GO d) 5% $RuCl_3$ /GO e) Ru complex equimolar amount to GO-Ru catalyst **2** and c) GO-Ru catalyst **2**

After the photocatalytic reaction, 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.

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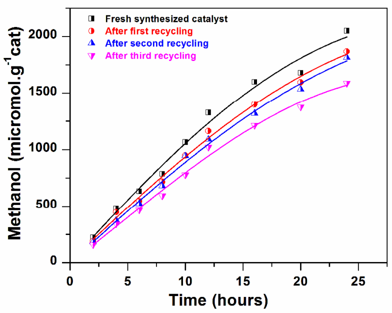


Fig. 2: Reuse experiments for catalyst **2**

Isotopic tracer experiments

For establishing the origin of methanol from CO_2, instead of organic matter presented in the reaction media or catalyst, we performed 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-Mass, giving $^{13}CH_3OH$ at m/z 33 instead of $^{12}CH_3OH$ m/z 32 (Fig. S19).

To explain the better photoactivity of catalyst, optical band gap values were calculated. Tauc plot of ruthenium complex **1** Fig. 3a gave the optical band gap value 1.90 eV to 2.29 eV, which was a strong indication of visible light active nature of complex **1**.[27] For GO Fig. 3b, instead of a sharp optical band gap, a range of band gap (2.9-3.7 eV) was obtained that was due to the uneven oxidation of sheets. This obtained value was in well conformity with the reported literature value.[21,28] While in case of GO-Ru catalyst **2,** the value of band gap 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 of ruthenium complex **1** to GO support enhanced the photoactivity of 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 the catalyst **2**.

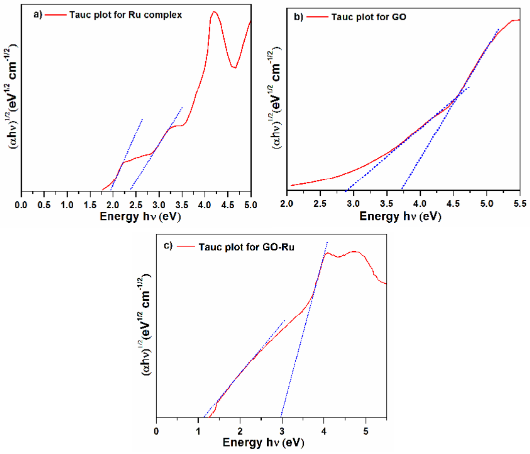


Fig. 3: Tauc plot for calculating band gap of a) Ruthenium complex **1** b) GO c) GO-Ru catalyst **2**

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

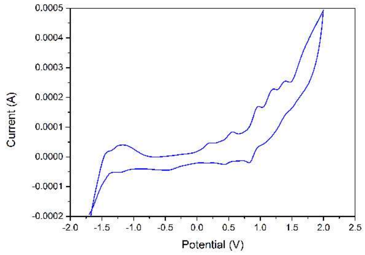


Fig 4: Cyclic voltametry curve of homogeneous Ru complex **1**

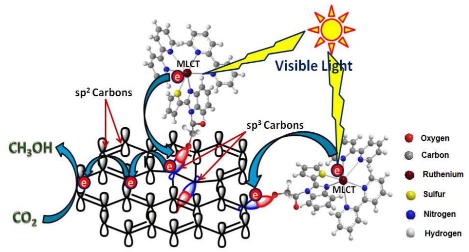
Based on the band gap values a plausible mechanism for the photoreduction of CO_2 to methanol is shown in Scheme 3. Oxygen containing functionalities in GO converts aromatic sp^2 carbon into sp^3 carbons so 2D network of sp^2 and sp^3 domain is created on GO's surface. Aromatic sp^2 hybridized carbon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

Ru(HOMO-LUMO) → Ru*($HOMO^+$ + $LUMOe^-$) **MLCT**

Ru*($HOMO^+$ + $LUMOe^-$)→ Ru*($HOMO^+$ + LUMO) + e^- (CB of GO)

Ru*($HOMO^+$ + LUMO) + e^-(derived from water splitting) → Ru(HOMO-LUMO)

$6e^-$ CB (GO) + CO_2 + $6H^+$(derived from water splitting) → $CH_3OH + H_2O$



Scheme 3: Plausible mechanism of photoreaction

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 sacrificial agent and under visible light irradiation. After the photoreduction, the catalyst was easily recovered by centrifugation and reused for subsequent runs. The recovered

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catalyst showed almost similar activity and provided similar yield of methanol in all the cases, which is a significant finding considering that immobilization of such photoactive complexes on 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 further promising from both environmental and industrial viewpoints.

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Notes and references

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†Electronic Supplementary Information (ESI) available: [Detailed experimental procedures and characterization of catalyst as well as reaction products are given in supplementary information]. See DOI: 10.1039/b000000x/

1. a) K. Maeda, *ACS Catalysis*, 2013, **3**, 1486-1503.; b) K. Nakata, T. Ochiai, T. Murakami and A. Fujishima, *Electrochim. Acta*, 2012, **84**, 103-111.; c) K. Maeda, J. Photochem. Photobiol. C: *Photochem. Rev.,* 2011, **12**, 237-268.; d) M. D. Hernandez-Alonso, F. Fresno, S. Suarez and J. M. Coronado, *Energy Environ. Sci*., 2009, **2**, 1231-1257.; e) Y. H. Hu, *Angew. Chem. Int. Ed.*, 2012, **51**, 12410-12412.; f) Y. Li, H. Liu and C. Wang, *Curr. Inorg. Chem.*, 2012, **2**, 168-183.
2. a) G. P. Smestad and A. Steinfeld, *Ind. Engineer. Chem. Res.*, 2012, **51**, 11828-11840.; b) P. D. Tran, L. H. Wong, J. Barber and J. S. C. Loo, *Energy Environ. Sci.*, 2012, **5**, 5902-5918.; c) A. Dhakshinamoorthy, S. Navalon, A. Corma and H. Garcia, *Energy Environ. Sci.*, 2012, **5**, 9217-9233.; d) E. V. Kondratenko, G. Mul, J. Baltrusaitis, G. O. Larrazábal and J. Pérez-Ramírez, *Energy Environ. Sci.,* 2013, **6**, 3112-3135.
3. a) S. Protti, A Albini, Nick Serpone *Phys. Chem. Chem. Phys*., 2014, **16**, 19790-19827.; b) K. Li, X. An, K. H. Park, M. Khraisheh and J. Tang, *Catal. Today,* 2014, **224**, 3–12.; b) S. N. Habisreutinger, L. Schmidt-Mende and J. K. Stolarczyk, *Angew. Chem. Int. Ed.*, 2013, **52**, 7372-7408.; c) 9. Y. Izumi, *Coord. Chem. Rev.*, 2013, **257**, 171–186.
4. A. Zaleska, Rec. *Pat. Engin*., 2008, **2**, 157-164.
5. S. M. Lam and A. R. Mohamed, *Rec. Pat. Chem. Engin*., 2008, **1**, 209-219.
6. B. Ohtani, *Rec. Pat. Engin*., 2010, **4**, 149-154.
7. G. Panayiotou, P. Gregoris, S. A. Kalogirou and S. A. Tassou, *Rec. Pat. Mech. Engin.*, 2010, **3**, 226-235.
8. G. Panayiotou, S. Kalogirou and S. Tassou, *Rec. Pat. Mech. Engin.,* 2010, **3**,154-159.
9. G. L. Chiarello and E. Selli, Rec. *Pat. Engineer*., 2010, **4**, 155-169.
10. Nippon Telegraph & Telephone, *Japanese Patent* JP2013035698A, 2013.
11. A. Yoshida, K. Kan, T. Kida, T. Harada and M. Isayama, *Japanese Patent* JP2004059507A, 2004.
12. *Taiwanese Patent* TW317301B, 2009
13. Nippon Telegraph & Telephone. *Japanese Patent* JP2013180943A, 2013.
14. Z. Yu, Y. Yuan and Z. Zou, *Chinese Patent* CN102532170A, 2012.
15. A. Yoshida, K. Kan and T. Kida, *Japanese Patent* JP2003275599A, 2003
16. P. O'Connor, G. H. Garcia and C. A. Corma, *World Patent* WO2012168355A1, 2012
17. a) C. D. Windle, M. V. Campian, A. K. D. Klair, E. A. Gibson, R. N. Perutz and J. Schneider, *Chem. Commun.,* 2012, **48**, 8189-8191.; b) P. D. Frischmann, K. Mahata and F. Wurthner, *Chem. Soc. Rev.,* 2013, **42**, 1847-1870.; c) J. Ettedgui, Y. D. Posner, L. Weiner, and R. Neumann, *J. Am. Chem. Soc.* 2011, **133**, 188-190.; d) M. Guttentag, A. Rodenberg, C. Bachmann, A. Senn, P. Hamm and R. Alberto, *Dalton Trans*., 2013, **42**, 334-337.
18. a) E. E. Benson, C. P. Kubiak, A. J. Sathrum and J. M. Smieja, *Chem. Soc. Rev.,* 2009, **38**, 89-99.; b) T. Morimoto, T. Nakajima, S. Sawa, R. Nakanishi, D. Imori, and O. Ishitani, *J. Am. Chem. Soc.* 2013, **135**, 16825-16828.
19. a) S. Liu, Z. Zhao and Z. Wang, *Photochem. Photobiol. Sci.*, 2007, **6**, 695-700.; b) T. M. Suzuki, H. Tanaka, T. Morikawa, M. Iwaki, S. Sato, S. Saeki, M. Inoue, T. Kajino and T. Motohiro, *Chem. Commun.,* 2011, **47**, 8673–8675.; c) F. Lakadamyali and E. Reisner, *Chem. Commun.* 2011, **47**, 1695-1697.; d) J. L. Wang, C. Wang, and Wenbin Lin, *ACS Catal.* 2012, **2**, 2630−2640.
20. a) M. Mahyari and A. Shaabani, *App. Catal. A: Gen.*, 2014, **469**, 524-531.; b) M. E. Ragoussi, J. Malig, G. Katsukis, B. Butz, E. Spiecker, G. Torre, T. Torres, and D. M. Guldi, *Angew. Chem. Int. Ed*. 2012, **51**, 6421-6425.; c) Y. Yu, M. Zhou, W. Shen, H. Zhang, Q. Cao, H. Cui, *Carbon*, 2012, **50**, 2539-2545.; d) X. Huang, X. Qi, F. Boey and H Zhang, *Chem. Soc. Rev*., 2012, **41**, 666-686.
21. H. C. Hsu, I. Shown, H. Y. Wei, Y. C. Chang, H. Y. Du, Y. G. Lin, C. A. Tseng, C. H. Wang, L. C. Chen, Y. C. Lin, and K. H. Chen, *Nanoscale*, 2013, **5**, 262-268.
22. a) P. Kumar, A. Kumar, B. Sreedhar, B. Sain, S. S. Ray, and S. L. Jain, *Chem. Eur. J.* 2014, **20**, 6154-6161.; b) P. Kumar, B. Sain and S. L. Jain, *J. Mater. Chem. A,* 2014, **2**, 11246-11253.
23. B Sammaiah, D Sumalatha, GS Reddy, M Rajeswari and LN Sharada, *Int. J. Ind. Chem*., 2012, **3**, 11-15.
24. T. Lundrigan, C. **L**. M. Jackson, Md. Imam Uddin, L. A. Tucker, Adeeb Al-Sheikh Ali, *A. Linden, T. S.* Cameron and A. Th*ompson, Can. J. Chem.***,** *2012,* **90**, 693-700.
25. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc*., 1958, **80**, 1339.
26. L. Ren, X. Wang, S. Guo, and T. Liu, *J. Nanopart Res.,* 2011, **13**, 6389-6396.
27. J. Tauc, and A. Menth, *J. Non-Cryst Solids*, 1972, **569**, 8-10.
28. G. Eda, and M. Chhowalla, *Adv. Mater.,* 2010, **22**, 2392–2415.
29. a) Ran Miao; Multimetallic Supramolecular Complexes; Ph.D thesis, Virginia Polytechnic Institute and State University, 2007.; b) C. M. Elliot, and E. J. Hershenhart, *J. Am. Chem. Soc.* 1982**, 104**, 7519-7526.; c) S. Rasmussen, M. Richter,E. Yi, H. Place, and K. Brewer, *Inorg. Chem.,* 1990, **29**, 3926-3932.
30. a) G. Eda, C. Mattevi, H. Yamaguchi, H. Kim, and M. Chhowalla, *J. Phys. Chem. C,* 2009, **113**, 15768–15771.; b) F. Bonaccorso, Z. Sun, T. Hasan and A. C. Ferrari, *Nature Photonics* , 2010, **4**, 611-622.; c) K. P. Loh, Q. Bao, G. Eda, and M. Chhowalla, *Nature Chemistry*, 2010, **2**, 1015-1024.; d) A. Mathkar, D. Tozier, P. Cox, P. Ong, C. Galande, K. Balakrishnan, A. L. M. Reddy, and P. M. Ajyan, *J. Phys. Chem. Lett.*, 2012, **3**, 986–991.
31. R. Argazzi, N. Y. M. Iha, H. Zabri, F. Odobel, and C. A. Bignozzi, *Coord. Chem. Rev.,* 2004, **248**, 1299.

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