

Photochemical Oxidative Coupling of 2-Naphthols using Hybrid rGO/MnO₂ Nanocomposite under Visible Light Irradiation

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Abstract: The present paper describes a simple, cost effective, efficient and high yielding photocatalytic approach for the oxidative self-dimerization of 2-naphthols using a semiconductor-metal hybrid consisting of intercalated manganese dioxide nanoparticles to reduced graphene oxide (rGO/MnO₂) under visible light irradiation. The desired photocatalyst was synthesized in a single step by mixing of MnO₂ nanoparticles with reduced graphene oxide under ultrasonication. The hybrid photocatalyst exhibited significantly higher activity as compared to neat MnO₂ NPs and rGO, which is believed to be due to the synergistic effect of its components. To our knowledge, hybrid rGO/MnO₂ nanocomposite is the first heterogeneous green photocatalyst for the oxidative coupling of 2-naphthols under mild conditions.

Introduction

BINOL is optically active, and its derivatives have been extensively used as chiral auxiliaries and ligands in asymmetric synthesis, and shown extremely high stereo-control property in a wide range of asymmetric transformations.^[1,2] There are several methods known for the oxidative coupling of 2-naphthols to give BINOL using stoichiometric oxidants, as well as transition metal based catalysts in conjunction with terminal oxidants.^[3,4] Also, very few photocatalytic asymmetric oxidative coupling reactions of 2-naphthols to BINOL derivatives under visible light irradiation are reported. Jana et al. reported β-MnO2 as a photocatalyst for the oxidative coupling of 2-Naphthol under visible light irradiations.^[5] Irie and co-worker have reported the asymmetric synthesis of chiral BINOL using chiral (NO)Ru(II)-salen complex as catalyst under irradiation of visible light.^[6] However, the known methods suffer from certain drawbacks such as expensive transition metal such as ruthenium, tedious recovery and inefficient recycling due to homogeneous nature and poor catalytic activity.[7,8]

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Inorganic and Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Hyderabad-500007, India. Manganese dioxide (MnO2) is a well known semiconductor material which has seevral fascinating properties like easy preparation, inexpensive and low toxicity.^[9,10] In addition the lower band gap (0.9-1.2 eV) and larger surface area of MnO₂ leads to its higher photocatalytic activity.^[11] However the bare MnO₂ has a narrow band gap which tends to show absorption in the infrared region. The composites prepared by the combination of MnO₂ with other semiconductors such as TiO₂, ZnO etc. has sufficient band gap to provide activity in the visible light region.^[12-13] Recently our group has established a concept to immobilize the metal nanoparticles/complexes/ salts or oxides to photoactive semiconductor supports either via in situ or post grafting approach to develop high-performance photocatalysts with the additional benefits of facile recovery and recycling of the catalyst for various transformations.[14-16] Graphene oxide/ graphene oxide, one of fascinating reduced carbon nanomaterials due to their extraordinary chemical, mechanical and optical properties, has become widely used as a semiconductor for immobilizing various sensitizers including metal NPs and metal complexes to develop improved photocatalysts resulting from the synergistic combination of the individual properties of the component materials.[17,18]

The present paper report a simple, cost effective, efficient and high yielding photocatalytic approach for the oxidative self dimerization 2-naphthols using a hybrid nanocomposite, synthesized via in situ grafting of MnO_2 nanoparticles to reduced graphene oxide (rGO/MnO₂) under visible light irradiation (Scheme 1). Importantly, the chemical interaction between the metal center of MnO_2 and semiconductor support produces a synergistic effect which provided higher activity, selectivity, and durability to the hybrid photocatalyst.



Scheme 1. Oxidative naphthol coupling by using rGO/MnO₂ as a photocatalyst

Results and Discussion

Synthesis and characterization of catalyst

The desired hybrid nanocomposite was obtained by grafting of MnO_2 NPs produced from $KMnO_4$ on rGO support as shown in Scheme 2.

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Scheme 2. Synthesis of rGO/MnO2 hybrid nanocomposite

The surface electronic state of elements and compositional analysis of rGO/MnO₂ was explained by X-ray photoelectron spectroscopy. XPS analysis indicated the presence of C, O and Mn elements in the composite material (Fig. 1a). High-resolution XPS spectrum of rGO/MnO₂ in the C_{1s} region exhibited three characteristic peak components at binding energies 284.1, 285 and 287.5 eV due to the C–C, C–O and O–C–O carbons, respectively (Fig. 1b).^[19] For the O_{1s} spectrum (Fig. 1c), the main peak was divided into two peaks located at 529.6 and 532.4 eV related to Mn-O-Mn and Mn-O-H of MnO₂, respectively.^[20] Figure 1d represented the high-resolution spectrum of Mn 2p, in which two peaks appeared at 653.6 and 642.3 eV with spin energy separation of 11.38 eV attributed to Mn 2p_{3/2} and Mn 2p_{1/2}, respectively.^[21,22] These results were found to be in good agreement with Mn(IV) characters in the phase of MnO₂.



Fig. 1 High-resolution XPS spectra of rGO/MnO_2 in a) survey spectrum, b) C1s, c) O1s and d) Mn2p region

The morphology of the prepared samples was determined by HR-TEM analysis (Fig. 2). The TEM images of rGO and rGO/MnO₂ at 200 nm scale showed the presence of layered and crystallite fringes corresponded to 0.24 nm interplaner d-spacing of 100 plane due to the presence of MnO₂ nanoparticles in graphitic sheets (Fig. 2a-f). The HR-TEM image of bare MnO₂ NPs revealed nearly spherical shaped particles of size in the range 16-20 nm (Fig. S1).



Fig. 2 HR-TEM images of rGO and rGO/MnO_2 a) and b) at 200 nm, c) at 100 nm, d) 50 nm and e) at 5 nm showing fringes, f) at 5 nm scale bar showing interplaner d-spacing.

HR-TEM elemental mapping of rGO/MnO_2 photocatalyst showed that all the elements namely, carbon, oxygen, and Mn were homogeneously distributed in the hybrid nanocomposite rGO/MnO_2 . Furthermore, EDX pattern of rGO/MnO_2 showed the presence of all the constituent elements like C, O, Mn (Fig. 3). SAED pattern of rGO/MnO_2 confirmed the presence of MnO_2 nanoparticles in the rGO/MnO_2 hybrid nanocomposite (Fig. 3d). The peaks for the copper were observed due to copper present in carbon coated copper TEM grid.



Fig. 3 HR-TEM Elemental mapping of rGO/MnO_2 a) Carbon, b) Oxygen, c) Manganese, d) SAED pattern and e) EDX Pattern showing elemental composition

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Fig. 4 illustrated the FTIR spectra of rGO and rGO/MnO₂. The spectrum of rGO showed the absorption peak at 1570 cm⁻¹ due to the C=C of the graphene sheets and the absorption peak at 1223 cm⁻¹ was attributed to C-OH stretching (Fig. 4a).^[23] After the intercalation of MnO₂ in between the rGO sheets, a new intense peak appeared at 558 cm⁻¹ related to the Mn-O of MnO₂ which confirmed the successful grafting of MnO₂ nanoparticles in between the rGO sheets (Fig. 4b).^[24]



Fig 4. FTIR Spectra of a) rGO, b) rGO/MnO2.

The crystalline and phase structure of the synthesized material was described by X-ray diffraction pattern (Fig. 5). XRD diffraction pattern of rGO revealed an intense broad peak at 25.4° and a small peak at 43.6°, 20 corresponding to (002) and (111) planes confirmed the formation of rGO from graphene oxide (Fig. 5a).^[25] XRD pattern of MnO₂ nanoparticles showed two characteristic peaks at 17.3° (001) and 36.8° indexed to 220 plane.^[26] In the case of rGO/MnO₂ (JCPDS No. 42-1317), the peak observed at 25.4° indexed to 002 planes with 0.24 nm interlayer distance was attributed to the presence of rGO in the nanocomposite (Fig. 5c). Other major peaks observed at 20 = 36.8° and 66° (020) were due to the manganese oxide, which was indexed to inter-atomic distances in materials consisted of edge-sharing MnO₆ octahedra.^[27]



Fig. 5 XRD Pattern of a) rGO, b) MnO2 NPs and c) rGO/MnO2.

Figure 6 showed the UV-visible spectra of rGO and rGO/MnO₂. The UV spectrum of rGO exhibited a characteristic band at 260 nm due to π - π * transitions of aromatic C-C bonds indicating the restoration of the extensive conjugated sp² carbon network in rGO. Also, a small hump around 350 nm due to n- π * transitions of C=O bonds was observed. For the comparison, UV-Vis spectrum of bare MnO₂ NPs is shown in Fig. S2. As shown a broad band in the range of 400 - 620 nm was observed which attributed to the d-d transition of Mn (Fig. S2).^[28] After the intercalation of MnO₂ NPs in between the rGO sheets in rGO/MnO₂, a new peak in the range 350-400 nm appeared. Hence, the deduction in the characteristic peak of rGO and the emergence of a new peak originating from MnO₂ NPs clearly indicated the interaction of MnO₂ nanoparticles with graphene surface.^[29]



Fig. 6 UV/Vis absorption spectra of a) rGO, b) rGO/MnO2.

To evaluate the light absorption capacity of the materials, Tauc plot was constructed for optical band gap determination (Fig. 7). The band gap of MnO_2 NPs was found to be 1.0 eV (Fig. 7a), which is unsuitable for the absorption in visible light. However in nanocomposite rGO/MnO₂ the band gap 1.3 eV (Fig.7b) indicated its higher activity in visible light.



Fig. 7 Tauc plot for band gap determination of a) MnO2; b) rGO/MnO2.

Raman spectroscopy is a powerful tool to characterize the structure and electronic properties of the synthesized material. The Raman spectrum of reduced graphene oxide (rGO) shows two characteristic peaks, one at 1335 cm⁻¹ for D band and another at 1594 cm⁻¹ for G bands (Fig. 8a). The D band is associated with first-order Raman scattering of the E_{2g}

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vibrational mode, and the G band corresponds to sp² bonded carbon atoms.^[30] Hence the integral intensity ratio of D to G bands (ID/IG) for rGO was found to be 0.98. In the case of rGO/MnO₂, both the D and G bands are found to be in slightly reduced intensity. The peaks arise at 484, 579, 620 cm⁻¹ shows the presence of MnO₂ NPs in the composite material (Fig. 8b).^[31] The characteristic peak arises at 620 cm⁻¹ due to the Mn-O lattice vibrations. The increased value of I_D/I_G in composite i.e. 1.2 indicated the presence of large number of defects and a decrease in the average size of the in-plane sp² domains of C-C in the composite.^[32,33]



Fig. 8 Raman spectra of a) rGO, b) rGO/MnO₂.

The specific surface properties of synthesized samples were determined by the adsorption and desorption of the nitrogen gas on the surface of the material with the help of the BET theory of multilayer adsorption and desorption (Fig. 9). The nitrogen adsorption-desorption isotherm for rGO was of type-(IV) which confirmed the mesoporous nature of the material. The higher absorption capacity of rGO could be attributed to the larger surface area of the material. The S_{BET} and pore volume for rGO were found to be 110.2 m^2g^{-1} and 1.50 $cm^3g^{-1},$ and for rGO/MnO2 the values were obtained as 165.2 m^2g^{-1} and 1.17 cm³g⁻¹, respectively.^[27] The large surface area and lower pore volume of composite rGO/MnO₂ was believed due to the intercalation of MnO₂ NPs in between the sheets of reduced graphene oxide, which led to the creation of enlarged gallery spaces in between the rGO sheets.^[34] In bare MnO₂ NPs the BET surface area was found to be 196.57 $m^2g^{\text{-}1},$ which is significantly higher than the commercial MnO2^[35] and MnO2 nanostructures reported in the literature [36,37]



Fig. 9 Adsorption desorption isotherm of a) rGO, b) rGO/MnO2 and c) MnO2

The thermal stability and degradation pattern of the samples was determined by thermo-gravimetric analysis (TGA). Under the air flow, TGA thermogram of rGO showed a weight loss in between 100-280 °C due to the evaporation of adsorbed water molecules and degradation of remaining oxygen-containing groups on rGO sheets (Fig. 10a).^[38] The thermogram of rGO/MnO₂ demonstrated two main weight loss regions; the first weight loss of about 6.5% below 230 °C, was corresponding to the interlayer water, while the second weight loss observed at 450 °C was corresponding to the phase transformation of MnO₂ due to the loss of oxygen.^[25]



Fig. 10 TGA diagram of a) rGO, b) rGO/MnO₂.

The photo-catalytic activity

The photocatalytic activity of the synthesized rGO and hybrid $r\text{GO}/\text{MnO}_2$ was tested for the oxidative coupling of naphthols

using toluene as a solvent under visible light irradiation at room temperature under an oxygen atmosphere. The reaction mixture was irradiated by using a 20W LED for 12 h under stirring condition. The results of these experiments are summarized in Table 1. In the absence of photocatalyst, there was no reaction occurred even after prolonged time (24 h) of visible light irradiation (Table 1, entry 1). The reaction was found to be very slow and afforded only 30% conversion of 2-naphthol to 1,1'-BINOL using rGO as a photocatalyst. However in case of rGO/MnO₂ composite, the reaction was occurred efficiently and afforded almost quantitative yield of the desired product. Higher activity of the composite suggested a synergistic effect of the components on photo activity. In order to check the synergistic effect of photocatalyst components on activity, we synthesized three rGO/MnO₂ samples using different amount of rGO (0.25, 0.5 and 1 g). The obtained composites were marked as 0.25rGO/MnO2, 0.5rGO/MnO2 and 1.0rGO/MnO2 and tested for the oxidative coupling of 2-naphthol under identical conditions. The activity of the composites was found to be in order _{0.25}rGO/MnO₂<_{0.5}rGO/MnO₂>_{1.0}rGO/MnO₂ (Table 1, entry 3). The poor activity of 0.25rGO/MnO2 attributed to the inefficient charge mobility and fast recombination. The composite 0.5rGO/MnO2 showed maximum activity, which was assumed due to the intimate contact between rGO and MnO₂ that accelerates the transfer of photogenerated electrons from MnO₂ to rGO and provides better charge mobility, effective charge antirecombination and higher photocatalytic activity. In 1.0rGO/MnO2 the slightly decreased activity was resulted to the less synergy between photocatalyst components due to the presence of excess rGO and isolated MnO2 NPs on the surface. Based on these results we have considered 0.5rGO/MnO2 as the optimum photocatalyst for further studies. In the absence of light, the reaction gave only trace yield of the product using 0.5rGO/MnO2 photocatalyst, which indicated that the reaction is truly photochemical in nature (Table 1, entry 3). The presence of oxygen was found to be vital, and in its absence, no reaction occurred even in the presence of 0.5rGO/MnO2 photocatalyst (Table 1, entry 3). Furthermore, among the different solvents such as acetonitrile, dichloromethane, and toluene studied, toluene was found to be optimum reaction medium for this transformation. For comparison, the reaction was also performed using bare MnO2 NPs; however, a very poor conversion observed which is most likely due to the agglomeration of NPs under the reaction conditions (Table 1, entry 4).



S.No	catalyst	Visible	Oxidant	Conv	[%]/t
		light		(%) ^[b]	
1		Yes	O ₂	-	-
2	rGO rGO + BQ	Yes Yes	O ₂ O ₂	30 Trac e	2.5
3	0.25rGO/MnO2 0.5rGO/MnO2 1.0rGO/MnO2 rGO/MnO2 + BQ	Yes Yes, - ^c Yes Yes	$ \begin{array}{c} O_2 \\ O_{2,} - d \\ O_2 \\ O_2 \end{array} $	72.8 97.2, 90.5 22.5	6.1 8.1, - ^c , - ^d 7.5 1.9
4	$MnO_2 NPs$ $MnO_2 + BQ$	Yes Yes	O ₂ O ₂	42.5 8	3.5

^[a]Reaction conditions: 2-naphthol 1.0 mmol, toluene 5 ml, room temperature, time 12h visible light (λ >400 nm); ^[b]determined by GC-MS; ^[c]In the absence of visible light; ^[d]in the absence of O₂ under N₂ atmosphere

BQ=p-benzoquinone (2%) was added as a radical scavenger

[%]/t= conversion vs time

Further, the reaction was generalized to various 0.5rGO/MnO2 substituted naphthol using derivatives photocatalyst under described optimized reaction conditions and the results of these experiments are summarized in Table 2. Among the various substrates, those bearing electron donating groups were found to be more reactive towards the coupling reaction and afforded excellent yields of corresponding coupling products (Table 2, entry 1-4). In all substrates corresponding 1,1'-BINOL was obtained selectively without any evidence for the formation of any by-product. In case of lower yield of the desired product, unreacted substrate was recovered at the end of the reaction (Table 2, entry 5-7).

Entry	Reactant	Product	Yield
			(%) ^[b]
1	ССС	C C C C C C C C C C C C C C C C C C C	
		ОН	97.0
2	OCH3	ОСН3	
	Un	ОН	92.0

Table 2: rGO/MnO2 catalyzed photochemical oxidative coupling of 2naphthols.^[a]

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^[a]Reaction conditions: 2-naphthol (1.0 mmol), toluene (5 ml), $_{0.5}$ rGO/MnO₂ (100 mg), room temp., time 12h, visible light (λ >400 nm); ^[b]Isolated yield.

Furthermore, we evaluated the recycling of the photocatalyst by considering the oxidative coupling of 2-naphthol under optimized conditions as a representative example. After completion of the reaction, the photocatalyst was separated by simple filtration, washed with methanol, dried and reused in subsequent experiments for five runs (Fig. 11). No significant loss was observed in the activity of the recycled photocatalyst, and the product yield remained almost unchanged, which confirmed that the developed rGO/MnO₂ photocatalyst is highly stable, leach-proof and truly heterogeneous in nature. Furthermore, the used photocatalyst recovered after fifth recycling experiment was characterized by FTIR, XRD and HR-TEM analyses (Fig. S3-S5). The almost similar data of recovered photocatalyst with fresh one further confirmed the higher stability of the photocatalyst under the described conditions.





The exact mechanism for this transformation is not clear at this stage, however, a plausible mechanism is shown in Scheme 3. It is believed that reduced graphene oxide (rGO) due to the sp² and sp³ carbon network acts as a semiconductor, and also provide better charge separation and higher mobility to suppress the recombination.^[39] After the absorption of visible light irradiation, the photogenerated electrons transfer from the valence band to the conduction band of MnO₂ NPs. These electrons passed through the conjugated network of rGO nanosheets and used for the conversion of O2 to O2. (superoxide radical).^[40] The superoxide radical abstracts hydrogen atom from naphthol radical cation to produce hydrogen peroxide (H₂O + $\frac{1}{2}$ O₂ = H₂O₂) as a byproduct. Selfdimerization of the naphthol radicals produces corresponding BINOL (Scheme 3). To confirm that a superoxide radical was involved in the photocatalyzed oxidative coupling of 2-naphthol reaction, p-benzoquinone (BQ), a well-known superoxide scavenger was added to the reaction mixtures containing MnO2. rGO and composite rGO/MnO2 under described conditions (Table 1, entry 2-4). The desired product was obtained in significantly poor yield, indicating that the formation of a superoxide radical is an essential step in the present study.^[41,42]



Scheme 3. (a) Plausible mechanism of aerobic oxidative coupling of 2-naphthol using rGO/MnO_2 photocatalyst, (b) band position of the components in the photocatalyst

Conclusions

An efficient semiconductor-metal hybrid photocatalyst consisting of manganese dioxide nanoparticles intercalated in reduced graphene oxide nanosheets was synthesized. The synthesized photocatalyst has been successfully exploited as an efficient photocatalyst for oxidative dimerization of 2-naphthols using molecular oxygen as oxidant. The hybrid photocatalyst exhibited excellent synergistic effect due to its components and therefore showed much higher activity as compared to neat MnO_2 NPs and rGO. The intercalation of metal nanoparticles in between the rGO sheets provides a facile approach to synthesize economical and active heterogeneous catalysts for photochemical transformations.

Experimental Section

Materials

Graphite flakes, potassium permanganate (99%), sodium nitrate (99%) and 2-naphthol was purchased from Sigma-Aldrich were of analytical grade and used without further purification. Buffer tablets pH 7.0 was purchased from Qualigens fine chemicals. Hydrazine mono hydrate, hydrochloric acid, ethanol, toluene, hydrogen peroxide (30%), sulphuric acid (H₂SO₄), water was of HPLC grade and procured from Alfa Aesar. All other chemicals were of A.R. grade and used without further purification.

Techniques used

X-ray photoelectron spectroscopy (XPS) measurement of photocatalyst was carried out using ESCA+ (omicron nanotechnology, Oxford instruments Germany) XPS system having an angle between analyzer to the source is 90 °. All of the binding energies were referenced to the C1s peak at 284.6 eV of the surface adventitious carbon. High-resolution transmission electron microscopy (HR-TEM) images were recorded with JEM 2100, Japan operated at an accelerating voltage of 200 kV and lanthanum hexaboride was used as a source of electrons. A very dilute suspension of the sample was deposited on the copper grid by sonication method to collect HRTEM images. The images were processed by using GATAN digital micrograph software. Fourier Transform Infrared (FT-IR) spectra were recorded on Perkin-Elmer spectrum RX-1 IR spectrophotometer using Potassium bromide window. The crystal structure of the material was characterized by Bruker D8 Advance diffractometer with Cu Ka radiation, (λ = 1.5418 Å) in the range of 2 θ = 20-80 and a scan rate of 4⁰ min⁻¹. The sample for XRD was prepared on a glass slide by adding well-dispersed catalyst in slot and drying properly. UV-visible spectra of samples were collected on Perkin Elmer lambda-19 UV-VIS-NIR spectrophotometer using a 10 mm quartz cell while absorption spectra of solid samples were recorded by using fine powder of BaSO₄ as a reflectance standard. Raman spectra of samples were collected at room temperature using a Raman Microprobe (HR-800 Jobin-Yvon) with 532 nm Nd-YAG excitation source. The specific surface area of materials was analyzed by nitrogen adsorption desorption isotherm at 77 K by using VP; Micromeritics ASAP2010. TG-DTA analysis for calculating the thermal stability of samples was carried out using a thermal analyzer TA-SDT Q-600 in the temperature range of 40 to 800 °C under nitrogen flow with a heating rate 10 °C/min. ¹H NMR and ¹³C NMR of the reaction products were collected at 500 MHz by using a Bruker Advance-II 500 MHz instrument.

Synthesis of reduced graphene oxide (rGO)^[43]

At first, the graphene oxide was synthesized according to the modified Hummers' method and then was mixed with water (3 mg/ml), sonicated for 3h to make a homogeneous suspension. Subsequently, hydrazine hydrate (1 µl for 3 mg of GO) was added to the above suspension, and the reaction was continued at 80 °C for 12 h. After that, the reaction mixture was cooled down to room temperature and the black precipitate

so obtained was filtered through a membrane filter (2 mm dia). The resulting black reduced graphene oxide was dried in vacuum oven for overnight.

Synthesis of in situ rGO/MnO2 hybrid nanocomposite^[44]

After some modifications in situ rGO/MnO₂ composite was synthesized. 0.5 g of reduced graphene oxide was dissolved in 20 ml solution of 1 M KMnO₄, and the volume of the mixture was adjusted to 50 mL with ultrapure water. The pH of the reaction medium was controlled by buffer tablet (pH=7.0), the mixture was sonicated for 30 min. After that, the separated light black, brown colloid (rGO/MnO₂) was collected by centrifuge and washed 3-4 times with ultrapure water for the removal of K⁺ ions present in the reaction mixture. Similarly, other rGO/MnO₂ samples having different rGO (0.25 and 1 g) were prepared for the comparative study.

Synthesis of pure MnO₂ nanoparticles [26]

The synthesis of MnO₂ nanoparticles occurred by a redox reaction of KMnO₄ and Mn(AC)₂. First 0.01 mol KMnO₄ and 0.015 mol Mn(AC)₂ were separately dissolved in two beakers that contained 50 mL distilled water. Then the Mn(AC)₂ solution stay at 60 °C under continuously and add the prepared solution of KMnO₄ dropwise. The temprature of mixture was maintained at 60 °C under continuously stirring for 24 h and pH of solution was adjusted to 7. After that, the solution was filtered and washed with deionized water until the filtrate was colorless and at 100 °C for 12 h.

Photocatalytic oxidative 2-naphthol coupling experiment

For the photocatalytic oxidative coupling reaction, 2-naphthol (1.0 mmol), toluene (10 ml) and photocatalyst (100 mg) were taken in a round bottomed flask, and the resulting mixture was irradiated with visible light (20 W LED) at room temperature with stirring for 12 h under oxygen atmosphere. After completion of the reaction, the catalyst was separated from reaction mixture via syringe filter. The obtained crude product was purified by column chromatography on the SiO₂ gel using ethyl acetate-hexane (4:6) as eluent. The pure products were characterized by ¹H NMR and ¹³C NMR.

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Full Paper

An economical and easily accessible semiconductor-metal hybrid, synthesized by grafting of MnO_2 NPs to reduced graphene oxide, has been reported for the self-dimerization of 2-naphthols using oxygen under visible light irradiation. The excellent synergy between MnO_2 with rGO support through metal- π interaction make the developed photocatalyst much more active as compared to the individual components.



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Photochemical Oxidative Coupling of 2-Naphthols using hybrid rGO/MnO₂ Nanocomposite under Visible Light Irradiation