



Visible light assisted reduction of nitrobenzenes using $\text{Fe}(\text{bpy})_3^{+2}/\text{rGO}$ nanocomposite as photocatalyst



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ABSTRACT

Visible-light-induced photocatalytic reduction of aromatic nitrobenzenes to the corresponding anilines at room temperature using reduced graphene oxide (rGO) immobilized iron(II) bipyridine complex as photocatalyst is described. The rGO-immobilized iron catalyst exhibited superior catalytic activity than homogeneous iron(II) bipyridine complex and much higher than metal free rGO photocatalysts. The heterogeneous photocatalyst was found to be robust and could easily be recovered and reused for several runs without any significant loss in photocatalytic activity.

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1. Introduction

The reduction of nitrobenzenes to the corresponding anilines is an industrially important reaction because anilines are important intermediates for the synthesis of dyes, biologically active compounds, pharmaceuticals, rubber, photographic and agricultural chemicals [1,2]. The traditional methods for reduction of nitrobenzenes include catalytic hydrogenation, electrolytic reduction, and metal catalyzed reductions [3–5]. However these processes suffer from certain drawbacks such as the use of potentially explosive H_2 gas, high pressure reactors, hazardous and harmful reagents like mineral acids etc. Furthermore, the catalytic reduction of a nitro compound using hydrogen gas is generally carried out at a high temperature (100–150 °C) and high pressure (10–50 bar) which provide low selectivity of the product mainly due to the nonselective hydrogenation of other functional groups [6,7].

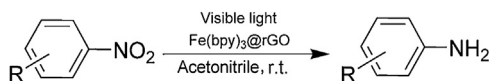
In recent years, photocatalytic reduction of nitrobenzene into aniline using semiconductor photocatalysts has gained considerable interest as these reactions occur under mild and ambient temperature conditions [8,9]. Among the known semiconductors, TiO_2 based heterogeneous photocatalysts have been widely used for reduction of nitrobenzenes [10–12]. However, these photocatalysts work only under UV irradiation, which is a small part of

the solar spectrum and also need special reaction vessels. In order to improve their efficiency in the visible region, surface modification of the TiO_2 photocatalyst by doping of metal or metal oxides, oxide halides i.e. PbPnO_2X (Pn = Bi, Sb; X = Br, Cl) and sensitization with dyes has also been demonstrated [13–15]. However, transition metal doping commonly generates a discrete level in the forbidden band of the photocatalyst, which causes low-mobility of electrons and holes in the dopant level and thus provide limited activity enhancement. Recently metal complexes owing to their fascinating properties such as higher stability in the reaction medium, higher visible light absorbance and better charge separation have been distinguished to be superior and efficient photocatalysts in organic transformations over conventional organic synthesis [16]. Among the known metal complexes, $[\text{Ru}(\text{bpy})_3]^{2+}$ complex has widely been used, however its limited accessibility, high cost and toxic nature makes its utility limited from practical viewpoints [17,18]. Furthermore, homogeneous nature of the catalyst and its higher solubility in common organic solvents along with water makes its recovery and recycling difficult. To address the issue associated with the catalyst recovery, immobilization of these metal complexes to photoactive semiconductor supports constitute a logical and promising approach [19]. The immobilization of metal complexes to photoactive support not only enhances their efficiency but also make their recovery and recycling feasible [20,21].

Since its discovery in 2004, graphene has attracted considerable interest owing to its unique mechanical, thermal, optical, and electrical properties [22]. The unique two dimensional structures

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Scheme 1. Visible light assisted photoreduction of nitrobenzenes.

with its high specific surface area have made graphene an attractive photocatalyst as well as ideal support for constructing new type of graphene-based photocatalysts for photocatalytic reactions [23]. In this regard, extensive research work has done on the development of novel graphene-based semiconductor photocatalysts for photocatalytic hydrogen generation and CO₂ reduction [24,25]. For example Xiang et al., recently published a review on semiconductor graphene based photocatalysts for solar fuel production including hydrogen generation and CO₂ reduction [26]. Putri et al., reviewed the applications of heteroatom doped graphene in photocatalysis [27]. Min et al., reported dye-cosensitized graphene/Pt photocatalyst for high efficient visible light hydrogen evolution [28]. Kong et al., reported novel Pt–Sn alloy decorated graphene nanohybrid [29] and amorphous CoSn_xO_y decorated graphene nanohybrid photocatalyst for highly efficient photocatalytic hydrogen evolution [30]. In another report they described dye-Sensitized NiS_x catalyst decorated on graphene for highly efficient reduction of water to hydrogen under visible light irradiation [31]. Similarly a number of reports are known on photocatalytic CO₂ reduction using graphene based photocatalysts [32]. In this regard, we have recently reported graphene oxide immobilized cobalt phthalocyanine [33] and ruthenium trinuclear polyazaine complex [34] for the photo-reduction carbon dioxide to methanol under visible light irradiation.

In the present paper we have synthesized a low cost, easily available and environmentally benign iron bipyridine [Fe(II)(bpy)₃]²⁺ complex which subsequently grafted to rGO support to make it recoverable and recyclable. The synthesized heterogeneous (Fe(bpy)₃@rGO **3**) catalyst was used for the photoreduction of nitrobenzenes to corresponding anilines using hydrazine hydrate at room temperature under visible light irradiation (Scheme 1).

2. Experimental section

2.1. Materials

Iron(II) chloride (98%), 2,2'-bipyridine (99%), graphite flakes, ammonium hexafluoro phosphate (99.9%) was purchased from Aldrich were of analytical grade and used without further purification. All other chemicals were of A.R. grade and used without further purification.

2.2. Synthesis of [Fe(II)(bpy)₃](PF₆)₂ complex [35]

In a typical synthesis, 0.80 mmol iron(II) chloride (0.1 g) was dissolved in a minimum amount of water and in another solution 2.56 mmol bipyridine (0.4 g) was dissolved in a minimum amount of ethanol. Both solutions were mixed together under stirring and then an aqueous solution of ammonium hexafluorophosphate was added to obtain a deep red color precipitate. The obtained precipitate was collected by filtration and washed with cold water and ethanol. Yield: 75%, UV–vis (λ_{\max}) = 285 nm, and 523 nm.

2.3. Synthesis of graphene oxide [36]

Exfoliated graphene oxide was synthesized by oxidation of graphite with KMnO₄ and H₂SO₄ according to the literature procedure. Briefly, in a round bottom flask immersed in a ice bath, 2 g graphite flakes were taken and then 68 mL H₂SO₄, 1.50 g sodium nitrate was added; the resulting suspension was stirred for 5 min.

Then 9.0 g KMnO₄ was added slowly to this mixture and the resulting mixture was stirred for additional 5 days. Next to this 5% diluted H₂SO₄ (100 mL) was added and heated at 90 °C for 2 h with continuous stirring. To this mixture 30 wt% H₂O₂ solution (approximately 5.4 mL) was added and stirred for 2 h at room temperature. The raw GO was isolated by centrifugation (6000 rpm) and washed with H₂SO₄ (3 wt%), H₂O₂ (0.5 wt%) and HCl (3 wt%). Final washing was done with distilled water until pH of filtrate became neutral to get exfoliated graphene oxide.

2.4. Synthesis of reduced graphene oxide [37]

Reduced graphene oxide was synthesized by hydrothermal method by using water and ethanol as a solvent. GO (400 mg) was dispersed in water/ethanol (60 mL/30 mL) mixture and sonicated for 2 h. The obtained suspension was transferred to a 100 mL teflon-sealed autoclave and maintained at 120 °C for 24 h. This hydrothermal treatment reduces oxygen carrying functionalities of graphene oxide. The resulting reduced graphene oxide (rGO) was recovered by filtration, washed by water, and dried at 60 °C for 24 h.

2.5. Synthesis of iron(II) bipyridine and reduced graphene oxide nanocomposite

For the synthesis of Fe(bpy)₃@rGO nanocomposite 0.25 g of [Fe(bpy)₃]PF₆ and 1.0 g reduced graphene oxide was added in 250 mL acetonitrile/water (1/1) mixture. This mixture was sonicated for 30 min to dispersing the reduced graphene oxide. Then obtained mixture was stirred for 24 h at room temperature. The obtained catalyst was filtered with PTFE filter and washed with acetonitrile and water. Fe content of synthesized catalyst was found to be 1.1 wt% (0.197 mmol/g) as determined by ICP-AES analysis. Thus the calculated value of loading of Fe(bpy)₃(PF₆)₂ complex in composite should be 16 wt%.

2.6. Photocatalytic reduction of nitrobenzene

The photocatalytic activity of synthesized catalyst was checked under visible light by using 20 W LED (Model No. HP-FL-20W-F-Hope LED Opto-Electric Co., Ltd., $\lambda > 400$ nm). In a borosil round bottom flask 25 mg of Fe(bpy)₃@rGO catalyst was taken and 25 mL of acetonitrile/DCM(dichloromethane)/methanol was added. The resulting mixture was sonicated for 10 min to disperse the catalyst. Next to this 0.1 mmol aromatic nitro compound and 1 mmol hydrazine monohydrate was added to round bottomed flask and sealed with a rubber septum. The reaction mixture was irradiated in visible light with the collection of samples at regular intervals. The collected samples were analyzed by TLC and GC to monitor the progress of reaction. After completion of reaction solvent was removed under reduced pressure and the crude product was purified by column chromatography. The identification of product was done by GC–MS and ¹H NMR.

2.7. Chemical and structural characterizations

The rough structure of materials was determined with the help of scanning electron microscopy (SEM) image collected on FE-SEM (Jeol Model JSM-6340F). To get fine morphologies of the synthesized materials, high resolution transmission electron microscopy was performed by using FEI-Tecnaig² TwinTEM operating at an acceleration voltage of 200 kV. The samples for HR-TEM were obtained by dispersing them into a minimum amount of water and deposited carbon coated copper grid. Vibrational spectra of samples for executing various functional groups was collected by using Fourier transform infrared spectroscopy and recorded on

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