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Nickel oxide nanoparticles grafted on reduced graphene oxide (rGO/NiO) as efficient photocatalyst for reduction of nitroaromatics under visible light irradiation

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Graphical Abstract

Nickel oxide nanoparticles grafted on reduced graphene oxide (rGO/Ni) as efficient photocatalyst for reduction of nitroaromatics under visible light irradiation



Highlights of the research

- Facile synthetic methodology for large scale production of nickel nanoparticles decorated reduced graphene oxide via simultaneous reduction of simultaneous chemical reduction of GO and NiCl₂ with sodium borohydride (NaBH₄)
- Photocatalytic reduction of nitroaromatics to corresponding amino compounds under visible light irradiation
- Facile recovery of the photocatalyst via external magnetic effect
- Efficient recycling of the photocatalyst without significant loss in activity.
- Cost effective and mild synthetic methodology for the decomposition of organic pollutants to safer compounds by visible light.

Abstract

Nickel oxide nanoparticles were grafted on reduced graphene oxide *via* simultaneous reduction of graphene oxide and nickel salt in a single step reaction. The synthesized material (rGO/NiO) was found to be efficient visible light active photocatalyst for the reduction of nitroaromatic derivatives to their corresponding amino compounds. Hydrazine monohydrate provided necessary protons and electrons for the targeted reaction. After completion of the reaction, the photocatalyst could readily be recovered by simple external magnet and could be reused for six runs without any significant loss of its activity. More importantly, the photocatalyst did not show any leaching during the reaction as confirmed by ICP-AES analysis of the recovered catalyst.

Keywords: Photocatalyst, reduced graphene oxide, nickel oxide nanoparticles, reduction, nitrobenzene

1. Introduction

Development of green and sustainable methodologies for organic transformations has become a prime need in current day chemistry. Among the known approaches, light assisted transformations particularly using visible light are of prime importance due to its plentiful availability and inexpensive nature [1, 2]. Apart from the photodegradation of organic pollutants and waste water treatments [3-5], the development of photocatalytic chemical conversions is gaining considerable interest and growing rapidly worldwide in current years [6, 7].

The reduction of nitrocompounds to the corresponding amines is an important transformation owing to the pharmaceutical importance of these compounds as reactive

intermediates in the synthesis of various bioactive compounds [8-10]. Apart from the conventional approaches which generate copious amounts of undesirable waste [11, 12], photocatalytic reduction using UV light in the presence of TiO₂ based semiconductor photocatalysts has also been well documented in the literature [13]. However, the main drawback is the use of UV radiation which consists of only 5% part of solar spectrum and requires special reaction vessels. Thus, the visible light assisted methodology for the reduction of nitrocompounds to amines is highly desired. To achieve this goal, a number of surface modifications of the TiO₂ photocatalyst by doping metal or metal oxides, oxide halides (*i.e.*, PbPnO₂X (Pn = Bi, Sb; X = Br, Cl) and sensitization with dyes have been reported to perform the reaction under visible light [14-17]. In addition to these reports, Ag/Bi₂MoO₆ [18], Fe(bpy)₂⁺³/rGO [19], Ni@npg-C₃N₄ [20] and Ni(II)-porphyrin metal-organic framework [21] have also been recently reported for this transformation. However, the tedious and multi-step synthesis of these photocatalysts leaves a scope for the further development in this area.

Graphene, owing to its outstanding thermal, mechanical and electrical properties has come out to be an exciting and promising material in recent decades for diversified applications in various fields, including adsorption, photocatalysis and heterogeneous catalysis, etc [22, 23]. Properties such as high surface area and absence of mass transfer barriers make this material extremely suitable in catalysis as a new form of carbon material [23]. The solution-based chemical reduction of exfoliated graphene oxide is the most suitable approach for the efficient production of reduced graphene oxide (rGO) sheets owing to its low-cost and massive scalability and an affordable technique for the large-scale production of rGO sheets. In addition, owing to the presence of sp² carbon sheets and sp³ carbons bonded with additional oxygen groups graphene oxide/reduced graphene oxide behave like a semiconductor. The sp² carbon network has mobile electrons due to π conjugated system that

behaves like conduction band while sp³ carbons have tightly held electrons which behave like valence band [24-25]. Thus, because of the presence of conduction and valence band, GO/rGO have a band gap and act like a semiconductor in photocatalytic transformations. The presence of oxygen functional groups in GO/rGO can also act as nucleation centers or anchoring sites for the landing of nanoparticles [26], limiting the nanoparticles growth and improving their stability and dispersion on the rGO surface. At the same time, these nanoparticles can help to enlarge the interplanar spacing of the rGO sheets, limiting their stacking, and thus maintain the excellent properties of individual rGO nanosheets [26]. Some of the current studies on graphene-based nanocomposites have shown that a synergistic combination of metal/metal oxide nanoparticles with graphene sheets enhances their properties and performances, which make them utilizable in various fields.

Nickel-based nanoparticles (Ni NPs) have received considerable attention recently, because of their low cost and remarkable catalytic performance in hydrogenation of nitrobenzene and nitrophenol, reduction of oxygen and oxidation of olefins [27-28], etc. Recently, several reports described the synthesis of Ni NPs/graphene nanocomposites. The most common synthetic methodology to produce these nanocomposites is based on the simultaneous reduction of both nickel salt and GO [29], or the reduction of nickel salt in the presence of rGO. For example, Ji and co-workers [30] synthesized reduced graphene oxide/Ni (rGO/Ni) nanocomposites *via* one step reduction of a mixture of nickel chloride (NiCl₂) and graphene oxide (GO) with hydrazine hydrate at 100 °C for 3 h under N₂ atmosphere. Yang et al. [31] used hydrothermal method for the preparation of rGO-Ni(OH)₂ composites from nickel nitrate [Ni(NO₃)₂·6H₂O] mixed with GO in DMF at 180 °C for 12 h. The dried rGO-Ni(OH)₂ composite was calcined at 250°C for 4 h in air to obtain the final black colored product, the rGO–NiO composite. Zhu et al. [32] prepared a rGO/NiO composite by homogeneous co-precipitation and subsequent annealing. Urea and NiCl₂

solutions were slowly and sequentially added to GO and heated at 90 °C for 1.5 h. However, long experimental time and high-temperature calcination are required during all the procedures.

Herein, we report a facile low-temperature solution method for the large-scale synthesis of rGO/NiO nanocomposites and their application as photocatalysts for reduction of nitrocompounds to corresponding amines under visible light irradiation (**Scheme 1**).

2. Experimental

Materials

The chemical reagents are of analytical grade and were used as received without further purification. Graphite powder (< 20 micron), potassium permanganate (KMnO₄), sulphuric acid (H₂SO₄), phosphoric acid (H₃PO₄), hydrogen peroxide (H₂O₂), nickel chloride (NiCl₂), sodium borohydride (NaBH₄) were purchased from Sigma-Aldrich. All substrates and solvents were purchased from Merck India Ltd (Mumbai, Maharashtra, India) and used without further purification.

Preparation of graphene oxide (GO)

GO was prepared from graphite according to the modified Hummers' method. Briefly, graphite flakes (2 g) were placed in a round bottom flask and the flask was immersed in an ice bath. Then H₂SO₄ (68 mL) and sodium nitrate (1.50 g) were added simultaneously and stirred for 5 min. After that KMnO₄ (9.0 g) was added slowly to this mixture and stirred for 5 days. 100 mL diluted H₂SO₄ (5 wt %) were added to this and heated at 90 °C for 2 h with continuous stirring. After that 30 wt % H₂O₂ solution (approximately 5.4 mL) was added and stirred for 2 h at room temperature. GO was collected by centrifugation (6000 rpm) of the mixture and washed with H₂SO₄ (3 wt%), H₂O₂ (0.5 wt%) and HCl (3 wt%). Finally washing was done with distilled water until pH of washing became neutral. A homogeneous yellow brown suspension (1 mg mL⁻¹) of GO sheets in deionized water (DI) was achieved by

ultrasonication for 3 h. Preparation of rGO/NiO nanocomposite was achieved by simultaneous chemical reduction of GO and NiCl₂ with sodium borohydride (NaBH₄). Typically, to 5 mL of GO (1 mg mL⁻¹) in DI water, sonicated for about 20 min to form a homogeneous dispersion, was added NiCl₂ (9, 19 or 38 mg) and the mixture was sonicated for 30 min. Then 5 mL of NaBH₄ (0.1 M) aqueous solution was added to the mixture at room temperature. A spontaneous formation of a black precipitate was observed. The precipitate was washed repeatedly with water and separated by centrifugation. The products were signed as rGO/NiO-1, rGO/NiO-2 and rGO/NiO-3 according to the feeding amount of 9, 19, and 38 mg of NiCl₂.6H₂O, respectively. The nickel content in the synthesized composites was found to be 0.2, 0.35 and 0.5 mmol/g as determined by ICP-AES analysis.

Characterization

X-Ray Diffraction (XRD)

X-ray diffraction patterns for determining the phase structure and crystalline properties of the materials were obtained on a Bruker D8 Advance diffractometer (Billerica, MA, USA) working at 40 kV and 40 mA with Cu K_a radiation ($\lambda = 0.15418$ nm).

Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) imaging was performed with a FEI Tecnai G2-20 twin operating at 200 kV. For that purpose, the rGO/NiO composites were dispersed on a thin carbon film of a 3 mm diameter copper grid. It was equipped with a CCD camera and a Digital Zicrograph software for the acquisition of electron diffraction patterns, and the dark-field and high-resolution imaging.

FTIR spectroscopy

Fourier transform infrared (FTIR) spectra were recorded using a Thermo Scientific FTIR instrument (Nicolet 8700). Dried rGO/NiO sample (1 mg) was mixed with KBr powder (100 mg) in an agate mortar. The mixture was pressed into a pellet under 10 tons load for 2–4 min,

and the spectrum was recorded immediately. Sixteen accumulative scans were collected. The signal from a pure KBr pellet was subtracted as the background.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) measurements were carried out in Al₂O₃ crucibles in a nitrogen atmosphere at a heating rate of 10°C/min using a TA Instruments Q50 thermogravimetric analyzer.

X-ray photoelectron spectroscopy (XPS)

For X-ray photoelectron spectroscopy (XPS) analysis, the samples were prepared by casting 50 μ L of an aqueous solution of rGO/NiO composite onto a clean silicon wafer followed by drying in an oven at 80°C to remove the solvent. XPS measurements were performed with an ESCALAB 220 XL spectrometer from Vacuum Generators featuring a monochromatic Al Ka X-ray source (1486.6 eV) and a spherical energy analyzer operated in the CAE (constant analyzer energy) mode (CAE=100 eV for survey spectra and CAE=40 eV for high-resolution spectra), using the electromagnetic lens mode. The detection angle of the photoelectrons is 30°, as referenced to the sample surface. After subtraction of the Shirley-type background, the core-level spectra were decomposed into their components with mixed Gaussian-Lorentzian (30:70) shape lines using the CasaXPS software. Quantification calculations were performed using sensitivity factors supplied by PHI.

Raman measurements

Micro-Raman measurements were carried out using a visible Labram HR spectrometer (Horiba Gr, France). The Raman backscattering was excited with 532 nm excitation wavelength. The beam was focused on the sample surface through an optical objective to a spot less than 1 μ m. The samples were prepared by casting 50 μ L of an aqueous solution of rGO/NiO composite onto a clean silicon wafer followed by drying in an oven at 80 °C to remove the solvent.

Experimental procedure for the photocatalytic reduction of nitroaromatics

Photocatalytic activity experiments were performed under visible light using a 20 watt LED (Model No. HP-FL-20W-F-Hope LED Opto-Electric Co., Ltd (Shenzhen, China), $\lambda > 400$ nm). Intensity of the light at vessel was measured by light meter (Lutron Electronic Light Meter) and was found to be 70 W/m². In a typical reaction, a round bottom flask was charged with 50 mg of rGO/NiO photocatalyst, 1 mmol of nitrobenzene and 2 mmol of hydrazine monohydrate in 20 mL solvent mixture of acetonitrile/DCM/methanol. The resulting mixture was subjected to sonication and then irradiated under visible light. All the experiments were performed under the inert atmosphere in the presence of nitrogen. Progress of the reaction was monitored by withdrawing the samples at certain time intervals and analyzed by gas chromatography-flame ionization detector (GC-FID). After the completion of the reaction, the photocatalyst was recovered by external magnet and the resulting filtrate was concentrated under reduced pressure. Thus obtained crude product was isolated using column chromatography. The identification of product was done by gas chromatography-mass spectrometry (GC-MS).

3. Results and discussion

Synthesis and characterization of rGO/NiO nanocomposites

In the present study, the required rGO/NiO nanocomposites having different nickel contents were prepared by simultaneous chemical reduction of GO and NiCl₂ with sodium borohydride (NaBH₄), as depicted in **Scheme 2**. The obtained products were signed as rGO/NiO-1, rGO/NiO-2 and rGO/NiO-3 according to the feeding amount of 9, 19 and 38 mg of NiCl₂.6H₂O, respectively. The nickel content in the synthesized composites was found to be 0.2, 0.3 and 0.5 mmol/g, respectively as determined by ICP-AES analysis. Among all the three composites, rGO/NiO-3 showed the highest catalytic activity, therefore its detailed characterization and catalytic results are discussed in the following section.

The HR-TEM images of the synthesized rGO/NiO-3 nanocomposite are displayed in **Fig. 1**. They reveal that the shape of the NiO NPs varies from nearly spherical to ellipsoidal and irregular morphologies; they are closely attached to rGO sheets with an average diameter of 2-10 nm.

The HRTEM image and SAED pattern of rGO/NiO-3 composite are provided to further reveal the structure of Ni. As shown in **Fig. 2** (**a**,**d**), the HRTEM images have atomic columns at positions (see the fast Fourier transform (FFT) in the insets of **Fig. 2b** and **c**) compatible with the structure of rGO with the lattice fringe spacing of 0.37 nm, corresponding to the interplanar spacing of (002) planes. The selected area electronic diffraction pattern (SAED) displays rings that reveal the ultra-small NiO NPs on rGO with a polycrystalline nature (inset of **Fig. 2d**), in accordance with reported data [33, 34].

X-ray photoelectron spectroscopy (XPS) analysis also confirms the formation of rGO/NiO-3 nanocomposite. The XPS survey spectrum of the nanocomposite comprises carbon (C_{1s}), oxygen (O_{1s}) and nickel (Ni_{2p}) in full accordance with the chemical composition of the material with a high Ni atomic concentration (14.58%) as shown in **Fig. 3A**.

The Ni_{2p} high resolution XPS spectrum comprises four distinctive peaks at 854.4, 860.4, 872.5 and 878.6 eV. The peaks at 854.4 and 860.4 eV are assigned to Ni_{2p_{3/2} and its satellite, while the features at 872.5 and 878.6 eV are due to Ni_{2p_{1/2} and its satellite. The binding energy values are consistent with those reported for NiO [35-37]. The absence of a peak at 852.6 \pm 0.4 eV indicates that the amount of Ni metal in the composite is negligible [37, 38]. Similarly, the absence of an XPS peak at 856.6 eV and its satellite at 862.4 eV due to Ni_{2p_{3/2} [37] suggests that Ni(OH)₂ was not formed during the chemical process.}}}

The C_{1s} high resolution XPS spectrum of the initial GO is displayed in **Fig. 4A**. It consists of peaks due to Csp^2 (283.9 eV), C-O (286.2 eV) and C=O (287.4 eV). After reaction of GO with NiCl₂ in the presence of NaBH₄, the peak at 283.9 eV becomes predominant, while the peaks at 286.2 and 287.4 eV are greatly decreased, suggesting that the chemical process removes most of the oxygen containing groups and therefore restores partially the graphenic network (**Fig. 4B**). A new peak at 290.8 eV appears in the C_{1s} XPS spectrum assigned to O-C=O.

The Raman spectra of GO and rGO/NiO-3 are depicted in **Fig. 5**. The Raman spectrum of GO displays two prominent peaks at 1345 cm⁻¹ (D band) and 1607 cm⁻¹ (G band), corresponding to the E_{2g} vibrational mode of sp²-bonded carbon atoms in a two-dimensional hexagonal lattice and the breathing mode of κ -point photons of A_{Ig} symmetry, respectively. The peak intensity ratio of the D and G band (I_D/I_G) is commonly used as a measure of the disorder degree in the materials. The starting GO shows an I_D/I_G of 0.72.

The Raman spectrum of rGO/NiO exhibits the D band (1358.6 cm⁻¹) and G band (1584.6 cm⁻¹) of the chemically reduced graphene oxide (rGO) with an intensity ratio (I_D/I_G) of 1.09, along with peaks at 360, 536, 681 and 1073 cm⁻¹ due to the shaking peaks of NiO [39-40]. The peaks at 360 and 536 cm⁻¹ could be assigned to the first order transverse optical (1TO) and longitudinal optical (1LO) phonon modes of NiO, respectively. The peaks at 680 and 1073 cm⁻¹ could be attributed to second order transverse optical (2TO) and longitudinal optical (2LO) phonon modes of NiO [39].

Comparing with GO, the G band of rGO/NiO is found to shift from 1607 to 1584.6 cm⁻¹, which is attributed to the recovery of the hexagonal network of carbon atoms in rGO/NiO as reported in the literature [41].

The thermal properties of the rGO/NiO-3 nanocomposite were investigated by TG–DSC analysis (**Fig. 6**). The rGO/NiO-3 nanocomposite exhibits a three-step thermal decomposition. The first mass loss (4.5 wt%) below 200 °C is due to the removal of adsorbed water and evaporation of the intercalated water molecules. The second weight loss (25.3 wt%) in the temperature range of 200–600°C is attributed to the decomposition of the labile oxygen-containing functional groups present in rGO. The weight loss (2.4 wt%) observed above 600 °C results from the pyrolysis of the carbon skeleton of rGO nanosheets.

The FTIR spectra of GO and rGO/NiO-3 nanocomposite are depicted in **Fig. 7**. The main peaks observed at 3412, 1742, 1630, 1422, 1232 and 1068 cm⁻¹ in the FTIR spectrum of GO are attributed to the stretching vibrations of O–H, C=O, C=C, C-C, C–O and C–O–C, respectively. The intensities of these peaks decreased significantly after formation of NiO nanoparticles on rGO sheets due to the reduction of the oxygen containing functional groups during the chemical process. Indeed, after reduction of GO with NaBH₄, the peaks due to O–H, C–O (epoxy) and C–O (alkoxy) stretchings decreased dramatically, some of them disappeared entirely. The disappearance of C=O peak at 1742 cm⁻¹ in the FTIR spectrum of rGO/NiO-3 further supports GO partial reduction to rGO. In addition, the appearance of the peak at 615 cm⁻¹ related to NiO confirmed the presence of NiO NPs on rGO sheets (Fig. 7)

The XRD patterns of the synthesized fresh and recovered rGO/NiO are shown in Fig. 8. It is clear from (Fig. 8) that the photocatalyst consists of crystalline NiO phases. All the diffraction peaks in this pattern can be indexed to a single phase of face-centered cubic NiO,

which matches well with JCPDS card no. 47-1049. The absence of peaks related to $Ni(OH)_2$ in the XRD pattern, confirmed that $Ni(OH)_2$ was not formed during the reduction process.

Photocatalytic reduction of nitrobenzenes

The photocatalytic activity of the synthesized NiNPs, rGO and rGO/NiO 1-3 was tested for the reduction of nitrobenzene as a model substrate using hydrazine monohydrate as a proton source under visible light irradiation. The results of these optimization experiments are summarized in **Table 1**. There was no conversion obtained with pristine nickel nanoparticles (Ni NPs) (Table 1, entry 1). However, the yield of product was found to be 15.6 % when rGO was used as a photocatalyst (Table 1, entry 2). In order to check the effect of nickel content on the photocatalytic reactivity, three samples having different Ni-content i.e. 9, 19, and 38 mg of NiCl₂.6H₂O, respectively were synthesized. The yield of product increased with the nickel content and was found to be 54.6 % and 72.6 %, respectively, when rGO/NiO-1 (0.2 Ni mmol/g) and rGO/NiO-2 (0.35 Ni mmol) were used as photocatalysts under identical conditions (Table 1, entry 3-4). In case of using rGO/NiO-3 (0.5 Ni mmol/g) as photocatalyst almost quantitative conversion with 97.2% yield of aniline was obtained within 8 h (Table 1, entry 5). Further increase in nickel content (0.75 mmol/g) did not show any significant effect on the activity and afforded almost similar yield (97.5 %). However, a large excess of Ni (1.0 mmol/g) on the GO surface makes the photocatalyst less reactive (78.5% conversion), which is believed to be due to increased electron-hole recombination and reaching of saturation point where further transfer of electrons from Ni to substrate might not be possible (Table 1, entry 7). Therefore, 0.5 mmol/g was the optimum loading and used for the detailed study. Furthermore, the reaction did not take place in dark conditions at ambient temperature in all cases as shown in Table 1 (entries 1-5). At higher temperature (65 °C) under identical

(62%) after 24 h. However, the use of visible light under mild conditions represents the

conditions in dark, the reaction was found to occur and afforded moderate product yield

advantage of the present methodology over thermally catalyzed reaction at higher temperature. These results indicated that although reaction may occur at thermally higher temperature, light illumination is essential to progress the reaction efficiently. The presence of hydrazine hydrate as a source of protons and electrons was found to be vital and no reaction occurred in its absence (Table 1, entry 5). Furthermore, 50 mg of photocatalyst amount was found to be optimum and further increase in catalyst amount did not influence the reaction to any significant extent. We have used solvent mixture (acetonitrile/dichloromethane/methanol) for the photocatalytic reactions owing to the better solubility of the substrates and good dispersion of the photocatalyst in the reaction medium. In case of using acetonitrile and methanol mixture, slightly poor product yield (88.5%) was obtained which we assume due to the poor mixing/solubility of the substrates. Whereas, the reaction was found to be slow in mixture of dichloromethane and methanol, which is attributed to the poor mixing/solubility in both solvents. The reaction in acetonitrile alone also provided poor conversion (65%) which is most likely due to the poor dispersion of the catalyst. The presence of methanol was found to be beneficial for better dispersion of the photocatalyst during the reaction. However, the mixing of ternary solvent system (acetonitrile, dichloromethane and methanol) provided better homogenous medium along with better solubility of the substrates and good dispersion of the photocatalyst for the reaction, thus we have chosen this combination as reaction medium for the experiments.

Further, the reaction was explored for various substituted nitrobenzene derivatives under optimized reaction conditions and the results are summarized in **Table 2**. All the substrates showed high to excellent conversion to corresponding amino derivatives within 8-10 h without revealing any significant effect of the substituents. More particularly, the substrates having electron donating groups required comparatively lesser reaction times than the

substrates having electron withdrawing groups. In the present study, hydrazine hydrate has been used as sacrificial agent that provided necessary electron and protons for the reduction of nitrocompounds.

Recycling experiments were also conducted in order to study the photocatalytic stability and activity. Under the above optimized reaction conditions, reduction of nitrobenzene was performed to check the recycling of the photocatalyst. After completion of the reaction, the photocatalyst was recovered by external magnetic effect and the resulting filtrate was subjected to usual workup and GC analysis. The recovered photocatalyst was washed with methanol, dried and used for subsequent runs. The recovered photocatalyst was reused for subsequent six runs. The results of these experiments are summarized in **Fig. 9**. No significant loss was observed in the activity of the recycled catalyst, and the product yield remained almost unchanged even after six recycling experiments, which confirmed the true heterogeneous nature of the developed photocatalyst. Furthermore, an inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis of the photocatalyst after six recycling experiments showed a nickel content of 0.48 mmol/g which is nearly similar to that of a fresh catalyst (0.5 mmol/g). These results confirmed that the developed photocatalyst had not shown any leaching and was truly heterogeneous in nature (**Fig. 9**).

Mechanism of the reaction

The exact mechanism of the reaction is not known at this stage; however, based on the analytical results and existing literature, a plausible mechanism is proposed as shown in Scheme 3. According to the existing reports, reduction of nitrobenzene to aniline can proceed by two possible reaction pathways [24,42]. The first direct route includes nitrosobenzene and N-phenylhydroxylamine intermediates, while second condensation route include

condensation of nitrosobenzene and N-phenylhydroxylamine to give azoxybenzene, azobenzene and hydrazobenzene intermediates. In order to confirm the reaction pathway, we had withdrawn aliquots from the reaction mixture after 8 and 16 h for HPLC analysis (Agilent 1120 compact LC equipped with a Qualisil BDS C-18 column with a flow rate of 1 mL/min and the eluent consisted of 70% methanol and 30% water solution) (Figure 10). The appearance of nitrosobenzene, N-phenylhydroxylamine and aniline peaks in the HPLC chromatogram confirmed the formation of these intermediates (direct route). Next, we performed the photoreduction of azobenzene under similar reaction conditions. After the reaction only hydrazobenzene can be obtained and no aniline was detected, which further confirmed that photoreduction of nitrobenzene proceeded through direct route with the formation of nitrosobenzene and N-phenylhydroxylamine as reactive intermediates.

Furthermore, rGO/NiO-3 exhibits a large absorbance in the 1.5-6.5 eV range (Figure 11). The peak close to 6 eV could be due to rGO and/or to NiO [43]. The very large absorption in the 1.5 - 4.7 eV range could result only from the presence to defects present in NiO [44] as the absorption of rGO at these low energies has much decreased. Under visible light, electronic transitions between the valence band (VB) and defects energy levels located in the band gap of NiO leave free holes in the VB. Similarly, transitions between defects energy levels and the conduction band (CB) create free electrons in the CB. Therefore free carriers are able to reach the NiO-rGO interface, thus becoming available for redox reaction.

Reduced graphene oxide (rGO) due to the presence of extensive network of conjugated sp² carbons provides excellent mobility of electrons which prevents the electron-hole recombination. Thus due to the better charge separation on the rGO sheets the electrons are easily available for the reduction of nitrobenzene however the holes generated in the valence band of NiO provide oxidation of hydrazine hydrate. Hydrazine works as sacrificial electron and proton donor for the reduction (Scheme 3).

Conclusion

The present paper demonstrated a facile methodology for large scale synthesis of nickel oxide nanoparticles decorated reduced graphene oxide (rGO/NiO) *via* simultaneous chemical reduction of GO and NiCl₂ with sodium borohydride (NaBH₄). The developed material was found to be as efficient visible light active photocatalyst for the reduction of nitroaromatic derivatives to their corresponding amino compounds. Hydrazine monohydrate was used as the source of protons and electrons for the targeted reaction. After completion of the reaction, the photocatalyst could readily be recovered by simple external magnet and could be reused for six runs without any significant loss of its activity. The developed synthetic procedure and application of rGO/NiO will provide a viable solution for the decomposition of organic pollutant such as nitrobenzenes under mild visible light irradiation.

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Fig. 1: High resolution transmission electron microscopy (HRTEM) images of rGO/Ni nanocomposite.



Fig. 2: HRTEM images (a), fast Fourier transform (FFT) (b), high profile of NiO NPs on rGO, and (d) SAED of rGO/NiO nanocomposite.



Fig. 3: X-ray photoelectron spectroscopy (XPS) analysis: (A) survey and (B) Ni_{2p} high resolution spectra of rGO/NiO-3.



Fig. 4: C_{1s} high resolution XPS spectra of (A) GO and (B) rGO/NiO-3 nanocomposite.



Fig. 5. Raman spectra of GO and rGO/NiO nanocomposite.



Fig. 6: TGA and DTG curves of rGO/NiO nanocomposite.



Fig. 7: FTIR spectra of GO and rGO/NiO-3 nanocomposite.



Fig.8: Wide angle XRD of: a) Fresh rGO/NiO; b) Recovered rGO/NiO.



Figure 9: The photocatalytic performance of rGO-NiO-3.



Figure 10: HPLC chromatograms of aliquots withdrawn from the reaction mixture after 8 and 16 h.



Figure 11: Absorbance plot of rGO-NiO-3.



Scheme 1: rGO/NiO-catalyzed photoreduction of nitrobenzenes.



Scheme 2. Schematic illustration of the synthesis of rGO/NiO nanocomposites.



Scheme 3: Plausible mechanistic pathway for the rGO/NiO-3 catalyzed photoreduction of nitrocompounds.

Entry	Catalyst	Conditions	Time (h)	Aniline yield (%)	TOF
				b	(h ⁻¹)
1	NiNPs	Dark	24	-	-
		Visible light	12	-	-
2	rGO	Dark	24	-	-
		Visible light	12	15.6	1.3
3	rGO/NiO-1	Dark	24	-	-
		Visible light	12	54.2	4.5
4	rGO/NiO-2	Dark	24	-	-
		Visible light	8	72.0	9.0
5	rGO/NiO-3	Dark	24	Trace	-
		Visible light	8	97.2	12.2
		Visible light	24 °	- ^c	_ c

Table 1. Results of optimization experiments ^a.

^a Reaction conditions: nitrobenzene, 1.0 mmol; photocatalyst 50 mg; hydrazine monohydrate, 2 mmol; Irradiation, White cold 20 W light emitting diode (LED) $\lambda > 400$ nm, Power at reaction vessel 70 W/m²; ^bIsolated yield; ^cwithout hydrazine monohydrate.

Entry	Reactant	Product	Time/h	Conversion (%) ^b	Yield (%) ^c	TOF (h ⁻¹)
1			8.0	98.0	97.2	12.2
2	H ₃ C-	H ₃ C-NH ₂	8.0	98.5	97.4	12.2
3			8.0	95.2	94.2	11.7
4	H ₃ CO-NO ₂	H ₃ CO-NH ₂	8.0	95.1	94.8	11.8
5			8.0	96.0	95.2	11.9
6			10.0	93.6	92.4	9.2
7	Br - NO ₂	Br - NH ₂	10.0	92.4	93.2	9.3
8		I-NH2	10.0	90.4	89.2	8.9
9	F ₃ C-V-NO ₂	F ₃ C-V-NH ₂	10.0	85.4	83.6	8.3

nes. ^a

^a Reaction conditions: nitro compound, 1.0 mmol; rGO/NiO-3, 50 mg; hydrazine monohydrate, 2 mmol; Irradiation, White cold 20 W LED $\lambda > 400$ nm, Power at reaction vessel 70 W/m²; ^bConversion was determined by gas chromatography (GC); ^c Isolated yield.