Biomolecule-Mediated Generation of Ru Nanocatalyst for Sustainable Reduction of Nitrobenzene

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ABSTRACT: A mild and sustainable synthetic route was followed for the generation of biomolecule-assisted Ru nanocatalyst under open as well as inert atmosphere using the polyphenol morin. The nanocatalyst was characterized thoroughly by powder X-ray diffraction, N₂ adsorption–desorption, high-resolution transmission electron microscopy, dynamic light scattering, X-ray photoelectron spectroscopy, absorption spectroscopy, Fourier transform infrared spectroscopy, fluorescence spectroscopy, thermogravimetric analysis, and inductively coupled plasma optical emission spectrometry. The nanocatalyst reveals excellent catalytic activity for the reduction of several substituted nitrobenzene to aniline derivatives under simple, mild, and environment-friendly conditions. The catalyst can be reused for four consecutive cycles without significant loss in its catalytic activity.

INTRODUCTION

Study related to nanocatalysts (NCs) is one of the most attractive and frontline areas of modern research due to their diverse applications in innumerable branches of science. The unique properties of NCs, including large surface-to-volume ratio and numerous accessible active sites compared to their bulk counterparts, make these materials most favorable for organic transformations. Organic transformations using NCs are in vogue as they offer several benefits like excellent atom economy, placid reaction conditions, ease of separation of the synthesized products as well as catalysts, etc. Therefore, extensive research for efficient design and sustainable production of highly active metal or metal oxide NCs is exceedingly worthwhile. Several literature reports are available describing novel methods for the synthesis of metal-based NCs.⁴⁻⁹ Nanodimensional noble metals, mainly palladium, platinum, and ruthenium have captured significant interest, due to their high activity and selectivity toward several catalytic processes,⁶⁻¹⁰ including selective hydrogenation of chloro nitrobenzene (p-CNBr).¹¹ Although ruthenium is a low-cost material, a recyclable Ru-based catalyst would make the methodology many-fold cost-effective, environment-friendly, and industrially efficient. The widely studied methods for the generation of nanodimensional Ru catalysts utilize the conventional reduction process with drastic reaction conditions.¹¹⁻¹²

Reduction using biomolecules has gradually captured the limelight of researchers due to the increasing environmental, economic, as well as industrial concern. In this connection, plant extract or plant-mediated materials have revealed their capability to convert metal ions into their nanostate often through a simple process without requirement of any rigorous experimental setup. Significantly, phytochemicals like polyphenols, phenolic acids, alkaloids, terpenoids, sugars, etc., present in plant metabolites, probably partake in the biosynthesis of metal and/or metal oxide nanoparticles (NPs). In an effort to harness such nanodimensional Ru, Kannan and Sundrarajan have reported the synthesis of ruthenium oxide NPs using Acalypha indica plant extract,¹³ wherein they studied the antimicrobial activity of the NPs. Ismail et al. have reported a green synthesis of ruthenium oxide NPs using aqueous extract of Aspalathus linearis and deposited over nickel foam to develop a supercapacitor.¹⁴ Synthesis of Se/Ru alloy was reported by Zhou et al., with the help of gallic acid as both reducing and stabilizing agent,¹⁵ which was further studied for the possibility of its biomedical applications. Reports on green syntheses of nanodimensional ruthenium for catalytic applications are scarce excepting a few.¹⁶⁻¹⁷ Generation of nanodimensional Ru employing the vast family of biomolecules still remains to be unveiled and explored for their magnificent catalytic properties. Some literature reports are tabulated here, which describe the syntheses of Ru-NCs under different conditions (Table 1).

Formation of aniline derivatives is of significant interest due to the pharmaceutical as well as industrial concerns.⁰²¹
Aniline and its derivatives widely participate in the synthesis of several valuable compounds, including pharmaceuticals, pigments, pesticides, herbicides, rigid polyurethane, etc. Aniline acts as the building block for the synthesis of different peptides, amino acids, etc. Moreover, synthesis of aniline derivatives is crucial due to its manifold applications in various fields such as production of consumer goods, adhesives/sealants, coatings, textile materials, pulp and care, rubber fields such as production of consumer goods, adhesives/sealants, coatings, textile materials, pulp and care, rubber

In the present study, we have described an efficient green synthesis of ruthenium nanocatalysts using a flavonoid-type biomolecule, morin as stabilizing agent at room temperature (Scheme 1). The synthesis has been done both in open atmosphere and in N₂ environment. Morin is a naturally available polyphenol commonly obtained from Maclura pomifera and Maclura tinctoria and from the leaves of Psidium guajava. It can act as a reducing agent as well as stabilizing agent during nanosynthesis. The as-synthesized nanomaterials have been employed for the reduction of nitroarenes to furnish aromatic amines and their derivatives with good to excellent product yields.

**CHARACTERIZATION**

**Absorption Spectroscopy.** Absorption spectroscopy was used to find the best condition for the preparation of NCs. The time scan data established the possible mechanism behind the formation of the NCs. To get the best condition of NC formation, 0.2 mL of 10 mM alcoholic solution of morin was taken in 2.5 mL solution of different pH values (viz., 5, 7, 9, and 12). The alcoholic solution of morin has its characteristic absorption maximum at ~330 nm. Then, 0.01 mL portion of 1 mM RuCl₃ solution was gradually added to the above morin-containing solution of different pH values.

**N₂ Adsorption–Desorption and BET Analysis.** N₂ adsorption–desorption was performed using the solid sample to determine the specific surface properties of the material. The specific surface area, pore size distribution, and pore volume of the solid material can be obtained after degassing the material at 300 °C in a surface area analyzer instrument for 3 h. Finally, the specific surface area of the NCs can also be obtained using Brunauer–Emmett–Teller (BET) method.

**TEM analysis.** The TEM analysis was performed after dispersing 2 mg of the NC in 2 mL of water–alcohol (1:1) mixture and sonicating for 1 h. Then, the dispersed solution was drop-cast on a carbon-coated Cu grid. Before getting the TEM images of the material, the grid was dried under an IR lamp.

**FTIR Analysis.** FTIR analysis was used to get an idea about the bond vibrations of the NCs. A very small amount of the solid material was thoroughly mixed with dry KBr using a mortar and pestle. The sample was then pelletized using pressure around 5 ton using a hydraulic press. The pellet was then loaded in the sample holder of the analyzer instrument.

**Powder XRD.** Powder XRD was used to determine the crystalline nature of the prepared NCs. Powder sample was taken in a rectangular metal holder and then the arrangement was lightly pressed before the X-ray crystallographic analysis.

**Dynamic Light Scattering (DLS).** Dynamic light scattering experiment was carried out to estimate the hydrodynamic radii of the NCs. The sample preparation method is similar to that of the TEM experiment. The dispersed solution obtained after sonication for 1 h was further diluted ~100 times to perform the experiment.

**Thermogravimetric Analysis (TGA).** The thermal properties of the NC were determined using the thermogravimetric analysis technique under N₂ atmosphere with a flow rate of 10 mL/min. An ~6 mg of solid sample was taken on a platinum pan and heated to ~439 °C at a heating rate of 10 °C/min to record the change of weight percentage with the change of temperature.

**X-ray Photoelectron Spectroscopy (XPS) Analysis.** The elemental composition and the oxidation state of the central metal ion were analyzed using this technique. A monochromated Al Kα was used as X-ray source with X-ray spot size of 900 × 900 μm² outfitted with the XPS instrument. A flood gun was used for uniform charge neutralization. The binding energies (BEs) of Ru 3d (~280 eV), C 1s (~285 eV), N 1s (~400 eV), and O 1s (~531 eV) were obtained using both full survey and narrow scan methods. The full survey scan was repeated five times with step size of 1 eV, pass energy of 150 eV, and dwell time of 50 ms, whereas the narrow scan was repeated 15 times with step size and pass energy of 0.1 and 20 eV, respectively, and dwell time of 100 ms. Due to the very close binding energy of Ru 3d and C 1s, Ru 3p (BE ~475 eV)
was also acquired using the narrow scan method. All of the data were examined using Thermo Advantage Software (version 5.952) taking a smart background.

**ICP-OES Analysis.** Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the amount of ruthenium in the catalyst and also the leaching percentage of the Ru from the catalyst after the reaction. To get the amount of ruthenium in the catalyst, 0.6 mg of solid catalyst was digested in hot and concentrated HNO₃. To achieve leaching of the catalyst, 6 mg of the catalyst was treated with nitrobenzene, water, and reducing agent as in the reaction mixture (as described in the following section). After the reaction was complete, the reaction mixture was centrifuged. The reaction mixture was collected separately, and the solid catalyst was again washed with water and then centrifuged again. Finally, the reaction mixture was digested with hot and concentrated HNO₃. After three successive addition and evaporation of concentrated acid, the solid masses so obtained were cooled to room temperature. Finally, the solid masses were treated with a requisite amount of Milli-Q water. Then, the aqueous solutions were filtered using a microsyringe filter (pore size, 0.22 μm). The filtrates were then diluted with water to a particular volume, and then the solutions were introduced in the ICP-OES instrument.

**Catalytic Activity for Reduction of Nitrobenzene to Aniline.** The NCs designated as Ru-morin@air and Ru-morin@N₂ were studied for their catalytic activities toward reduction of nitrobenzene to aniline in the presence of NaBH₄ as a reducing agent and water as a solvent at 100 °C. After completion of the reaction (as indicated by TLC), and separation of the catalyst, the reaction mixture was extracted using ethyl acetate (3 × 10 mL). The organic part was washed with water and dried using anhydrous sodium sulfate. Then, the solvent was evaporated under reduced pressure to get the solid mass that was purified by column chromatography using pet ether and ethyl acetate as eluent to get the pure product. The identity of the product was confirmed by ¹H and ¹³C NMR spectroscopy.

**Recycling Experiment.** At the end of the reaction, Ru-morin@N₂ NC was separated from the reaction medium by centrifugation. Particularly, Ru-morin@N₂ NC was chosen for the recycling experiment as it showed better catalytic activity. The collected NC was repetitively rinsed with water and ethyl acetate, followed by diethyl ether. Finally, the NC was dried at 80 °C temperature for 1 h to activate for the next run.

# RESULTS AND DISCUSSION

**Absorption Spectroscopy.** The best condition for the formation of the NC was pH 12, as indicated by the absorption spectra. At this pH, a sharp increase in the absorbance (λ_max = 330 nm) occurred with gradual addition of RuCl₃ solution to the morin solution of pH 12. The Benesi–Hildebrand (B–H) (Figure 1 and inset) plot indicates that the stoichiometry and association constant for the interaction between ruthenium and morin at pH 12 were 1:1 and 1235.83 M⁻¹, respectively, using eq 1

\[
\frac{1}{A - A_0} = \frac{1}{A_1 - A_0} + \frac{1}{(A_1 - A_0)K_a[M]}
\]

where \(A_0\) is the absorbance of morin solution in the absence of ruthenium, \(A_1\) is the absorbance of morin solution when it is completely bound with ruthenium, \(A\) is the absorbance of morin solution with gradual addition of ruthenium, [M] is the concentration of ruthenium, and \(K_a\) is the binding or association constant.38

The absorption spectral changes of morin solution at pH values 5, 7, and 9 with increasing Ru concentration were insignificant and are pictorially described in supplementary figures (Figures S1–S3).

**Mechanism of Formation of NCs.** The possible mechanism for the formation of NC was established using time-dependent absorption spectroscopy. To study the mechanism, the metal solution and alcoholic solution of morin were taken in equimolar ratio at pH 12 in a cuvette and then the absorbance value of the resulting solution was measured at 330 nm continuously up to 4.5 h (Figure 2). The initial hike followed by achieving a maximum suggested an increase in monomer concentration which resulted due to burst nucleation governed by the LaMer mechanism. Thereafter, a steady increase in the absorbance for ruthenium-morin NC proposed a rapid autocatalytic growth according to the Finke–Watzky model.39

**N₂ Adsorption–Desorption and BET Analysis.** The catalytic activity of porous materials may be related to their surface activity, which is again dependent on their pore diameter. This can be found in agreement with earlier studies.40,41 The catalyst in this was also found to be mesoporous as can be seen from the results of BET analysis. Figure 3 represents the N₂ adsorption–desorption curve of the

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**Figure 1.** UV interaction data and B–H plot (inset) between morin (79–76 μM) and ruthenium (4–30 μM) at pH 12.

**Figure 2.** Time scan profile for Ru-morin@air NC material at pH 12.
Ru-morin@air and Ru-morin@N2 NCs. From the figure, it is clear that the surface properties of Ru-morin@air show a convex type of isotherm with a blunt knee at a lower P/P₀ value and an elevated adsorption at higher P/P₀ value. This type of isotherm (type II) is generally obtained for unhampered monolayer–multilayer adsorption at high P/P₀. The small knee indicates a major overlap of monolayer adsorption and initiation of multilayer adsorption. The width of the adsorption layer increased at P/P₀ = 1. An H3 hysteresis loop was obtained for Ru-morin@air which is typical for nonrigid platelike assembly at the surface of the NCs. The adsorption–desorption study for Ru-morin@N2 shows type IV isotherm with H4 hysteresis loop. This type of isotherm is common for mesoporous adsorbent in which the adsorbent–adsorptive interaction plays a key role in determining the adsorption behavior of the adsorbent. Similar to type II isotherm, the monolayer–multilayer adsorption takes place by the pore condensation phenomenon. The H4 hysteresis loop has the characteristics of aggregated particles as obtained from TEM study also (discussed in the following section). For Ru-morin@N₂, the change of the nature of the isotherm and the hysteresis loop is also in agreement with the change of surface morphology in inert atmosphere. The BET specific surface areas of Ru-morin@air and Ru-morin@N2 NCs are 4.72 and 24.11 m²/g, respectively. The porous nature of each of the adsorbent is obtained from this characterization and shows the average pore diameter for Ru-morin@air and Ru-morin@N₂ to be 8.33 and 7.82 nm, respectively.

**TEM Analysis.** Figure 4 represents the TEM images of the prepared NCs, Ru-morin@air, and Ru-morin@N₂ and confirms that they are formed in nanodimensions. The TEM images indicate significant differences for Ru-morin@air and Ru-morin@N₂. For Ru-morin@air, frail lattice fringes with nanocrystalline and fine porosity were observed. However, for Ru-morin@N₂, the TEM image shows an aggregated mass of the NCs with hardly any nanocrystallinity. The selected area electron diffraction (SAED) pattern (Figure 5) of the NCs reflected the same observation as from the TEM images. The particle size of the NCs was estimated using histogram analysis. From the histogram data, we obtained that the average particle size of Ru-morin@air and Ru-morin@N₂ lies in the range of 20–10 nm (Figure 6). There is a slight decrease in average particle size in N₂ atmosphere. However, there is an enhanced tendency for agglomeration in inert atmosphere, which arises due to higher interparticle interactions in the inert atmosphere. These results are in good agreement with the literature reports that suggest the change of surface morphology with the implementation of inert atmosphere.

**FTIR Analysis.** To get information about the bond vibrations of the NCs, the solid-state FTIR spectroscopy was performed. We tried to compare the bond frequencies present in the NC to that of the pure morin molecule to get a clear idea about the change, appearance, or disappearance of bond vibrations. Figure 7 represents the FTIR spectra of pure morin, Ru-morin@air, and Ru-morin@N₂ NCs. On inspection of the three spectra, we found that, on NC formation, a clear change is observed in the 1612–831 cm⁻¹ region. For Ru-morin@air, the peak at 1612 cm⁻¹ for C═C stretching vibration present in morin was shifted to 1619 cm⁻¹. The two peaks at 1515 and 1445 cm⁻¹ for aromatic C═C stretching and in-plane C–C–H bending present in morin moiety completely disappeared in Ru-morin@air. The peak at 1376 cm⁻¹ for –OH bending vibration and in-plane bending vibration of the C–O–H group present in morin molecule was shifted to 1383 cm⁻¹ in Ru-morin@air. Two peaks of morin at 1294 and 1163 cm⁻¹ for asymmetric stretching of Ph–O bond and aromatic C–H bending, respectively, absolutely disappeared in Ru-morin@air. Rather a new peak at 1121 cm⁻¹ for in-plane C–H bending.

**Figure 3.** N₂ adsorption–desorption isotherm of Ru-morin@air and Ru-morin@N₂ NCs.

**Figure 4.** TEM images of Ru-morin@air and Ru-morin@N₂ NCs.

**Figure 5.** SAED pattern of Ru-morin@air and Ru-morin@N₂ NCs.

**Figure 6.** Histogram of Ru-morin@air and Ru-morin@N₂ NCs.
vibration appeared upon NC formation in open atmosphere (Ru-morin@air). Another new peak at 1867 cm\(^{-1}\) appeared due to metal–CO bond vibration in Ru-morin@air NC. The peak at 831 cm\(^{-1}\) for twisting vibration of the C–O bond was absent in the NC materials. For Ru-morin@N\(_2\), although the change in bond frequency is less prominent than that for Ru-morin@air, yet we tried to elaborate the situation. The peak at 1612 cm\(^{-1}\) in morin was shifted to 1625 cm\(^{-1}\) in the Ru-morin@N\(_2\) NCs. The peak at 1515 cm\(^{-1}\) in the morin moiety remained unaltered on NC formation, whereas the intensity of the peak at 1445 cm\(^{-1}\) was measurably lowered and a new peak at 1417 cm\(^{-1}\) appeared owing to =C–H bending vibration in the NC. The peak at 1163 cm\(^{-1}\) in the morin was shifted to 1182 cm\(^{-1}\) upon NC formation. Another new peak at 989 cm\(^{-1}\) due to C–H bond vibration appeared in the Ru-morin@N\(_2\) NC. The peak at 831 cm\(^{-1}\) in morin was shifted to 836 cm\(^{-1}\) in the Ru-morin@N\(_2\) NC material. One new peak at 1805 cm\(^{-1}\) appeared in this NC owing to the metal–CO bond vibration. The results with individual band identifications are presented in Table 2. The FTIR data suggest that although there is bonding between functionalities of morin and metal, no subsequent oxidation of morin could be observed, suggesting that morin is acting as a stabilizing agent.

**Powder XRD.** Figure S4 represents the powder X-ray diffraction pattern of Ru-morin@air and Ru-morin@N\(_2\) NCs. No major diffraction pattern in the PXRD of either of the two materials was observed. Although the TEM image and SAED pattern of Ru-morin@air indicate the nanocrystalline nature of the material, the PXRD pattern grossly reflects its amorphous nature. This can be attributed to the experimental setup of the two characterization tools. For TEM or SAED, we generally focus on a very particular portion of the NC in its microenvironment. But for PXRD, the result is basically the average behavior of a larger portion of the material. For Ru-morin@N\(_2\) both the results are in agreement with each other and indicate the amorphous nature of the material.

**DLS Measurement.** From DLS analysis, the hydrodynamic radii of Ru-morin@air and Ru-morin@N\(_2\) NCs were obtained.
as 614 and 46 nm, respectively (Figure 8). The anomalies in the particle size compared to the TEM experiment are due to the enhanced hydrodynamic radius of the NCs in solution phase present in the colloidal solution.53 The larger increase in the hydrodynamic radius for Ru-morin@air compared to Ru-morin@N2 may be attributed to the involvement of oxygen in the atmosphere that results in the generation of oxide-type particles with a resultant increase in the hydration environment. This trend in deviation is in good agreement with the results obtained from TEM experiment.

TGA Analysis. Figure 9 describes the TGA graph of the Ru-morin@N2 NC. The plot shows a gradual weight loss of the NC with the increase of temperature. But it is only 14% from the ambient temperature to 100 °C, which may be due to the presence of polyphenol moiety, which degrades upon heating. Although a significant mass loss was observed after 200 °C, as our reaction is carried out at ∼100 °C, we can say that up to this temperature, the catalyst is stable enough and is able to catalyze the reaction successfully.

XPS Data. The narrow scan XPS images of Ru 3d and C 1s of the two NCs are plotted in Figure 10. In spite of very close proximity of Ru 3d and C 1s binding energy, Ru 3d3/2 remains outside from that of the C 1s region and hence both of them can be analyzed simultaneously in the presence of one another. From the figure, it is clear that in both of the NCs, ruthenium is present in the form of RuCl3 and RuO3 although the atomic percentages are different. The table associated with Figure 10 reflects the atomic percentages of RuCl3 and RuO3 present in the two NCs. The lower atomic percentage of RuO3 for Ru-morin@N2 NC is quite obvious as the material is prepared in inert atmosphere. The participation of morin toward the formation of NCs was also varied upon change in the preparation environment. This was confirmed from the variation of atomic percentage of sp3 carbon, sp2 carbon, C=O, −O−C=O, and C−O−C carbons, as reflected in the table of Figure 10.

ICP-OES Analysis. From the ICP-OES technique, the amount of ruthenium in the catalyst was found to be 1.97 × 10⁻³ mol %. After the first run, the catalyst was regenerated from the reaction mixture, which was further analyzed for the amount of Ru that could have been leached from the catalyst during the reaction. It was found that only 1.28% of Ru has leached from the catalyst after the first cycle. Therefore, there was a fair possibility of recyclability of the catalyst, which was further confirmed by actually recycling it four times. The experiment is described below.

Catalytic Activity of the Ru-Based NCs. After the synthesis and thorough characterization, the reactivity of the NC was examined for the hydrogenation of nitroarenes to furnish aniline derivatives. We commenced our study by performing a series of experiments to screen the catalysts using nitrobenzene (1a) as the model substrate and sodium borohydride as the reducing agent (Table 3). During our preliminary experiments for the screening of the catalysts, Ru-morin NC formed under nitrogen atmosphere (Ru-morin@N2) has been shown to be the best catalyst followed by Ru-morin@air.

![Figure 8. DLS pattern of Ru-morin@air and Ru-morin@N2 NCs.](image-url)

![Figure 9. TGA graph for Ru-morin@N2 NC.](image-url)

![Figure 10. XPS images of Ru-morin@air and Ru-morin@N2 NCs.](image-url)

![Table 3. Screening of the Catalysts for the Nitrobenzene Reduction Using NaBH₄](table-url)
N₂) produced better product yields than Ru-morin@air (entries 1 and 2, Table 3). This is due to the fact that the NC entitled as Ru-morin@N₂ has a smaller particle size as well as a larger surface area (24.11 m²/g) than Ru-morin@air, which help to speed up the reaction rate through the binding of increasingly more reactant molecules over the surface of the NC. Besides, it was interesting to find that the newly synthesized NC (Ru-morin@N₂) is to some extent more reactive than the homogeneous RuCl₃ catalyst (entry 3, Table 3). Moreover, reduction reaction using only 6 mg of pristine morin as the active catalyst gave back the substrate 1a after 3 h (entry 4, Table 3). This signifies the inactivated nature of morin in this reaction.

After screening of the catalyst, Ru-morin@N₂ NC was employed to optimize the reaction conditions (Table 4). The reaction did not take place without any catalyst that ensures the principal role of the ruthenium NC in this reduction reaction (entry 1, Table 4). Several solvents, including ethanol, water—ethanol mixture (1:1), toluene, DMF, water, etc. (entries 2–6, Table 4), were screened, but except water, rest of them showed a detrimental effect on the product yield. The reactions were found to proceed satisfactorily under reflushing conditions (entries 6–8, Table 4). Besides, 6 mg of Ru-morin@N₂ NC (1.97 × 10⁻³ mol % of Ru) was found the best for this reduction reaction (entries 6, 11–12, Table 4).

Similar to that of the catalyst, reducing agent is also another important parameter for this reaction. The reaction did not furnish any product without any reducing agent (entry 1, Table 5). Several types of reducing agents were examined for this reaction (Table 5). Among them, SnCl₂, D-glucose, D-galactose, ascorbic acid, formic acid, and disodium tartrate remained unsuccessful to furnish any desired products (entries 2–7, Table 5). It was found that hydrazine monohydrate produced only around 60% yield, while sodium borohydride gives 91% yield under the same condition (entries 8 and 9, Table 5). The amount of NaBH₄ was also screened (entries 9–11, Table 5), and the best result was obtained in the presence of 0.5 mmol NaBH₄ using 6 mg of Ru-morin@N₂ (1.97 × 10⁻³ mol % of Ru) in water as the green solvent after 1.5 h of stirring under reflushing conditions.

After the attainment of the best reaction conditions, scope and efficiency of this methodology were further extended for the reduction of several substituted nitrobenzenes. Except aniline products, no side products were formed during the course of this reduction reaction, which undoubtedly signifies the selectivity of our newly synthesized methodology. The results are given in Table 6. Substrates having the phenyl ring substituted by electron-donating groups as well as electron-withdrawing groups bestowed good to best product yields using our optimized reaction conditions. Reduction of 1-methyl-3-nitrobenzene and 1-methoxy-2-nitrobenzene produced their corresponding amino products with 93 and 91% yields (entries 2 and 3, Table 6). The nitro group of 1-bromo-3-nitrobenzene was successfully reduced to furnish the amino product 3-bromoaniline with 89% yield (entry 4, Table 6). Our optimized reaction condition was found to be very selective toward the nitro group, keeping the −CN group unaffected in the case of 4-nitrobenzonitrile (entry 5, Table 6).

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<th>Table 4. Screening of Reaction Parameters for Nitrobenzene Reduction Using Ru-morin@N₂(^a)</th>
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\(^a\)Condition: PhNO₂ (0.1 mmol), NaBH₄ (0.5 mmol), Ru-morin@N₂, solvent (1.0 mL). \(^b\)Isolated yield.

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<th>Table 5. Screening of Reaction Parameters for Nitrobenzene Reduction Using Ru-morin@N₂(^a)</th>
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\(^a\)Condition: PhNO₂ (0.1 mmol), Ru-morin@N₂ (6 mg, 1.97 × 10⁻³ mol % of Ru), reducing agent (0.5 mmol), water (1.0 mL), 100 °C, 1.5 h. \(^b\)Isolated yield. 0.25 mmol NaBH₄ 1.0 mmol NaBH₄.

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<th>Table 6. Synthesis of Aniline Derivatives(^a),(^b),(^c),(^d)</th>
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\(^a\)Conditions: PhNO₂ (0.1 mmol), Ru-morin@N₂ (6 mg, 1.97 × 10⁻³ mol % of Ru), NaBH₄ (0.5 mmol), water (1.0 mL), 100 °C, time. \(^b\)NMR spectra are given in the Supporting Information (Figures S5–S9). \(^c\)Isolated yields. \(^d\)TOF = TON/time [TON = moles of substrate converted per mole of active site].


**RECYCLABILITY**

Capability of recycle and reuse are the principal advantages of a heterogeneous catalyst. To examine the recycling efficiency of the NCs, reduction reaction was performed using nitrobenzene as the model substrate. The recyclability chart of the NCs is presented in Figure 11. Further, the stability of the reused catalyst was examined by FTIR analysis (Figure 12) (Table 7), and from this spectrum and the table, it is quite clear that the newly synthesized Ru-morin@N₂ NC is significantly stable up to four cycles without a considerable loss in its activity.

The importance and efficiency of our methodology were compared to the literature reports.

**CONCLUSION**

In conclusion, a newly designed ruthenium-based nanocatalyst has been synthesized through a mild and eco-friendly methodology under inert atmosphere. Interestingly, the nanocatalyst provides excellent catalytic activity for the synthesis of several substituted anilines using water as green solvent. Our newly generated methodology showcases a number of advantages: (a) significantly lower time of reaction; (b) use of water as green solvent; (c) scope of wide functionalization; (d) small particle size of the NC; (e) ease of catalyst as well as product separation; (f) excellent turnover frequency; and (g) hassle-free technique for the synthesis of the NC. We have summarized a comparison of our work with the previously reported reduction methodologies of similar aromatic nitro compounds using Ru-based catalyst in Table 8. The all round advantage of water-based catalyst generation and reaction conditions together with a wide suitable ratio of reducing agent to starting material, product yield, and catalyst reusability make the method fairly attractive.

**EXPERIMENTAL SECTION**

Materials. Ruthenium(III) chloride hydrate (RuCl₃·xH₂O, MW: 207.43), morin hydrate [(2-(2,4-dihydroxyphenyl)-3,5,7-trihydroxychromen-4-one)], nitrobenzene (≥99.0%), and CDCl₃ were obtained from Sigma-Aldrich. All other reagents required for this study were of AR grade and used as obtained. All of the solvents used were distilled and dried before the actual use. Triple-distilled water was used throughout the experiment.

Apparatus. Absorption spectral data were acquired using PerkinElmer Lambda 25 UV−Vis spectrophotometer. Nitrogen adsorption−desorption isotherms were analyzed at liquid nitrogen temperature (77 K) using a Quantachrome surface area analyzer. The specific surface area and pore diameter were calculated using the Brunauer−Emmett−Teller (BET) method. Transmission electron microscopy (TEM) images were obtained using a Jeol JEM 2100 HR with electron energy loss spectroscopy (EELS). Fourier transform infrared (FTIR) spectra of the samples were recorded in the range 400−4000 cm⁻¹ on a PerkinElmer FT-IR 783 spectrophotometer having a resolution of 1 cm⁻¹ and PerkinElmer FT-IR Spectrum Two Spectrophotometer having a resolution of 0.5 cm⁻¹ using KBr pellets. A Mettler Toledo digital balance correct up to fourth decimal place was used for measuring the weights. A centrifuge machine Remi Elektrotechnik Ltd. R-4C was used to separate the supernatant solution of the nanoparticle. X-ray diffraction (XRD) was measured using X-PERT-PRO Panalytical diffractometer to confirm the actual phase of the prepared material. X-ray photoelectron spectroscopy (XPS) measurement was carried out using a Thermo Scientific Escalab 250 Xi system. The hydrodynamic radii of the NCs were estimated using Malvern Zetasizer Nano S, model ZEN 1600 dynamic light scattering (DLS) instrument. The thermogravimetric analysis of the NCs was conducted using Diamond TG/DTA Thermogravimetric/Differential Thermal Analyzer of PerkinElmer Instruments in the temperature range of 28−439 °C. A digital Mettler Toledo Seven Compact pH/ion meter was used to measure and adjust the pH of the solutions. The mol % of ruthenium present in the NCs was estimated using ICP-OES instrument (ICAP duo 6500, Thermo Fisher Scientific; RF power, 1150 W; flush pump rate, 50 rpm; analysis pump rate, 50 rpm; auxiliary gas flow, 1.0 L/min, Nebulizer gas flow, 0.60 L/min; coolant gas flow, 12 L/min; and wavelength, 287.876 nm). Thin-layer chromatography (TLC) analysis was performed on TLC silica gel 60 F₂₅⁴. The products were purified using silica gel (60−120 mesh) column chromatography. NMR spectra were recorded on a 300 and 400 MHz...
Table 8. Comparison Table for Previously Reported Method for Reduction of Nitrobenzene Using Ru-Based Catalyst with Our Method of Reduction

<table>
<thead>
<tr>
<th>starting material</th>
<th>corresponding amine derivative</th>
<th>catalyst</th>
<th>solvent</th>
<th>reducing agent(s)</th>
<th>reduction agent:starting material</th>
<th>reaction condition</th>
<th>yield (%)</th>
<th>no. of cycles</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-chloro nitrobenzene</td>
<td>p-chloro aniline</td>
<td>Ru/RGO(^a) composite</td>
<td>water:alcohol mixture((=1))</td>
<td>3 mPa H(_2) pressure((as \text{ H}_2\text{ source}))</td>
<td>60 (^\circ) C, 2 h in an autoclave</td>
<td>96</td>
<td>5</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>p-chloro nitrobenzene</td>
<td>p-chloro aniline</td>
<td>Ru(II)–Schiff-base catalyst</td>
<td>water</td>
<td>NaBH(_4)</td>
<td>4:1</td>
<td>RT(^b), 24 h</td>
<td>92</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>aniline</td>
<td>SBA-supported Ru catalyst</td>
<td>ethanol</td>
<td>N(_2)H(_4)</td>
<td>17:1</td>
<td>80 (^\circ) C, 21 h, air (&gt;99)</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R(^1)-NO(_2) + R(^2)-OH</td>
<td>R(^1)-NH-R(^2)</td>
<td>[Ru(p)-cymene)](_2)Cl(_2)</td>
<td>alcohol</td>
<td></td>
<td></td>
<td>DPPB(^d), K(_2)CO(_3), 130 (^\circ) C, Ar atm., 12 h</td>
<td>95</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>p-substituted nitrobenzene</td>
<td>p-substituted aniline</td>
<td>[Ru((bpy(_3))(_2(MeCN)(_2)])</td>
<td>methanol</td>
<td>NaBH(_4)</td>
<td>17:1</td>
<td>(\lambda &gt; 300 \text{ nm}, 5\ h)</td>
<td>99</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>aniline</td>
<td>Ru-CMK(^e)–3 nanoconjugate</td>
<td>water</td>
<td>NaBH(_4)</td>
<td>4:1</td>
<td>1200 rpm, 30 (^\circ) C, 1 h</td>
<td>56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nitro derivative of substituted</td>
<td>corresponding substituted</td>
<td>RuCl(_2(PPh(_3))(_3)</td>
<td>dioxane</td>
<td>SnCl(_2)2H(_2)O</td>
<td>1:2</td>
<td>18 (^\circ) C, 20 h, Ar atm.</td>
<td>61</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>benzene + (R'\text{CH}_2\text{CH}_2)(_3) (\text{NBr})</td>
<td>amine derivative</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>substituted nitrobenzene</td>
<td>substituted aniline</td>
<td>Ru/C nanoparticle</td>
<td>tetrahydrofuran</td>
<td>ethanol((as \text{ hydrogen source}))</td>
<td>3:1 to 15:1</td>
<td>KOH, toluene, 120 (^\circ) C, 12 h, 1 atm H(_2)</td>
<td>99</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>Ph-NO(_2) + PhCH(_2)OH</td>
<td>N-substituted amine</td>
<td>Ru(acac(_g))(_3)</td>
<td>chlorobenzene</td>
<td></td>
<td></td>
<td>DPPB(^f), KHCO(_3), PhCl, 150 (^\circ) C, 16 h, Ar atm.</td>
<td>94</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>aniline</td>
<td>ionic liquid-containing Ru catalyst</td>
<td>toluene</td>
<td>((\text{Cl}_2\text{)}_2\text{NHBH}_3)((as \text{ hydrogen source}))</td>
<td>6:1</td>
<td>RT(^b), 2−6 h</td>
<td>99</td>
<td>4</td>
<td>60</td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>N-substituted amine</td>
<td>Ru catalyst</td>
<td>toluene</td>
<td></td>
<td></td>
<td>KOrAmyl, benzyl alcohol, 120 (^\circ) C, 7 h</td>
<td>95</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>p-substituted nitrobenzene</td>
<td>p-substituted aniline and</td>
<td>polystyrene-conjugated Ru catalyst</td>
<td>chloroform or ethanol</td>
<td>N(_2)H(_4)</td>
<td>2.3:1 to 4.5:1</td>
<td>RT(^b), 30−90 h ((corresponding \text{ hydroxyl amine}))</td>
<td>98</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>corresponding hydroxyl amine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Reduced graphene oxide. \(^b\)Room temperature. \(^c\)Santa Barbara amorphous. \(^d\)1,2-Bis(diphenylphosphanyl)benzene. \(^e\)Bipyridine. \(^f\)Ordered mesoporous carbon. \(^g\)Acetylacetone. \(^h\)1,2-Bis(diphenylphosphino)ethane.
NMR instrument using CDCl₃ as solvents. The ¹H chemical shifts are reported in ppm relative to TMS.

**Synthesis of Ruthenium NCs at Open Atmosphere (Ru-morin@air).** Initially, 5 mL of 10 mM aqueous solution of RuCl₃ was prepared at ~18 °C. Then, it was added to 5 mL of 10 mM ethanolic solution of morin. Thereafter, the resulting solution was kept undisturbed overnight after adjusting the pH to ~12 using NaOH solution. The solution was then centrifuged at 2000 rpm for 10 min, and the supernatant solution was discarded. The residue was washed several times with a water:EtOH (1:1) mixture and case, the NC was washed several times with a water:EtOH (Ru-morin@air).

Initially, 5 mL of 10 mM aqueous solution (Ru-morin@N₂). Similar to that of Ru-morin@air. The only difference lies in the atmospheric condition of synthesis. Here, preparation of all of the solutions and the total synthesis procedure were carried out in a glovebox under N₂ atmosphere. As in the previous case, the NC was washed several times with a water:EtOH (1:1) mixture and finally dried before taking out of the N₂ atmosphere and designated as Ru-morin@N₂.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b02770. UV interaction between morin and ruthenium at pH 5, 7, and 9; PXRD pattern of Ru-NC; ¹H and ¹³C NMR spectra of the synthesized products; and related references (PDF)

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Notes

The authors declare no competing financial interest.

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**REFERENCES**


