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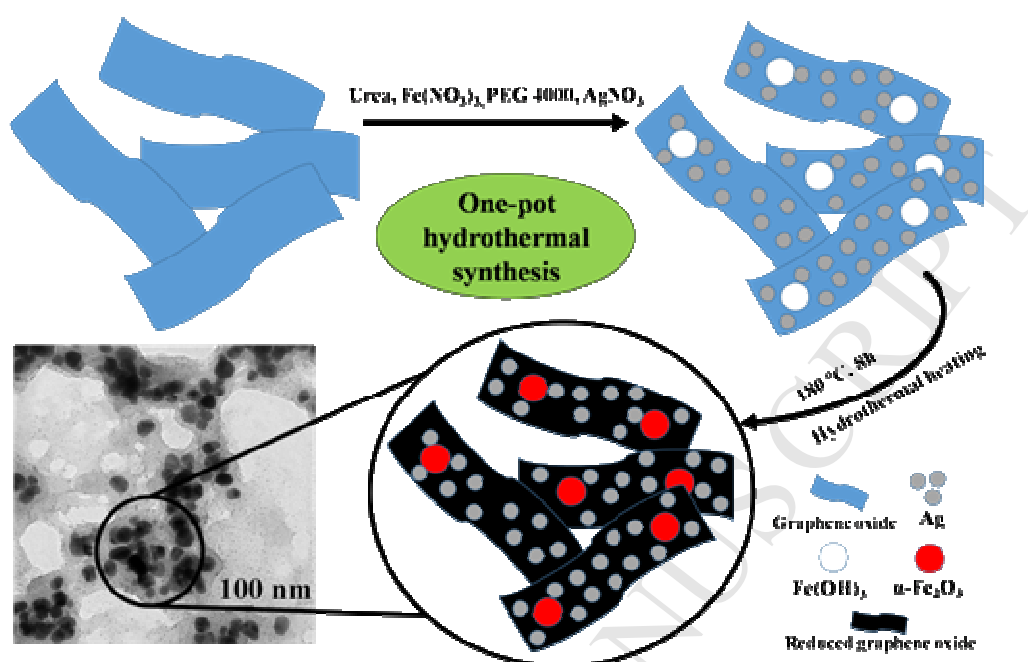
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Graphical abstract

One pot in-situ synthesis of Ag/Fe$_2$O$_3$ anchored rGO assisted by urea and PEG 4000 is described. The novel nanohybrid material (Ag/Fe$_2$O$_3$-rGO) is used as highly efficient magnetically separable heterogeneous catalyst for chemoselective reduction of nitroarenes to corresponding amines.

1 **Facile one-pot strategy to prepare Ag/Fe$_2$O$_3$ decorated reduced graphene oxide**

2 **nanocomposite and its catalytic application in chemoselective reduction of nitroarenes**

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9 **Abstract**

10 The present work reports about one-pot hydrothermal synthesis of a composite of Ag/Fe$_2$O$_3$

11 anchored on reduced graphene oxide (rGO) via homogeneous chemical precipitation of

12 Fe(OH)$_3$.and simultaneous reduction of Ag(I).The pristine aqueous suspension of graphene

13 oxide (GO) synthesized by Hummers method is mixed with Fe(NO$_3$)$_3$.9H$_2$O, AgNO$_3$, urea and

14 polyethylene glycol (PEG 4000).The mixture under hydrothermal conditions transforms into

15 Ag/α-Fe$_2$O$_3$-rGO nanohybrid. Here PEG 4000plays dual role of surfactant as well as reducing

16 agent for Ag(I). The synthesized Ag/Fe$_2$O$_3$-rGO nanocomposite was used as magnetically

17 recoverable catalyst for room-temperature chemoselective reduction of aromatic nitro groups to

18 the corresponding amines.

19 Keywords: Reduced graphene oxide; Magnetic catalyst; Nitroarenes; Chemoselective.

20 **1. Introduction**

21 Selective reduction of aromatic nitro compounds to amines is one of the highly useful organic

22 transformations[1]. Functionalized aromatic amines are important feedstock for the synthesis of

23 agrochemicals, dyes, pharmaceuticals, polymers, and various other industrially important fine

24 chemicals[2-4]. In industry, the reduction of nitroaromatics is carried out in the gas phase using a

25   nickel, copper or iron catalyst in the presence of various hydrogen sources[5,6]. The most

26   commonly used method for the production of aromatic amines is the reduction of corresponding

27   nitro substrates, using stoichiometric amounts of reducing agents. However, these traditional

28   noncatalytic processes are environmentally non-sustainable because of generation of the large

29   amount of waste[6-8]. Homogenous catalysts generally dissolve in reaction media, thus

30   providing more readily-accessible active catalytic sites, which results in mild reaction conditions

31   and good selectivity. These catalysts, however, have limited usages due to problems in

32   separating the products contaminated with unstable residuesas well asrecycling of the expensive

33   catalysts[9].Whereas the catalytic reductions of nitro groups in the presence of metal complexes,

34   metal sulfides or metal powder have various practical drawbacks, such as toxic by-products and

35   inefficient reusability[4,10-12]. Magnetic nanoparticles (NPs) can play a dual role in serving

36   both as catalysts as well as magnetic carriers of catalysts. Noble metal NPs possess fascinating

37   physicochemical properties and their catalytic activities have been extensively explored in recent

38   times. However, these NPs tend to aggregate due to their high surface energy during reaction

39   which eventually diminish their catalytic activity[13]. Industrial applications of these NPs are

40   also limited due to their high cost and poor recoverabilityfrom the reaction medium. These

41   problems are usually overcome by immobilizing noble metal NPs of specific shapes and sizes on

42   various solid supports[14-16]. Among the solid supports, magnetic NPs and porous carbon

43   materials have received great attention in recent past[17-18]. Magnetic nanoparticles are easy to

44   separate from the reaction medium by use of external magnet while carbon materials possess

45   high specific surface area. The combination of these types of materials may significantly can

46   further improve activity and dispersibility of noble metal NPs[19-22]. Recently, heterodimeric

47   nanocrystals with noble metals and iron oxides have been synthesized and used as magnetic

2

48 reusable catalyst. Park and co-workers synthesized Au-Fe$_3$O$_4$ heterodimer nanocatalysts and

49 applied them for the chemoselective reduction of nitro compounds[23]. Jang et al. reported a

50 simple and one pot synthesis of Rh-Fe$_3$O$_4$ heterodimer nanocatalyst and demonstrated their

51 application as magnetically recoverable catalyst for efficient and selective reduction of

52 nitroarenes[24]. A core-shell magnetic Fe@Au NPs anchored graphene oxide have been recently

53 reported for chemoselective and regioselective reduction of aromatic nitro group[19].

54 Recently,copper nanoparticles loaded on Fe$_3$O$_4$@SiO$_2$have been designed and catalytic

55 performance was investigated in the reduction of aromatic nitro compounds[25]. Although above

56 cited noble metal supported on iron oxide magnetic nanocatalysts have various advantages, such

57 as easy recovery and good efficiency, however their activity and selectivity are affected by steric

58 and diffusion factors[6]. Therefore, such heterodimeric nanocatalysts if supported on porous

59 carbon material, the surface area is substantially increased and nanocatalyst can be evenly

60 dispersed in the pores[26]. Graphene oxide has been proven to be one of the most important

61 porous carbon supports for anchoring metal nanoparticles[27-31].Graphene oxide possesses very

62 large specific surface area (up to 400 to 1500 m^2 g^{-1}) and also exhibits high utilization of its

63 surface area because both sides of its nanosheets are accessible[28,32].Therefore, there exists a

64 great possibility of high synergistic effect between noble metals and GO, which can greatly

65 enhance the performance of the material. Ag NPs supported on various metal and metal oxides

66 nanoparticles including magnetically recoverable nanoparticles have been the subject of

67 considerable interest for past several years[33]. To the best of our knowledge, Ag supported

68 Fe$_2$O$_3$ embedded on rGO has not been reported.As a part of our ongoing research on synthesis

69 and application of nanocatalysts[34-37], herein, we report development of one-pot hydrothermal

70 synthesis of Ag/Fe$_2$O$_3$ embedded rGO and studies of its catalytic activity for room-temperature

71 chemoselective reduction of aromatic nitro groups. The morphology, structure and composition

72 of as-prepared catalyst were characterized by various analytical techniques. The catalyst showed

73 superior performance and good selectivity for reduction of nitroarenesto amines by hydrazine

74 hydrate.

75 **2. Experimental**

76 2.1 Materials and physical measurements

77 Graphite powder, ferric nitrate and silver nitrate were purchased from Sigma Aldrich. Urea and

78 PEG 4000 were purchased from Merck India Ltd. Double distilled water was used throughout

79 the experiment. FT-IR spectrum was recorded on KBr matrix with Bruker 3000 Hyperion

80 Microscope with Vertex 80 FT-IR system. Thermogravimetric analysis (TGA) was performed in

81 air on a Netzsch STA449F3 thermal analyzer maintaining flow rate of 20 mL/min and heating

82 rate of 10°C/min. XRD measurements were carried out on a Bruker AXS D8-Advance powder

83 X-ray diffractometer with Cu-Kα radiation (λ=1.5418Å) with a scan speed of 2°/min.

84 Transmission electron microscopy images were obtained on a JEOL, JEM2100 equipment. The

85 sample powders were dispersed in ethanol under sonication and TEM grids were prepared using

86 a few drops of the dispersion followed by drying in air. Nitrogen adsorption-desorption

87 isotherms were obtained with a Micromeritics ASAP 2010 surface area and porosity analyzer.

88 Magnetism of the material was studied using a Lakeshore VSM 7410 at 300 K.

89 2.2 Synthesis of Graphene Oxide

90 Graphite powder (GP) was oxidized by modified Hummers method[38,39].In detail,

91 concentrated H_3PO_4 and concentrated H_2SO_4 were mixed in a 250 mL round bottomed flask

92 (RB), followed by addition of graphite powder. The RB was put in a preheated 50°C water bath

93 under magnetic stirring, followed by slow addition of $KMnO_4$ and the stirring was continued for

4

94 another 6 h.This was followed by addition of diluted H_2O_2 into the solution without interruption

95 until no bubbles were produced,while the color of the solution changed from black to purple and

96 finally became bright yellow. The mixture was stirred for another 3 h. The solid product thus

97 obtained was cooled to room temperature and separated by centrifuge. Product was then washed

98 with HCl (5%), alcohol, and deionized water to obtain the graphene oxide. The collected

99 sediment was dispersed in alcohol and treated ultrasonically. Subsequently, the concentration of

100 the graphene oxide suspension was calculated by weighing the mass of the sample after drying at

101 90°C for 24 h.

102 2.3 Synthesis of Ag/α-Fe$_2$O$_3$-rGO nanocomposite

103 An amount of 0.80 g of Fe(NO$_3$)$_3$.9H$_2$O (2 mmol) and 0.084 g of AgNO$_3$ (0.5 mmol) were added

104 to 20 mL of a 1.8 mg mL^{-1} GO aqueoussolution while stirring.To this 1.08 g of urea(0.0018 M)

105 and 2 g of PEG 4000 (0.5 mmol) were added and the above mixture was sonicated for 15 min at

106 25°C. After sonication for 15 min about 80 mL deionized water was added to the resulting

107 solution and transferred into a 100 mL Teflon-lined stainless steel autoclave, and heated at 180

108 °C in an electric oven for 8 h. The resulting black product was cooled to room temperature,

109 washed withdeionized water and ethanol several times. Finally, the productwas dried at 50°C in a

110 vacuum oven for 3 h. For comparison, bare nano Ag/α-Fe$_2$O$_3$ material without GO was also

111 prepared under the similar condition.

112 2.4General procedure for the room temperature reduction of nitroarenes

113 In a typical procedure, 1.0 mmol of aromatic nitro compound was slowly added to the stirred

114 aqueous suspension of 50 mg of freshly prepared nanoparticles catalysts (Ag/α-Fe$_2$O$_3$-rGO)and

115 the contents was stirredat room temperature for about 5 min. A total of 0.2 mL of hydrazine

116 monohydrate was then added to the mixture and the reaction contents was further stirred. Stirring

117   was continued for required time (Table 2) till complete conversion was achieved. Progress of the

118   reaction was monitored by thinlayer chromatography. After completion of the reaction, the

119   catalyst was separated magnetically from the reaction mixture and the product was extracted by

120   ethyl acetate (3×5 mL).The organic layer was dried over anhydrous Na_2SO_4 and filtered off, and

121   the solvent was evaporated at reduced pressure. All of the products were characterized by ^{1}H

122   NMR (400 MHz with TMS as the standard).

123   **3. Results and Discussion**

124   Synthesis of a composite of Ag/Fe_2O_3 anchored on rGO has been successfully achieved by

125   hydrothermal heating of a ferric hydroxide ($Fe(OH)_3$) precursor obtained by a homogeneous

126   chemical precipitation and simultaneous reduction of Ag(I) (Scheme 1). Here, urea was used for

127   hydroxylation. Urea decomposes at the experimental temperature to NH_3 and CO_2. NH_3

128   combines with water to produce ammonium (NH_4^+) and hydroxide (OH^-) ions. Here, hydroxide

129   anions are produced by hydration of urea, which cause a uniform rise in pH of the solution till

130   the solubility limit. The free OH^- ions then combines with Fe^{3+} ions forming $Fe(OH)_3$. It is

131   pertinent to mention here that polyethylene glycol (PEG) with uniform and ordered chain

132   structure can act as a very useful surfactant to control size and morphology of the nanomaterials.

133   Normally for reduction of GO to rGO, a reducing agent such as sodium borohydride, aluminium

134   hydride, hydrohalic acid, hydrazine etc. is required, but the main advantage of using urea lies in

135   the fact that no extra reducing agent is required. In the present synthesis, hydroxylating agent

136   urea also served as reducing agent for GO. Here, PEG 4000 also plays dual role assurfactant in

137   order to control the particle size, size distribution of the nanoparticles and as well as reducing

138   agent for $AgNO_3$.The Ag/α-Fe_2O_3 nanoparticles are grown on the surfaces of the reduced

139   grapheme oxide nanosheets through *in situ* reduction of the pristine GO under a hydrothermal

6

140 treatment at 180°C for 8 h. The main advantage in this process is that uniform rise in pH

141 prevents the occurrence of high local supersaturation, allowing nucleation to occur

142 homogeneously throughout the solution.

143   **<Scheme 1.>**

144 **3.1 Catalyst characterization**

145 **XRD analysis of the catalyst**

146   **<Fig.1.>**

147 The powder XRD pattern was recorded for identification of phases exhibited by the synthesized

148 material. Fig.1 shows the powder XRD pattern of the synthesized Ag/α-Fe$_2$O$_3$-rGO

149 nanocomposite. The diffraction peaks matches well with the reported data of α-Fe$_2$O$_3$ (JCPDS

150 File no. 87-1166). α-Fe$_2$O$_3$ possess a rhombohedrally centered hexagonal structure of the

151 corundum type with a close-packed oxygen lattice in which two thirds of the octahedral sites are

152 occupied by Fe(III) ions[40]. In addition, two diffraction peaks at 2θ values 38.19° and 44.46°

153 corresponds to (111), and (200) planes of face-centered cubic Ag (JCPDS File no. 87-0720).

154 This indicates formation of pure Ag/α-Fe$_2$O$_3$ nanoparticles. The Ag/α-Fe$_2$O$_3$-rGO nanocomposite

155 also showed an additional diffraction peak at 25.5° which can be attributed to (002) plane of

156 rGO. The average crystallite size of the synthesized Ag/α-Fe$_2$O$_3$-rGO nanocomposite was

157 estimated by the Debye-Scherrer equation [34], $d=k\lambda/\beta Cos\theta$, where'd' is the average crystallite

158 size, 'λ' is the wavelength of Cu-Kα radiation, 'β' is the full width at half maximum (FWHM) of

159 the highest intensity diffraction peak, 'θ' is the Bragg diffraction angle and 'k' is the shape

160 factor, whose value is about 0.9. The average crystallite size of the synthesized Ag/α-Fe$_2$O$_3$-rGO

161 nanocomposite was found to be 25.1 nm.

162 **TEM and EDSanalysis of the catalyst**

7

163   **<Fig.2.>**

164   The TEM image of the synthesized Ag/α-Fe$_2$O$_3$-rGO nanocompositeis shown in Fig.2. From the

165   TEM image it can be seen that the α-Fe$_2$O$_3$ and Ag nanoparticles are distributed homogeneously

166   in the rGO sheets. Fig.2b shows irregularly shaped particles of α-Fe$_2$O$_3$ with diameter 10-35 nm

167   and Ag NPs of size 2-5 nm. It can be seen from Fig.S1 in ESI Ag nanoparticles are in close

168   contact with α-Fe$_2$O$_3$ nanoparticles.The spacing of the lattice fringes werefound to be separated

169   by 0.251 and 0.234 nm, possibly due to (110) plane of α-Fe$_2$O$_3$ and (111) plane of metallic Ag

170   respectively.The ED pattern indicated polycrystalline nature of the material. The EDS pattern

171   (Fig.3) showed Fe, C, Ag and O, which confirms the formation of Ag/α-Fe$_2$O$_3$-rGO

172   nanocomposite.

173   **<Fig.3.>**

174   **Raman spectra of the catalyst**

175   **<Fig.4.>**

176   Fig.4 shows the SERS signal of GO and Ag/α-Fe$_2$O$_3$-rGO nanocomposite in the range of 1000-

177   1800 cm^{-1}.The materials showed two prominent peaks at 1352 and 1590 cm^{-1}, which correspond

178   to D-band (defect (D) peak) and G-band (graphite (G) peak), respectively. The values are

179   consistent with literature reports [41]. The D-band/G-band intensity ratio (I_D/I_G) of these peaks

180   provide the disorder levels of the materials. The I_D/I_G of GO and Ag/α-Fe$_2$O$_3$-rGO

181   nanocomposite were determined to be 0.826 and 1.001, respectively. The increase in the ratio of

182   I_D/I_G of Ag/α-Fe$_2$O$_3$-rGO was recognized due to the reduction of GO to rGO in the process of

183   synthesis of Ag/α-Fe$_2$O$_3$-rGO.

184   **TGA of the catalyst**

8

185   **<Fig.5.>**

186   The TGA curves of GO and Ag/α-Fe$_2$O$_3$-rGO nanocomposite are shown in (Fig.5 (a,b)). The

187   mass loss of 5 % at around 100-170°C which may be attributed to the removal of water molecule

188   trapped inside the GO and a maximum weight loss of 65 %in the temperature range of 170-

189   525°C may be ascribed to the pyrolysis of the labile oxygen-containing groups in the forms of

190   CO, CO$_2$ and steam. Ag/α-Fe$_2$O$_3$-rGO exhibits overall weight loss of only 17% when the sample

191   was heated up to 800°C at the heating rate of 10°C per minute. This weight loss corresponds to

192   loss of residual oxygen-containing groups of rGO from Ag/α-Fe$_2$O$_3$-rGO.

193   **N$_2$adsorption-desorption isotherm analysis of the catalyst**

194   **<Fig.6.>**

195   TheN$_2$ adsorption-desorption isothermof Ag/α-Fe$_2$O$_3$-rGO nanocomposite (Fig.6) follows the

196   characteristics of a type IV isotherm with a type H$_3$ hysteresis loop associated with aggregates of

197   plate-like particles forming slit-like pores [42]. The material showed high BET specific surface

198   area and pore volume of 772.65(m^2/g) and 1.47(cm^3/g), respectively. The Barrett Joyner Halenda

199   (BJH) pore size distribution indicates that most of the pores range from 5 to 20 nm as shown in

200   inset of Fig.6.

201   **VSM analysis of the catalyst**

202   **<Fig.7.>**

203   The magnetic hysteresis measurement Fig.7 of Ag/α-Fe$_2$O$_3$-rGO nanocomposite was carried out

204   at 300 K with the applied magnetic field sweeping from -20000 to +20000 G. The magnetic

205   hysteresis loops showed a ferromagnetic behavior with a remnant magnetization (M$_r$) of 15.13

206   emu g^{-1} and coercivity (H$_c$) of 572.03 G. The saturation magnetization of Ag/α-Fe$_2$O$_3$–rGO

207   catalyst is 57.2 emu g^{-1}. The nature of the hysteresis loop and value of saturation magnetization

208   clearly indicate strong ferromagnetic property of the nanocomposite.

209   **3.2 Catalytic activity of Ag/α-Fe$_2$O$_3$–rGO nanocomposite for reduction of nitroarenes using**

210   **hydrazine monohydrate at room temperature.**

211   After successful synthesis and full characterization of Ag/α-Fe$_2$O$_3$-rGO nanocomposite, we

212   examined its catalytic activity for reduction of nitroarenes to aromatic amines by hydrazine

213   hydrate. In order to get best results, the reaction variables such as solvent, and amount of catalyst

214   were optimized. For this purpose, nitrobenzene was chosen as a model substrate. The experiment

215   was conducted under different solvents *viz.* acetonitrile, dichloromethane, toluene and water. It is

216   evident from the optimization studies that water is the best solvent for the present catalytic

217   system. The reaction was also studied at different mole ratios of substrate, reducing agents and

218   catalyst (Table 1). A blank run in absence of the catalyst gives a very poor yield of the product

219   after a long reaction time.

220   **<Table 1.>**

221   Best results were obtained when catalyst amount is 50 mg and ratio of substrate to reducing

222   agent is 1:4. Increasing the amount of reducing agent beyond four equivalents did not improve

223   the yield significantly. To demonstrate the scope of the catalyst, a range of aromatic nitro

224   compounds were reduced to corresponding amines employing optimized reaction conditions and

225   the results are summarized in Table 2. Expectedly nitroarenes with both electron withdrawing as

226   well as electron donating functional groups, afforded good to excellent yields. All the products

227   were characterized by IR spectroscopy and melting point determination.To ascertain the role of

228   the catalyst, we have prepared Ag NPs and α-Fe$_2$O$_3$ NPs separately using our reported

229   methods[34,35] and used them separately as catalyst for reduction of nitroarenes to aromatic

230   amines and observed that independently they also show catalytic activity but efficiency is

231   significantly less compared to the nanocomposite. We then mixed these NPs (Ag NPs and α-

232   Fe_2O_3 NPs) at room temperature and used this mixture as catalysts for reduction of nitroarenes

233   but we have not seen any improvement of the yield of the product. The Ag/α-Fe_2O_3 (Ag

234   supported α-Fe_2O_3) was also synthesized and used as catalysts but some improvement in the

235   catalytic performance was observed butstill no way comparable to the performance of the Ag/ α-

236   Fe_2O_3-rGOnanocomposite. This clearly indicates Ag NPs and α-Fe_2O_3 NRs in isolation, a simple

237   random mixture of these components as well as Ag/α-Fe_2O_3 have significantly lowercatalytic

238   effect on reduction of nitroarenes. Therefore it can be concluded that role of rGO as a support in

239   Ag/α-Fe_2O_3-rGO is very important in enhancing the performance of the composite catalyst.A

240   comparison between the present catalyst and some of the previously reported catalytic methods

241   for reduction of nitroarenes to aromatic amines is summarized in Table 3.The comparison reveals

242   thatcatalytic reaction presented hereinis better than to the some of the most efficient catalytic

243   reductions of aromatic nitroarenes to amines. The added advantage of the present catalyst is its

244   easy recovery and recyclability.

245   **<Table 2.>**

246   **<Table 3.>**

247   **3.3. Recyclability of the catalyst**

248   After completion of the reaction, the solid catalyst was separated magnetically from the reaction

249   mixture and washed thoroughly with acetone and reused for multiple cycles to check the

250   efficiency of the recycled catalyst. The catalytic reduction of nitroarenes to aromatic amines was

251   carried out with the reused catalyst under the same reaction condition. The activity of the

252   recovered catalyst after 5 consecutive runs did not show any significant decline (Fig.8). The

253   TEM image of the spent catalyst showed an almost similar size and shape to that of the fresh

254   catalyst (Fig.S2 in ESI).Leaching test has been carried out by procedure reported[41]. To

11

255 confirm that there is no leaching of Ag particles during the reaction, we have removed the

256 catalystmagnetically after 15min of the reaction. The yield of the product obtained at 15

257 minuteswas noted. The reaction was further continued without the catalyst for another 15

258 minutes but we did not observe any increase in the yield. Since Ag is one of the catalytically

259 active components of the composite, so if there had been leaching of Ag NPs, we would have

260 observed some rise in yield. Therefore it can be stated that there is no leaching of Ag NPs from

261 the Ag/α-Fe$_2$O$_3$-rGO catalyst during the reaction.

262 <center>**<Fig.8.>**</center>

263 **4. Conclusion**

264 In summary Ag/α-Fe$_2$O$_3$-rGO nanocomposite has been successfully synthesized by the one-pot

265 hydrothermal method. The role of urea as hydroxylating agent and PEG 4000 as surfactant as

266 well as reducing agent are important features of the synthesis method. This novel

267 nanocomposite, Ag/α-Fe$_2$O$_3$-rGO, is used as recyclable catalyst in reduction of range of aromatic

268 nitroarenes to amines. To the best our knowledge, such rGO embedded nanocomposite has not

269 been previously used for conversion of nitroarenes to amines. This catalytic protocol has various

270 advantages such as high yields, elimination of homogeneous catalysts, simple work-up and easy

271 separation and recycling of the catalyst. The catalyst also shows true heterogeneity as its

272 efficiency remains almost same after five cycles of reuse.

273

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342   **Scheme caption**

343   **Scheme 1.** Synthesis of Ag/α-Fe$_2$O$_3$-rGOnanocomposite.

344   **Figure captions**
345   **Fig.1.** Powder XRD pattern of Ag/α-Fe$_2$O$_3$-rGOnanocomposite.

346   **Fig.2.** (a, b) TEM images (c) HRTEM image and (d)ED pattern of Ag/α-Fe$_2$O$_3$-rGO

347   nanocomposite.

348   **Fig 3.** EDS pattern of Ag/α-Fe$_2$O$_3$-rGOnanocomposite.

349   **Fig.4.** Raman spectra of GO and Ag/α-Fe$_2$O$_3$-rGOnanocomposite.

350   **Fig.5.** TGA curve of (a) GO and (b) Ag/α-Fe$_2$O$_3$-rGOnanocomposite.

351   **Fig.6.** (a, b)N_2adsorption-desorption isotherms of Ag/α-Fe_2O_3-rGOnanocomposite.

352   **Fig.7.** Room temperaturemagnetization hysteresis loop of Ag/α-Fe_2O_3-rGOnanocomposite.

353   **Fig.8.** Catalytic activity of Ag/α-Fe_2O_3-rGO nanocompositeagainst number of cycles.

354   **Table captions**

355   **Table 1.** Optimization of reductionof nitroarenes.

356   **Table2.** Reductionof nitroarenesin presence of Ag/α-Fe_2O_3-rGO catalyst.

357   **Table 3.** Comparison of the literature reported catalyst with the present catalyst.

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364   **<Scheme 1.>**

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382 **Table 1.**

Entry	Substrate (equiv)	Catalyst (mg)	Reducing agent (equiv)	Time(min)	Temperature (°C)	Yield(%)
1	1	100	4	60	27	95
2	1	50	8	60	27	96
3	**1**	**50**	**4**	**15**	**27**	**98**
4	2	50	4	60	27	76
5	1	30	4	60	70	92
6	1	50	4	60	80	76

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389 **Table2.**

Entry	Substrate	Product	Time (min)	Yield (%)	Selectivity(%)
1	NO_2 (benzene)	NH_2 (benzene)	30	98	>99
2	NO_2, Br (benzene)	NH_2, Br (benzene)	25	98	>99
3	NO_2, Cl (benzene)	NH_2, Cl (benzene)	45	97	>99
4	NO_2, I (benzene)	NH_2, I (benzene)	30	95	>99
5	NO_2, F (benzene)	NH_2, F (benzene)	20	98	>99
6	NO_2, CH_3 (benzene)	NH_2, CH_3 (benzene)	60	95	>99
7	NO_2, NH_2 (benzene)	NH_2, NH_2 (benzene)	30	99	>99
8	NO_2, Br (benzene)	NH_2, Br (benzene)	45	92	>99
9	NO_2, CH_3 (benzene)	NH_2, CH_3 (benzene)	40	95	>99
10	NO_2, NH_2 (benzene)	NH_2, NH_2 (benzene)	90	92	>99

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392 **Table 3.**

Entry	Catalyst	Solvent	Temp °C	Time (min)	Yield/conversion (%)	Ref
1	Ni NPs	Water	rt	75	99 conversion	4
2	Co NPs	Water	rt	300	50 conversion	4
3	Au/TiO_2	EtOH	rt	180	99 conversion	43
4	$Ni-Fe_3O_4$	Glycerol	80	180	94 yield	44
5	$Au-Fe_3O_4$	EtOH	rt	10	GC yield 99	23
6	$Rh-Fe_3O_4$	EtOH	80	60	99 yield	24
7	$Pd-Fe_3O_4$	EtOH	rt	60	90 yield	45
8	$Fe_3O_4@SiO_2/EP.EN.EG@Cu$	Water	rt	15	85 yield	25
9	Reduced graphene oxide	$N_2H_4.H_2O$ /H_2O	30	2880	97 yield	46
10	$Ag/\alpha-Fe_2O_3–rGO$	Water	rt	30	98 yield	Present Work

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Highlights

- ➤ One pot in-situ synthesis of Ag/Fe_2O_3 anchored rGO.

- ➤ PEG 4000 as surfactant and reducing agent for Ag(I).

- ➤ Formation of Ag/Fe_2O_3-rGO is confirmed by TEM, XRD, EDS and Raman spectroscopy.

- ➤ As-synthesized novel material exhibits pronounced activity as magnetic catalyst.

- ➤ The catalyst used for chemoselective reduction of aromatic nitro groups.