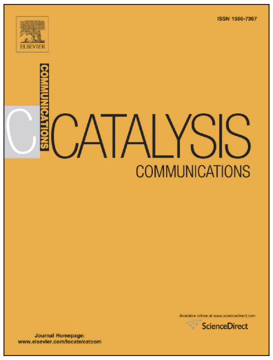


Room temperature catalytic reduction of nitrobenzene to azoxybenzene over one pot synthesised reduced graphene oxide decorated with Ag/ZnO nanocomposite

Bappi Paul, S. Vadivel, Nishant Yadav, Siddhartha Sankar Dhar

PII: S1566-7367(19)30060-3
DOI: https://doi.org/10.1016/j.catcom.2019.02.026
Reference: CATCOM 5637

To appear in: *Catalysis Communications*

Received date: 8 February 2019
Accepted date: 26 February 2019

Please cite this article as: B. Paul, S. Vadivel, N. Yadav, et al., Room temperature catalytic reduction of nitrobenzene to azoxybenzene over one pot synthesised reduced graphene oxide decorated with Ag/ZnO nanocomposite, Catalysis Communications, https://doi.org/10.1016/j.catcom.2019.02.026

Room temperature catalytic reduction of nitrobenzene to azoxybenzene over one pot synthesised reduced graphene oxide decorated with Ag/ZnO nanocomposite

Bappi Paul[a]*, S. Vadivel[b], Nishant yadav[c], Siddhartha Sankar Dhar[a]*

[a]Department of Chemistry, National Institute of Technology Silchar, Silchar-788010, Assam, India

[b]Department of Chemistry, PSG College of Technology, Coimbatore 641004, India

[c] Department of Chemistry, Pandit Prithi Nath College, kanpur- 208001, India

*Corresponding authors. Tel: +91-03842-242915; fax: +91-03842-224797

Email: bappipaulnits@gmail.com (B. Paul); ssd_iitg@hotmail.com (S.S. Dhar)

Abstract

We report herein, a one-pot synthetic route for the synthesis of reduced graphene oxide decorated Ag/ZnO nanocomposite and studied its catalytic activity as simple, recyclable and efficient catalyst for one-pot conversion of nitrobenzene to azoxybenzene. It was observed that 5–10 nm Ag-nanoparticles supported on 40–60 nm ZnO nanorod decorated on reduced graphene oxide was formed with a silver loading of 1.6 wt %. The effect of different reaction parameters were investigated and studied in detail. A nitrobenzene conversion of 96% with 98% selectivity of azoxybenzene was achieved without the use of any external additives.

Keywords: Nitrobenzene; Selective reduction; Azoxybenzene; High conversion; High selectivity.

Introduction

Selective catalytic reduction of nitrobenzene into valuable intermediates such as aniline, azobenzene, nitroso benzene and azoxybenzene are one of the challenging reactions in the field of pharmaceutical industries ranging from dyes, polymer stabiliser and food additives [1-3]. Among those, the preparations of azoxybenzene have attracted special importance due to its use as precursor for Wallach rearrangement that has been applicable in coloration of resin, dye, lacquer and also provide a simple route for synthesizing hydroxyazobenzene[4]. Azoxybenzene is produced as an intermediate in the reduction of nitroarenes or the oxidation of aniline. These reaction steps are quite complex and lead to different reaction intermediates. Therefore, the challenge lies in controlling the selectivity to the target product *via* manipulation of reaction conditions at a reasonable substrate conversion has becomes an important research interest [5,6]. Various methods have been reported for oxidative coupling of aniline and reducing nitroarenes using homogenous and heterogeneous catalyst.[6, 7-9] However, in most of the cases product separation from the reaction mixtures and the recyclability of the catalysts become two major issues in liquid-phase reaction. Therefore, development of more benign recyclable catalyst that works under mild conditions in reducing nitroarenes is in high demand.

Nanostructured ZnO continues to draw significant attention because of its potential application in energy generators, sensors, lasers as well as catalysts in chemical reactions [10]. Recent studies have shown that ZnO NPs modified with noble metals such as Ag or Au enable larger area of active sites for improved catalytic activity [11]. Noble metal supported ZnO nanostructured materials although have shown better activity due to synergistic effect between metal and metal oxides, however due to poor diffusion and steric factors, their activity and selectivity might be affected. Therefore, such heterodimeric nanocatalysts if supported on porous carbon, surface area may substantially be increased due to their highly even distribution in the pores. Graphene oxide (GO) has proved to very efficient porous carbon support for anchoring metal nanoparticles due to its large specific surface area and both sides accessible of its nanosheets [12]. Recently, some studies have demonstrated that transition metal nanoparticles supported on porous carbon nanosheets work as efficient catalysts for organic transformation [13-16]. We report herein, a one-pot hydrothermal synthesis of Ag/ZnO embedded rGO and studies of its catalytic activity for selective reduction of nitrobenzene to azoxybenzene using hydrazine hydrate ($N_2H_4.H_2O$) as reducing agent. In this study, hydrazine hydrate ($N_2H_4.H_2O$) is considered as a very suitable reagent for the reduction of nitrobenzene, since only water and N_2 are generated as by-products [17].

2. Experimental

2.1 Synthesis of Ag/ZnO-rGO

Graphene oxide (GO) nanosheets were prepared by our previously reported method [18]. 0.68 g of $ZnCl_2$ (5 mmol) and 0.084 g of $AgNO_3$ (0.5 mmol) were slowly added to 20 mL of 1.8 mg mL^{-1} GO aqueous solution while stirring. Subsequently, 1.20 g of urea (20 mmol) and 4 g of PEG 4000 (1 mmol) were slowly added to the aqueous mixture and was further sonicated for 30 min. Subsequently 60 ml of deionized water was added followed by hydrothermal heating at 180°C for about 24 h. The resulting solid was cooled to room temperature, washed with deionized water and ethanol several times. Finally the product was dried at 70°C in a vacuum oven for 6 h.

2.2 Catalytic activity measurements

The catalytic activity of Ag/ZnO-rGO catalyst was tested in the selective reduction of different aromatic nitro where nitrobenzene was taken as model substrate for reduction reaction as summarised in Table 2. Reduction of nitrobenzene was carried out in a double neck round bottom flask at room temperature (25 °C) using 20 mg catalyst, 15 mmol nitrobenzene and 5 mL ethanol as solvent, where 22.5 mmol hydrazine was added dropwise as reducing agent. Small aliquots were collected from the reaction mixture at regular intervals for analysis. At the end of the reaction, the solid catalyst was separated by filtering and products were analysed using a gas chromatograph (GC, Agilent 7890) connected with a HP-5 capillary column (30 m length, 0.28 mm id and 0.25 μm film thickness) and a flame ionization detector (FID).

3. Results and Discussion

<Fig.1>

The amount of Ag present in Ag/ZnO-rGO catalysts were estimated by ICP-AES. The crystalline nature and exposed phase of prepared catalyst were determined by powder X-ray diffraction (XRD) analysis (Fig.1). The diffraction peaks are found to be consistent with those of the reported data of ZnO (JCPDS File no. 89-1397) (Fig.1 (c)). The Ag/ZnO-rGO nanocomposite of catalyst showed two additional peaks at 2θ values 38.13° and 25.4° corresponds to (111) planes of face-centered cubic Ag (JCPDS File no. 89-3722), and (002) plane of rGO (Fig. 1(d)). It is also observed from the XRD pattern of the spent catalyst that the metallic Ag does not change its phase even after the catalytic reaction (Fig.1(e)). The physicochemical properties of the fresh and spent catalyst is summarised in Table S1 in ESI.

<Fig. 2.>

The TEM image of Ag/ZnO-rGO nanocomposite synthesized is shown in Figure 2. From the TEM image it can be seen that Ag particles are distributed homogeneously on the ZnO nanorod and anchored uniformly over rGO. TEM showed a rod-like structure of ZnO with diameter 40-60 nm and Ag NPs of sizes approximately 5-10 nm randomly attached to it. The high magnification TEM image of Ag/ZnO-rGO nanocomposite (Fig.S1 in ESI) and the EDS spectrum showed the existence of Zn, O, Ag and C in the material, which clearly indicates the formation of Ag/ZnO-rGO composite (Fig.S2 in ESI).

To characterize the ordered and disordered crystal structure of GO, Raman spectra were recorded (Fig.S3 in ESI). Both GO and Ag/ZnO-rGO shows two prominent peaks at 1298 and 1595 cm^{-1}, which correspond to D-band (defect (D) peak) and G-band (graphite (G) peak) respectively[19]. The D-band/ G-band (I_D/I_G) intensity ratio of these peaks provide the disorder levels of the GO. The I_D/I_G of GO was determined to be 1.12 whereas upon hydrothermal reduction, the I_D/I_G of Ag/ZnO-rGO is increased to 1.46.

Ag/ZnO-rGO nanohybrid featured characteristics of a type IV isotherm with H_3 hysteresis loop associated with aggregate of plate-like particles forming slit-like pores with a surface area and pore volume of 522.15 (m^2/g) and 1.07(cm^3/g), respectively (Fig.S3 in ESI). The pore size distribution as indicated by Barrett Joyner Halenda (BJH) shows that most of the pores range from 5 to 60 nm with an average pore size of 27.12 nm (Fig.S4 inset in ESI).

<Fig. 3.>

The valence state of Ag species in Ag/ZnO-rGO was estimated by X-ray photoelectron spectroscopy (XPS), where we can clearly see the presence of metallic silver in the form of corresponding Ag $3d_{5/2}$ and Ag $3d_{3/2}$ with binding energy values of 367.4 eV and 373.4 eV, respectively (Fig. 3). The XPS spectra of Zn 2p with binding energy at 1021.4 eV ($2p_{3/2}$) and 1044.5 eV ($2p_{1/2}$) confirms the existence of Zn element is in the state of Zn^{2+}. The high resolution C 1s spectra were deconvoluted into three distinct peaks, that correspond to the C–C bond at 285.6 eV and the carbon atoms bonded to different functional moieties of arginine C–O at 286.2 eV and C=O at 290.1 eV. The corresponding XPS analysis of the spent catalyst confirms that the oxidation state of Ag 3d binding energy remains same during the catalysis (Figure S5 in ESI).

2.3 Catalytic activity

After successful synthesis and characterization of nanostructured Ag/ZnO-rGO, we examined its catalytic activity for one-pot reduction of different aromatic nitro compound where nitrobenzene was taken as model substrate and various parameter such as time, temperature, nitrobenzene: $N_2H_4.H_2O$ molar ratio and catalyst amount were studied in order to get best yield and selectivity of azoxybenzene. When the catalytic experiments were carried out in presence of $N_2H_4.H_2O$ as the reducing agent and ethanol as a solvent keeping the nitrobenzene: $N_2H_4.H_2O$ mole ratio constant (1:1.5) at room temperature for 120 min the catalyst showed maximum nitrobenzene conversion of 96% with 98% selectivity towards azoxybenzene at room temperature where aniline, and azobenzene were detected as the side products. The effect of reaction time was also studied and the results also showed an increasing trend in both the nitrobenzene conversion and azoxybenzene selectivity with increasing time (Fig. 4). The results indicated that after 120 min of reaction, the maximum selectivity of azoxybenzene (~98%) was achieved, but after 150 min the selectivity of azoxybenzene dropped to ~92% due to formation of azobenzene. The conversion of nitrobenzene was found to be 100% with 54% azoxybenzene selectivity, whereas with increase in the temperature up to 70 °C, although the conversion increases steadily the selectivity drops down due to the formation of azobenzene as the major by-product which may be due to the over reduction of nitrobenzene which takes place at high temperature (Fig. S6 in ESI). When the molar ratio of nitrobenzene and $N_2H_4.H_2O$ was 1 : 0.5, we observed very low conversion of nitrobenzene (74%) with 80% azoxybenzene selectivity, which may be due to the lesser interaction between the reactant and active reducing species for catalysis. On increasing the mole ratio of nitrobenzene and $N_2H_4.H_2O$ up to 1:2.5), the conversion reached up to 100% and the selectivity dropped to up to 80% with the increase in azobenzene formation, because of over reduction of nitrobenzene (Fig. S7 in ESI).

<Fig. 4.>

In order to explore the individual role of Ag, ZnO and reduced graphene oxide in its catalytic activity, a series of experiments were conducted. A blank run in the absence of the catalyst does not show any catalytic activity under the optimized reaction conditions (Table 1, entry 13). When the Ag/ZnO catalyst was synthesized by the conventional impregnation method (imp), it showed very poor catalytic activity due to larger particle sizes and excessive leaching of the metals (Table 2, entry 5). Furthermore, the Ag/ZnO-rGO nanostructured catalyst showed a greater conversion for azoxybenzene production, compared to bare Ag or ZnO catalyst (Table 2, entries 3 and 4). The reasons for excellent catalytic activity of Ag/ZnO-rGO prepared by the present method is believed to be due to higher specific surface area and higher dispersion of very small sized Ag NPs supported on ZnO leading to easy accessibility of reactants on active catalytic sites. Thus, taking into account of all the reaction parameters as a standard Ag/ZnO-rGO as a catalyst the scope of the reaction was explored next. The results are summarized in Table 2. Various substituted nitroarenes bearing electron withdrawing and electron donating groups were examined. It was observed that a variety of structurally different aromatic nitroarenes were selectively transformed to their corresponding products in high to excellent yield.

<Table 1.>

<Table 2.>

The activity of the recovered catalyst after 5 consecutive cycle did not show any significant decline (Fig.5). Negligible amount of leaching of Ag and ZnO was detected (concentration of both metals were <2 ppb). To confirm that there is no leaching of Ag particles during the reaction, we have performed the conventional hot filtration test, where we have removed the catalyst after 90 min of the reaction and the yield of the product obtained at 90 min was noted [20]. The reaction was further continued without the catalyst for further 150 min more hours but we did not observe any increase in the yield. This confirms that there occurs no leaching of Ag NPs from the ZnO during the reaction.

<Fig. 5.>

4. Conclusion

In conclusion, one-pot synthetic route for the synthesis of reduced graphene oxide (rGO) decorated Ag/ZnO nanocomposite via homogeneous precipitation of Zn(II) and simultaneous reduction of Ag(I). The catalyst was found to be efficient catalyst for the selective reduction of nitrobenzene to azoxybenzene with 96% nitrobenzene conversion and 98% azoxybenzene selectivity at room temperature with hydrazine as reducing agent. The catalyst also shows true heterogeneity as its effectiveness remains almost same after five cycles of reuse.

Acknowledgements

The authors are thankful to SAIF IIT Bombay and SAIF North Eastern Hill University for providing analytical results. Director, NIT Silchar, is acknowledged for his support and encouragement.

References

[1] A. Grirrane, A. Corma, H. García, Science 322 (2008) 1661-1664.

[2] E.R. Burkhardt and K. Matos, Chem. Rev. 106 (2006) 2617-2650.

[3] J. Zhang, G. Lu, C. Cai, Catal. Commun. 84 (2016) 25–29

[4] E. Buncel, Acc. Chem. Res. 8 (1975) 132-139.

[5] H. Zhu, Y. Lu, F. Fan, S. Yu, Nanoscale 5 (2013) 7219.

[6] M.N. Pahalagedara, L.R. Pahalagedara, J. He, R. Miao, B. Gottlieb, D. Rathnayake, S.L. Suib, J. Catal. 336 (2016) 41–48.

[7] E. Wenkert, B. Wickberg, J. Am. Chem. Soc. 84 (1962) 4914–4919.

[8] A. Grirrane, A. Corma, H. García, Science 322 (2008) 1661-1664.

[9] S. Ghosh, S. S. Acharyya, T. Sasaki and R. Bal, Green Chem. 17 (2015) 1867–1876.

[10] Y. Chang, Catal. Commun. 56 (2014) 45–49

[11] Y. Hartadi, D. Widmanna, R. J. Behm, Phys. Chem. Chem. Phys. 18 (2016) 10781-10791

[12] W.H. Lee, J. Park, S.H. Sim, S. Lim, K.S. Kim, B.H. Hong, K. Cho, J. Am. Chem. Soc. 133 (2011) 4447-4454.

[13] S. Verma, D. Verma, S.L. Jain, Tetrahedron Lett. 55 (2014) 2406–2409.

[14] X. Liu, C. Wang, S. Cheng, N. Shang, S. Gao, C. Feng, C. Wang, Y.Qiao, Z. Wang, Catal. Commun. 108 (2018) 103-107

[15] S. Verma, M. Aila, S. Kaul, S.L. Jain, RSC Adv. 4 (2014) 30598-30604.

[16] S. Verma, D. Tripathi, P. Gupta, R. Singh, G.M. Bahuguna, L.N. Shivakumar, R.K. Chauhan, S. Saranb, S.L. Jain, Dalton Trans. 42 (2013) 11522-11527.

[17] D. Cantillo, M.M. Moghaddam, C.O. Kappe, J. Org. Chem. 78 (2013) 4530.

[18] B. Paul, D.D. Purkayastha, S.S. Dhar, S. Das, S. Haldar, J. Alloys Compd., 681 (2016) 316-323.

[19] A. Liu, W. Zhou, K. Shen, J. Liu, X. Zhang, RSC Adv. 5 (2015) 17336-17342.

[20] H. E. B. Lempers, R. A. Sheldon, J. Catal. 175 (1998) 62–69.

Figure, and table captions

Figure1. Powder XRD patterns of (a) standard Ag(0), (b) standard ZnO, (c) synthesized ZnO nanoparticle (d) Fresh Ag/ZnO-rGO nanocatalyst and (e) Spent Ag/ZnO-rGO nanocatalyst.

Figure2. TEM images of Ag/ZnO-rGO nanoparticles.

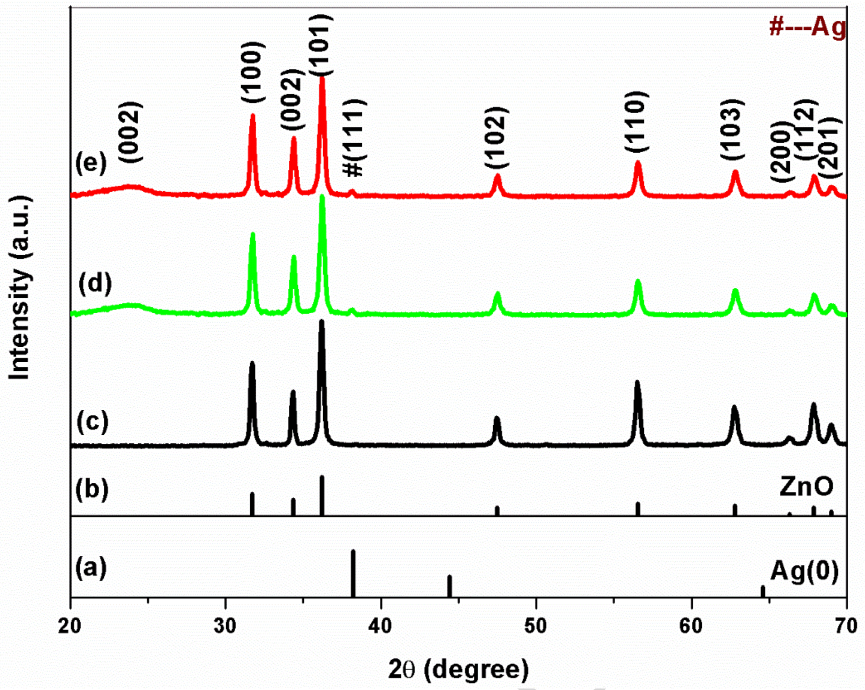
Figure 3. XPS spectrum of the Ag/ZnO-rGO nanoparticles**.**

Figure 4. Effect of time on nitrobenzene reduction. [■] Conversion of nitrobenzene, [🟥] selectivity to azoxybenzene, [🟦] selectivity of aniline, [🟩] selectivity to azobenzene. Reaction Condition solvent = ethanol; nitrobenzene = 15 mmol; the weight of the catalyst = 20 mg; substrate : hydrazine molar ratio = 1 : 1.5.

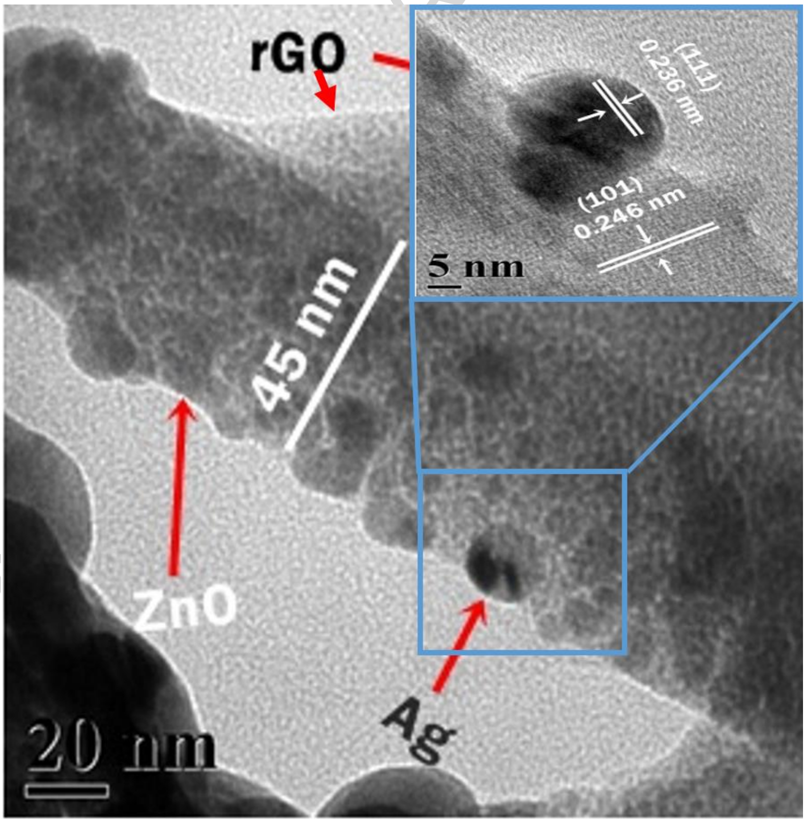
Figure 5. Recyclability test of Ag/ZnO-rGO nanoparticals

Table 1. Reductive coupling of nitrobenzene to azoxybenzene[a]

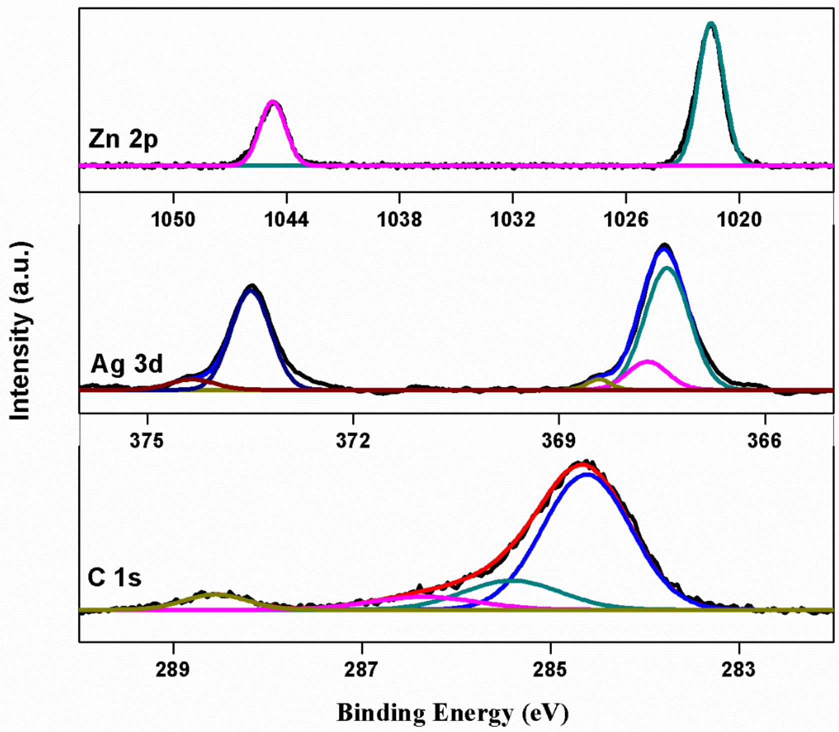
Table 2. Reductive coupling of various nitrobenzene catalyzed by Ag/ZnO-rGO nanocomposite


#---Ag
(e)
(002)
(100)
(002)
(101)
#(111)
(102)
(110)
(103)
(200)
(112)
(201)
(d)
(c)
(b)
ZnO
(a)
Ag(0)
Intensity (a.u.)
20
30
40
50
60
70
2θ (degree)

<Fig.1>

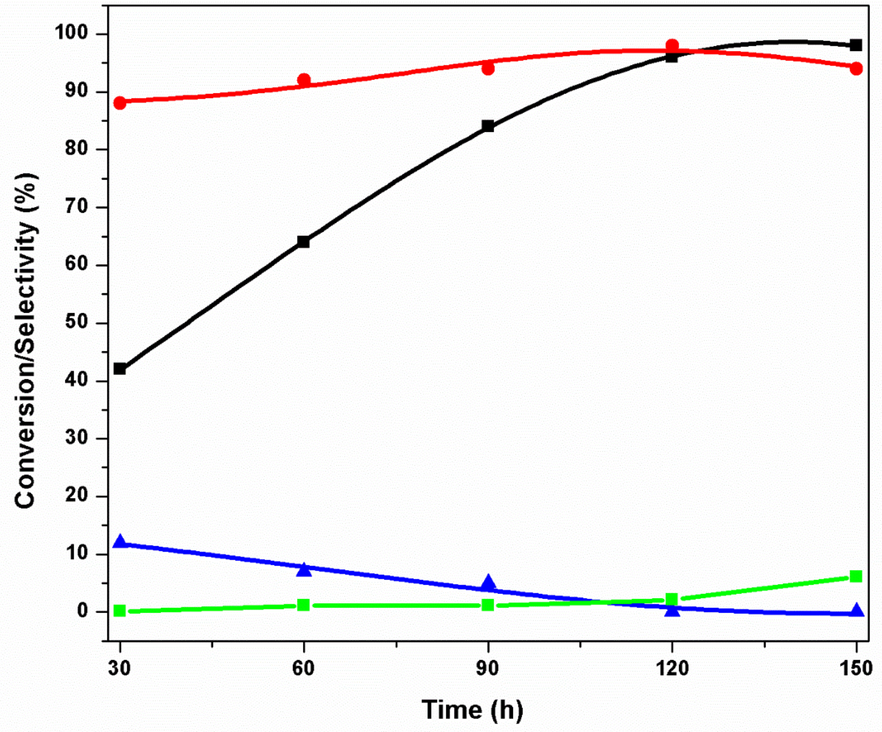

rGO
(111)
0.236 nm
(101)
0.246 nm
5 nm
45 nm
ZnO
Ag
20 nm

<Fig.2>



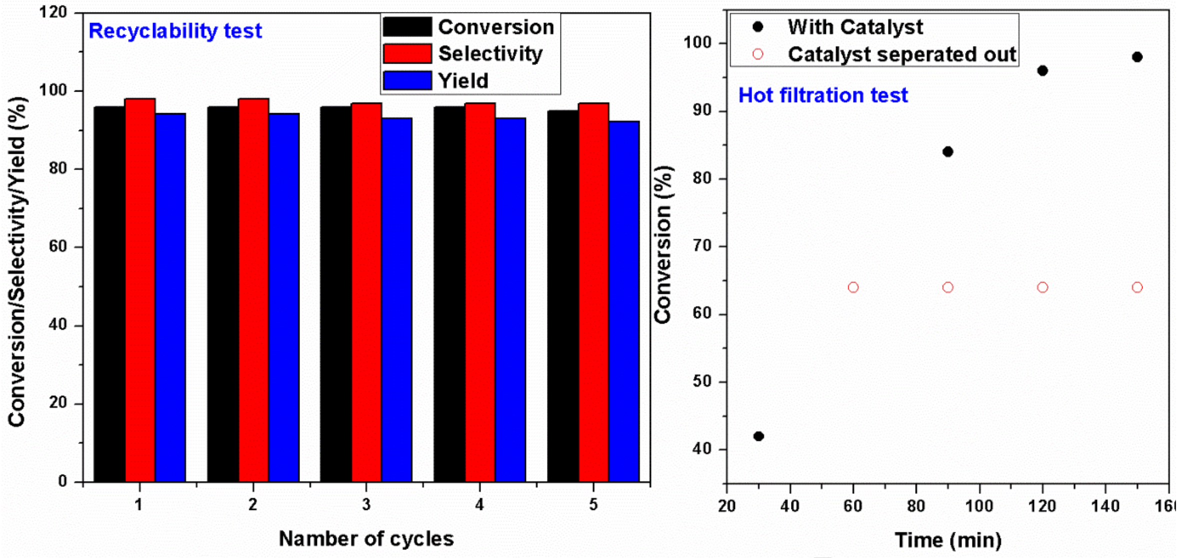
Zn 2p
Ag 3d
C 1s
Intensity (a.u.)
1050
1044
1038
1032
1026
1020
375
372
369
366
289
287
285
283
Binding Energy (eV)

<Fig.3>



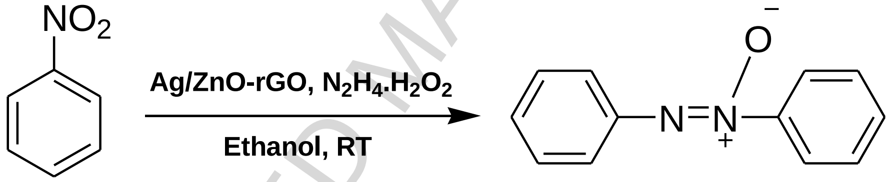
Conversion/Selectivity (%)
100
90
80
70
60
50
40
30
20
10
0
30
60
90
120
150
Time (h)

<Fig.4>



<Fig.5>

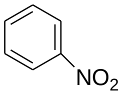
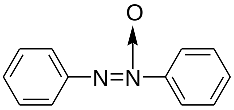
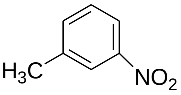
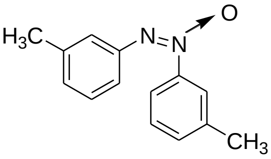
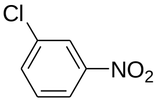
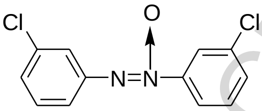
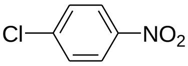
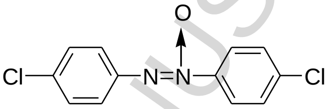
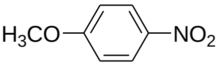
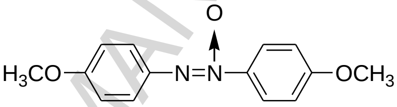
Table 1.



Entry	Catalyst	C_T^b (%)	Selectivity S_P^c (%)			Yield Y_A^d (%)
			Aniline	Azo benzene	Azoxy benzene	
1	Ag^{com}	6.8	43	47	-	-
2	ZnO^{com}	18	51	31	18	3
3	Ag^{us}	24	38	56	6	1
4	ZnO^{us}	27	64	14	22	6
5	Ag/ZnO^{imp}	22	16	58	26	6
6	rGO	6	100	-	-	-
7	Ag/ZnO-rGO [e]	96	-	2	98	94
8	Ag/ZnO-rGO [f]	96	-	3	97	93
9	Ag/ZnO-rGO [g]	100	2	44	54	54
10	Ag/ZnO-rGO [h]	74	14	6	80	59
11	Ag/ZnO-rGO[i]	100	-	20	80	80
13	No Catalyst	1	-	-	-	-

[a] Reaction conditions: solvent (ethanol) = 5 ml, substrate (nitrobenzene) = 15 mmol, the weight of the catalyst = 20 mg, silver loading = 1.6 wt%, reaction temperature = room temperature; time = 120 min; nitrobenzene : hydrazine molar ratio = 1 :1.5; [b] C_T: conversion of nitrobenzene based upon the FID-GC results = [moles of nitrobenzene reacted/initial moles of nitrobenzene used] × 100. [c]SP: selectivity of the product calculated by total moles of the product formed/total moles of nitrobenzene converted; [d] YA (Yield of azoxybenzene) = conversion × selectivity/100; [e]~Ag nanoparticles supported on ZnO-rGO. [f] Catalyst after 5 reuse; Ag/ZnO-rGO nanocatalyst. [g] When the reaction temperature was 80 °C. [h]When nitrobenzene: hydrazine (molar ratio) = 1:0.5; [i]when nitrobenzene: hydrazine (molar ratio) = 1:2.5. com = commercial; us = bare Ag and ZnO prepared by our method; imp = impregnation method.

Table 2.

Entries	Substrate	C_T (%)	Product	Selectivity (%)	Yield (%)
1		96		98	
2		74		84	62
3		90		94	85
4		90		92	83
5		90		86	77

[a] Reaction conditions: solvent (ethanol) = 5 ml, substrate = 15 mmol, the weight of the Ag/ZnO-rGO catalyst = 20 mg, silver loading = 1.6 wt%, time = 120 min; nitrobenzene: hydrazine molar ratio = 1: 1.5.

Highlights

- One-pot hydrothermal synthesis of reduced graphene oxide decorated Ag/ZnO
- 5–10 nm Ag-nanoparticles supported on 40–60 nm ZnO nanorod
- Room temperature catalytic reduction of nitrobenzene to azoxybenzene.
- Nitrobenzene conversion of 96% with 98% selectivity of azoxybenzene.