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Short Communication

Transition metal nanoparticles supported on mesoporous polyaniline catalyzed reduction of nitroaromatics

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ABSTRACT

Transition metal nanoparticles supported on mesoporous polyaniline (Meso-PANI) were synthesized by the self assembly of dual surfactants followed by the in situ reduction of metal precursors in aqueous solution. Catalysts were investigated in the reduction of nitroaromatics in the presence of $NaBH_4$ as a reducing agent. Among the catalysts investigated, Cu(10%)-Meso-PANI exhibited the highest activity. Cu supported on Meso-PANI exhibited significantly high activity compared to Cu supported on conventional PANI. Recycling experiments suggest that catalysts can be reused without significant loss in catalytic activity.

1. Introduction

Amines are important synthetic intermediates for the production of several organic compounds used in dye, pigment, agrochemical, polymer, and pharmaceutical industries [1–4]. Several routes are known for the synthesis of aliphatic amines, which includes reductive amination [5], reduction of nitriles [6], and direct amination of alcohols [7,8]. The most common approach for the synthesis of aromatic amine is based on the reduction of nitroaromatics. In conventional approach, catalytic hydrogenation is adopted to prepare aromatic amines [9–13]. High temperature and high H_2 pressure are some of the limitations associated with the catalytic hydrogenation process. To overcome these limitations, the precious noble metal catalysts have been used in combination with various reducing agents [14–17]. However, the high cost and limited availability of these metals led researchers to find more economical, easily available, and environmentally friendly alternatives. Recently, several studies based on transition metal mediated catalytic routes (including metal complexes) have been developed [18–24]. Although some advancement has been made in the catalytic reduction of nitroaromatics using heterogeneous catalysts [9–24], still the development of fast, cost effective, and mild catalytic route for the reduction of nitroaromatics with negligible metal contamination is of high demand.

Conducting polymer–metal nanocomposite materials have been widely used in catalysis [25–27]. Metal particles govern the catalytic properties, whereas the polymer matrix provides flexible functionalities to control host–guest interaction, thereby, ensuring the growth and distribution of metal nanoparticles [25–27]. Among the conducting polymers, polyaniline (PANI) has been proved to be an excellent candidate due to its unique redox property and high electrical conductivity [25–29]. Recently, we reported the morphological controlled synthesis of micro-/nano PANI [28]. Very recently, we developed the synthesis protocol for the preparation of Meso-PANI and its application is shown in H_2O_2 and glucose sensing [29]. We are exploring the possibility of supporting various transition metal nanoparticles on Meso-PANI and find their applications in catalysis. In this study, we report a novel method to synthesize transition metal nanoparticles supported on Meso-PANI and investigate their application in the reduction of nitroaromatics (Scheme 1) and compared the activity with metal nanoparticles supported on PANI.

2. Experimental

PANI and Meso-PANI were prepared according to the reported procedures [29]. PANI and Meso-PANI were decorated with metal nanoparticles by the in situ reduction of metal halide in aqueous solution. In this study, a variety of transition metal nanoparticles supported Meso-PANI were prepared (represented as M(x%)-Meso-PANI; where M = Cu, Ni, Co, Fe, and Mn; and x = input metal loading). In a typical synthesis of Cu(10%)-Meso-PANI, Meso-PANI (500 mg) was dispersed in 500 ml of deionized water with magnetic stirring at room temperature for 0.5 h and then with ultrasonication for another 0.5 h to obtain a uniform solution. $CuCl_2.2H_2O$ (150 mg) was added to the resultant solution and stirred for another 5 min to ensure complete mixing. Further, 100 ml of 0.2% $NaBH_4$ was added and the reaction mixture was stirred at ambient condition for 24 h. The resulting hybrid material was collected by centrifuging with an

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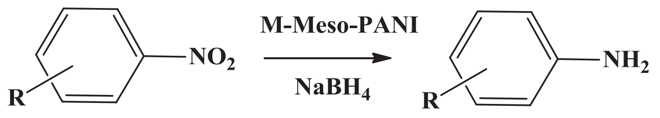


R = H, NH$_2$, OH, CH$_3$, Cl
M = Cu, Ni, Co, Fe, Mn

Scheme 1. Reduction of nitroaromatics over transition metal nanoparticles supported on Meso-PANI.

Table 1
Textural properties of materials synthesized in this study.

Sample	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Metal content (%)
PANI	35.4	0.034	-
Meso-PANI	83.6	0.085	-
Cu(10%)-Meso-PANI	76.3	0.075	7.80
[a]Cu(10%)-Meso-PANI	71.6	0.072	7.55
Cu(1%)-Meso-PANI	80.4	0.081	0.85
[a]Cu(1%)-Meso-PANI	78.8	0.076	0.83
Cu(1%)-PANI	33.2	0.030	0.82

[a] Recovered catalyst after 5th recycle.

ultracentrifuge. Atomic absorption spectroscopy was used to determine the metal loading in the materials (Table 1). For the comparative study, Cu(1%)-PANI was also prepared by following the procedure mentioned above.

Details about the materials, catalysts characterization, and procedure adopted for the catalytic investigation have been provided in the supporting information.

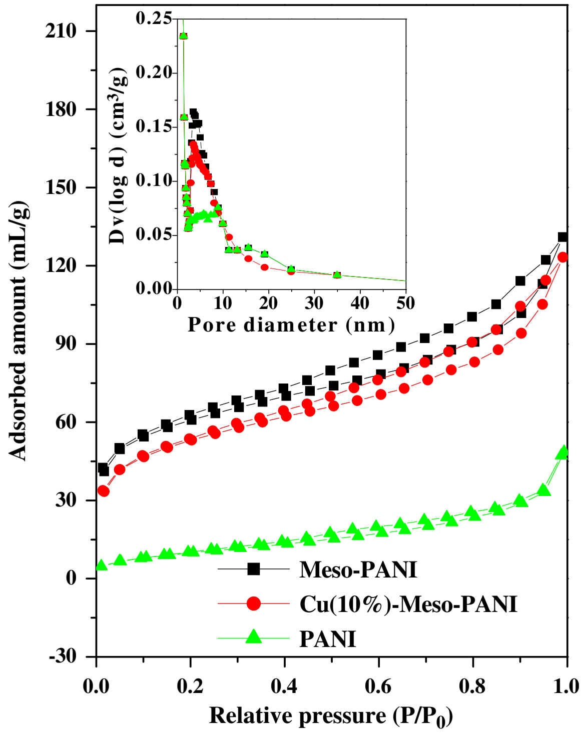


Fig. 2. N$_2$ adsorption–desorption isotherms of PANI, Meso-PANI, and Cu(10%)-Meso-PANI samples (Inset shows their pore size distributions).

3. Results and discussion

3.1. Synthesis and characterizations of catalysts

XRD patterns for PANI and Meso-PANI matched well with the reported literature (Fig. 1a) [29]. In the XRD pattern of Meso-PANI, two peaks at 2θ = 20.5° and 25.3° were observed. First peak is related to the periodicity parallel to the polymer chain, while the latter peak represent the periodicity perpendicular to the polymer chain [29] (Fig. 1(a)). A broad low-angle peak for Meso-PANI confirmed the existence of the ordered mesostructured PANI (Inset, Fig. 1a). Besides reflections corresponding to Meso-PANI [29], several more reflections were also observed in the XRD pattern of Cu(10%)-Meso-PANI. The diffraction peaks located at *2θ* values of 43.3°, 50.4°, 74.0°, and 90.0° correspond to (111), (200), (220), and (311) respectively, for metallic Cu in the fcc lattice (JCPDS, File No. 85-1326) (Fig. 1(b)). Cu(1%)-Meso-PANI sample shows XRD reflections only corresponding to Meso-PANI. No reflection for Cu-nanoparticles was observed in the XRD pattern of Cu(1%)-Meso-PANI confirming that Cu nanoparticles are incorporated

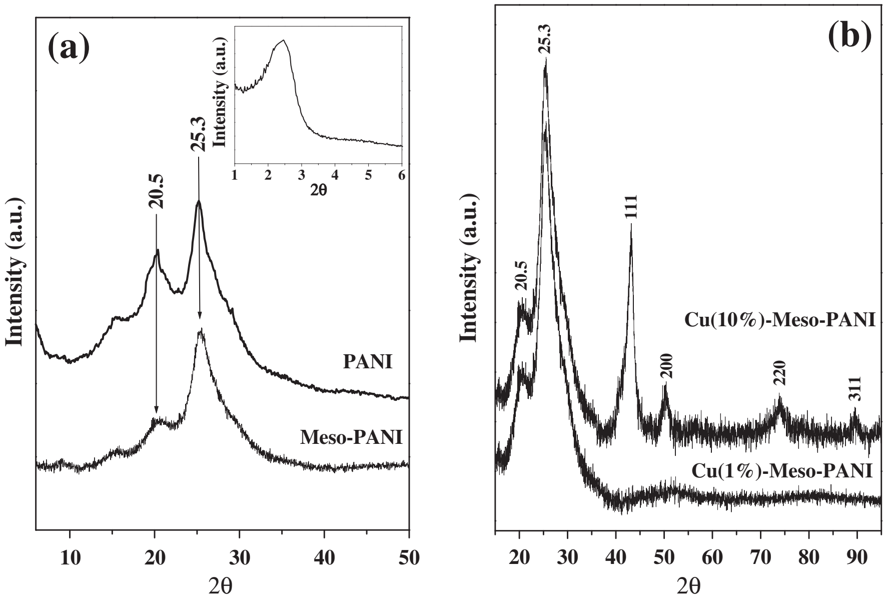


Fig. 1. XRD patterns of (a) PANI and Meso-PANI (Inset shows the low-angle XRD pattern of Meso-PANI) (b) Cu(10%)-Meso-PANI and Cu(1%)-Meso-PANI samples.

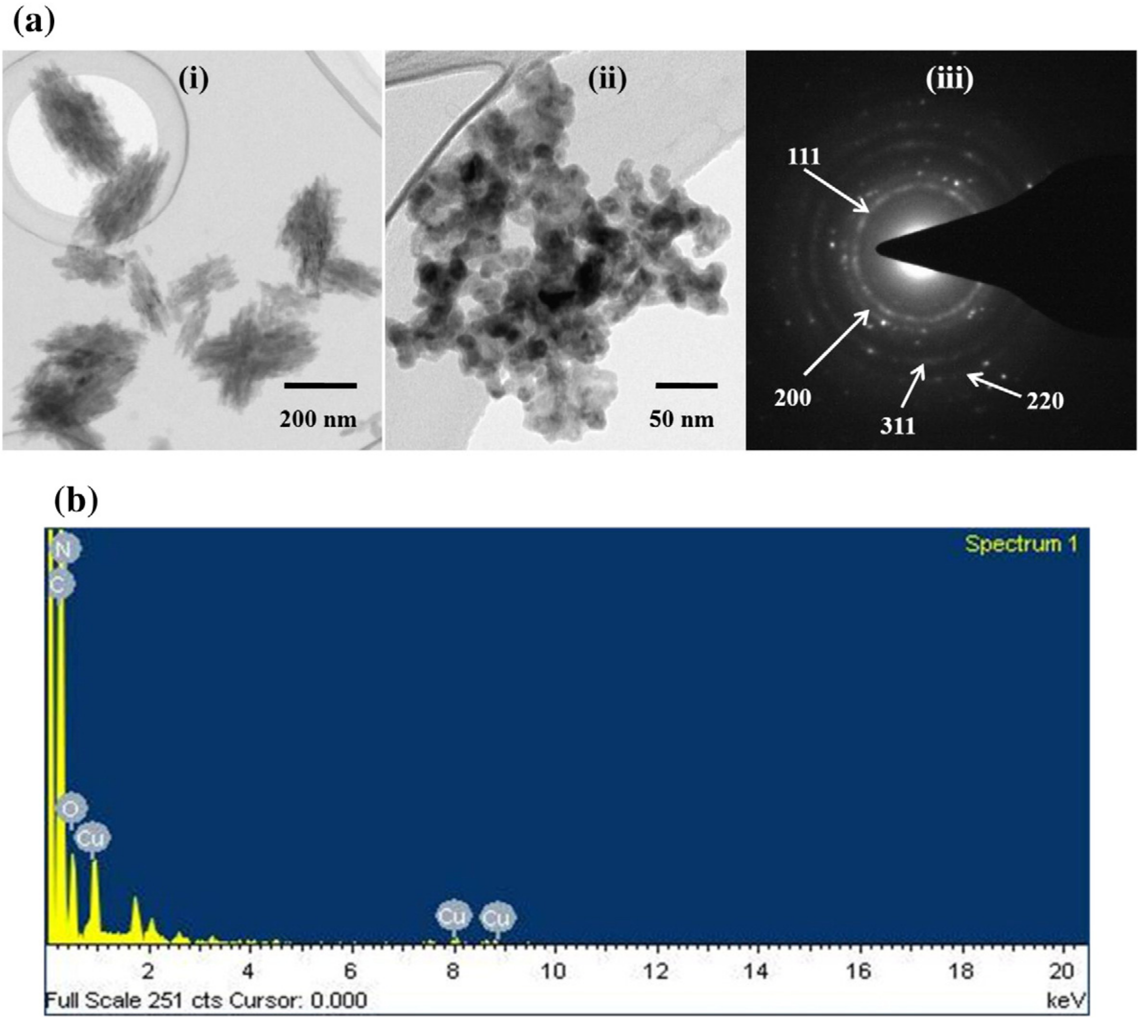


Fig. 3. (a) TEM images (i and ii) of Cu(10%)-Meso-PANI and corresponding diffraction pattern (iii) of Cu nanoparticles. (b) Energy-dispersive X-ray spectra of Cu(10%)-Meso-PANI.

inside the mesoporous wall of Meso-PANI. XRD patterns of M(1%)-Meso-PANI samples were found to be similar to that of Cu(1%)-Meso-PANI. Among the materials investigated, catalytic activity for Cu(10%)-Meso-PANI was found to be the best; therefore, the detailed characterization for only Cu(10%)-Meso-PANI is provided.

Table 2
Comparative catalytic activity in the reduction of *p*-nitroaniline over various catalysts investigated in this study.

S. No.	Catalyst	Time	[c]Product yield (%)
1	Cu(10%)-Meso-PANI	45 min	100
2	Cu(10%)-Meso-PANI[a]	45 min	98
3	Cu(1%)-Meso-PANI	45 min	55
4	Cu(1%)-Meso-PANI	1.5 h	100
5	Cu(1%)-Meso-PANI[a]	1.5 h	96
6	Cu(1%)-PANI	1.5 h	32
6	Ni(1%)-Meso-PANI	1.5 h	52
7	Co(1%)-Meso-PANI	1.5 h	50
8	Fe(1%)-Meso-PANI	1.5 h	18
9	Mn(1%)-Meso-PANI	1.5 h	12
10	$CuSO_4$[b]	2.5 h	100
11	$CuCl_2$[b]	2.5 h	100
12	$Cu(NO_3)_2$[b]	2.5 h	100
13	$Cu(OAC)_2$[b]	3.5 h	100
14	CuI[b]	3 h	100

Reaction condition: *p*-nitroaniline (1 mmol), solvent (10 ml, EtOH: water = 1:1), catalyst (50 mg), $NaBH_4$ (5 mmol), temperature (313 K).

[a] Catalytic activity results after 5th recycle.

[b] 0.01 mmol of the catalyst was used.

[c] GC yield.

Surface area and pore volume of catalysts were calculated from the N_2 adsorption–desorption studies. PANI samples synthesized in this study exhibited type IV isotherm but with different hysteresis loops (Fig. 2). Meso-PANI and Cu(10%)-Meso-PANI exhibited H3 hysteresis loops, which show that materials are having non-rigid aggregates like particles and signify the presence of slit shape pores, whereas, PANI exhibited H4 hysteresis. Materials exhibited broad pore size (4–10 nm) distribution (Fig. 2, inset). BET surface area for Cu metal decorated Meso-PANI was found to be less than Meso-PANI but

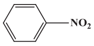
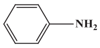
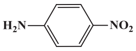
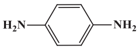
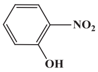
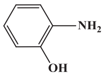
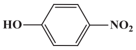
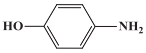
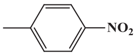
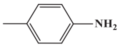
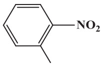
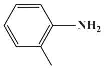
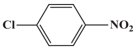
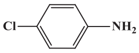
Table 3
Influence of solvent in the reduction of *p*-nitroaniline over Cu(10%)-Meso-PANI.

S. No.	Solvent	[a]Product yield (%)
1	Ethanol	100
2	Methanol	24
3	Water	88
4	Ethanol: Water (1:1)	100
5	THF	10
6	Isopropanol	12
7	Acetonitrile	0
8	Dichloromethane	0
9	Toluene	0

Reaction condition: *p*-nitroaniline (1 mmol), solvent (10 ml), catalyst (50 mg), $NaBH_4$ (5 mmol), temperature (313 K), reaction time (45 minutes).

[a] GC yield.

Table 4
Catalytic reduction of nitroaromatics over Cu(10%)-Meso-PANI and Cu(1%)-Meso-PANI.

S. No.	Substrate	Product	Cu(10%)-Meso-PANI	Yield (%)	Cu(1%)-Meso-PANI	[b]Yield (%)
1.			3 hr	100	[a]24 h	52
2.			45 min	100	1.5 h	100
3.			2.0 h	100	3.0 h	95
4.			1.5 h	100	2.5 h	93
5.			2.0 h	100	4.0 h	96
6.			2.5 h	100	4.0 h	90
7.			2.0 h	100	3.0 h	80

Reaction condition: reactant (1 mmol), solvent (10 ml, EtOH: water = 1:1), catalyst (50 mg), $NaBH_4$ (5 mmol), temperature (313 K).

[a] Reaction was conducted at 353 K.

[b] Isolated yield.

much higher than Cu metal decorated on PANI (Table 1). Uniform dispersion of Cu nanoparticles in the Meso-PANI matrix was confirmed using TEM (Fig. 3a), however, in the TEM image, it was noticed that the particles were not clearly monodispersed. The selected area electron diffraction patterns show diffuse ring pattern for the Cu nanoparticles present in Cu(10%)-Meso-PANI (Fig. 3a). EDS analysis further confirms the incorporation of Cu in Cu(10%)-Meso-PANI (Fig. 3b). UV–visible study also confirms the formation of Cu nanoparticle decorated Meso-PANI material (See Fig. S1 and other details in supporting information).

3.2. Catalytic activity

4-Nitroaniline was chosen as a model substrate to find the optimum reaction condition. The reduction of 4-nitroaniline by $NaBH_4$ in the absence of metal catalyst was quite slow and the reaction was not initiated even after 8 h at 313 K. Thus a combination of catalyst and $NaBH_4$ was investigated. The combination of Cu(10%)-Meso-PANI and EtOH:H_2O (1:1) was found to be very effective for the reduction of 4-nitroaniline using $NaBH_4$ as a reducing agents, which gave 100 % yield for *p*-phenylenediamine in 45 min (Table 2). Among the solvents investigated, EtOH:H_2O (1:1) was found to be the best for the reduction of nitroaromatics, when dissolution of reactants and catalytic activities are taken into account (Table 3).

Support plays an important role for the uniform dispersion with suitable dimension of metal nanoparticles, which is very important for high catalytic activity [30]. It is interesting to note that the activity of Cu(1%)-PANI is lower than that of Cu(1%)-Meso-PANI (Table 2). High catalytic activity of Cu(1%)-meso-PANI can be correlated with the high surface area of Meso-PANI compared to PANI, which provides favourable high dispersion of Cu nanoparticles and enhance the accessibility of reactant molecules to catalytic active sites. For comparative study, several M(1%)-Meso-PANI were prepared and investigated in the reduction of 4-nitroaniline. Among the M(1%)-Meso-PANI, Cu(1%)-Meso-PANI exhibited the highest activity, whereas Mn(1%)-Meso-PANI exhibited the lowest activity (Table 2). It was very interesting to note that commercially available Cu(II) and Cu(I) salts were also found to be active for the reduction of 4-nitroaniline in the presence of $NaBH_4$, however, their activity was found to be lower than that of Cu(1%)-Meso-PANI (Table 2).

It is known that Cu nanoparticles form CuH by transfer hydrogenation in the presence of reducing agent under the reaction conditions [31]. It may further be noted that the formation of CuH by the reaction of Cu and H_2 needed high pressure [32]. CuH is thermally unstable and undergoes decomposition under the reaction conditions to generate Cu and hydrogen to accomplish the reduction of nitro groups via a transfer-hydrogenation process [33].

Catalysts were found to be recyclable. After completion of the reaction, catalyst was separated by the centrifugation from the reaction mixture, which was washed first with ethyl acetate (thrice) followed by washing with water (twice). Recovered catalyst was dried in vacuum at 353 K for 8 h and used in the fresh reaction. No significant loss in catalytic activity was observed even after 5 recycle (Table 2). Hot-filtration method further confirmed that no catalytic species was leached into the reaction mixture. Cu(1%)-Meso-PANI and Cu(10%)-Meso-PANI were found to be stable even after their reuse, which was confirmed by XRD (Fig. S2, supporting information) and N_2-adsorption studies (Table 2).

Scope of this reaction was extended to other nitroaromatics such as nitrobenzene and substituted nitrobenzene. A wide range of substituted nitroaromatic compounds were reduced by this procedure to produce the corresponding aromatic amines. Reduction of nitrobenzene required much longer time than the reduction of substituted nitrobenzene (Table 4). It may be noted that high Cu loading is required to obtain the quantitative yield of aniline upon the reduction of nitrobenzene. In general, *ortho*-substituted nitrobenzene took longer time than *para*-substituted nitrobenzene during the reduction process (Table 4). The reduction of *p*-chloro nitrobenzene proceeded selectively, without any dehalogenation (Table 4).

In general, the reactions were very clean, giving the amines in high yields. No intermediate product was observed during or after the reaction for various nitroaromatics. However, an intermediate product was observed during the reduction of nitrobenzene using Cu(1%)-Meso-PANI. Intermediate product was separated by column chromatography and identified by using IR and NMR. Isolated intermediate product was identified as azobenzene. To understand the mechanistic pathway, two parallel reduction reactions of nitrosobenzene and azobenzene were conducted. Under this condition, nitrosobenzene gave aniline whereas, azobenzene gave 1,2-diphenylhydrazine as major product and aniline as a minor product. Since we did not observe any intermediate during the reaction (except in the case of the reduction of nitrobenzene over Cu(1%)-Meso-PANI), hence, we can conclude that this reaction proceeds via nitrosobenzene derivative, which consumed instantly as soon as it formed during the reaction and therefore, we did not identify nitrosobenzene as intermediate. Whereas, the reduction of azobenzene is very slow process, and hence, it was detected in the case of Cu(1%)-Meso-PANI.

4. Conclusion

In summary, we reported the reduction of nitroaromatics to aromatic amines by using transition metal incorporated Meso-PANI. Among the catalysts investigated, Cu(10%)-Meso-PANI exhibited the highest activity. The simple operation, use of economical catalyst & reducing agent, mild reaction conditions, short reaction time, high yields of amines, reduction of wide range of substituted nitroaromatics, and recyclability of the catalyst make this protocol an attractive route for the reduction of aromatic nitro compounds.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2013.03.034.

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