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# Encapsulation of silver nanoparticles into graphite grafted with hyperbranched poly(amidoamine) dendrimer and their catalytic activity towards reduction of nitro aromatics

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# ABSTRACT

Hyperbranched polyamidoamine (PAMAM) dendrimer have been successfully grafted on the graphite surface and silver nanoparticles (AgNPs) were readily synthesized within the graphite grafted PAMAM dendrimer templates and applied as nanocatalysts in the reduction of nitro aromatics. Three generations of PAMAM dendrimers with varying chain branches have been utilized in order to serve this purpose. The grafting of PAMAM dendrimer on graphite surface has been monitored using TGA, Raman and FT-IR spectra and the AgNPs/GR-G<sub>1.0</sub>PAMAM, AgNPs/GR-G<sub>2.0</sub>PAMAM, AgNPs/GR-G<sub>3.0</sub>PAMAM nanocatalysts were characterized using XRD, UV-visible spectra, SEM, TEM and EDX spectral analysis. The prepared catalysts were found to exhibit enhanced catalytic activity towards the reduction of 4-nitrophenol and the reaction rate constant for our third generation catalyst was estimated to be  $21.7 \times 10^{-3} \, \text{s}^{-1}$ , which is the highest reported heterogeneous system so far. The efficiency of the system has been further demonstrated through the reduction of halonitroarenes without dehalogenation in the halo-substituted nitro benzenes and reduction of nitro groups in the presence of imine functionalities under mild condition.

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# 1. Introduction

Aromatic amines are versatile synthetic intermediates due to their application in the preparation of dyes, pharmaceuticals, agricultural products, surfactants and polymers [1–3]. At both laboratory and industrial scale, the preparation of aromatic amines is conventionally accomplished by the reduction of corresponding nitro compounds using catalytic hydrogenation and a variety of other reduction conditions [4,5]. Numerous reducing agents have been utilized for the reduction of nitro compounds with the most classic being metallic reagents in the presence of an acid. However, this methodology is messy and environmentally hazardous [6] and therefore synthetic routes involving clearer and cheaper alternatives are necessary. One such methodology is to employ NaBH<sub>4</sub> in water as the hydride source. However, reduction of nitro groups with NaBH<sub>4</sub> in the absence of any catalyst is highly tedious and hence many different metal catalysts have been used to carry out this reduction [7-9].

Noble metal nanoparticles have attained great attention in catalysis research since they possess high surface area than that of their bulk counterparts leading to improved catalytic activities [10–12]. The highly active surface atoms of these nanoparticles could lead to aggregation of the naked nanoparticles and consequently resulting in diminished catalytic activity. Metal nanoparticles based on different methods have been developed to solve this issue and utilized for the catalytic reduction of nitrophenols to amines. Yang et al. have employed gold nanoparticles doped in mesoporous organic gel based on polymeric phloroglucinol carboxylic acid-formaldehyde as a nanocatalyst for the catalytic reduction of 4-nitrophenol, with a reduction rate constant of  $7.4 \times 10^{-3} \text{ s}^{-1}$ [13]. Hayakawa et al. reported that gold nanoparticles prepared by laser irradiation methods have shown a rate constant of  $1.78-13.2 \times 10^{-3} \text{ s}^{-1}$  [14] and Panigrahi et al. have reported gold nanoparticles supported by polystyrene anion resin which exhibited a rate constant of  $0.16 \times 10^{-3} \text{ s}^{-1}$  [15]. Lu et al. have reported the tree-type spherical polymer supported silver nanoparticles (AgNPs) and their estimated rate constant was  $0.33 \times 10^{-3} \text{ s}^{-1}$  [16]. However, these procedures suffer from selectivity, for instance, reduction of halo substituted nitro aromatics resulted in dehalogenated amines [17,18]. To overcome this problem, Chen et al. and Raja et al. have prepared Ag, Au, Co and Pd nanoparticles embedded in silica matrix to achieve reduction of nitro selectivity with high yield [19-21]. This methodology requires high temperatures ( $\sim$ 140 °C) and high pressure ( $\sim$ 120 atm) conditions which might be due to smaller available metal sites on the surface of SiO<sub>2</sub> matrix.

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Therefore, the need of the day is to encapsulate the metal nanoparticles in a heterogeneous system that permits easy passage of the substrates and products of the catalytic reaction. One such way is to stabilize the nano particles in an organic dendrimer matrix which provides open and flexible structure. Polyamidoamine (PAMAM) dendrimers are highly branched, well-defined, synthetic macromolecules available in nanometer dimensions [22]. Synthetic methodologies for dendrimer structure are difficult and expensive [23] and hence alternative methods have been adopted by constructing dendrimer branches on solid support such as chitosan, carbon nanotubes, silica, polymer surface [24-28]. These matrices are again found to be expensive and hence our focus was to synthesize PAMAM dendrimer branches on graphite surface. In addition to its cost-effectiveness, graphite grafted organic dendrimer structures provide the property that can bridge the gap between homogeneous and heterogeneous phase.

Hence, in the present investigation we have synthesized novel nanocatalysts based on AgNPs encapsulated on three generations of PAMAM dendrimers with varying chain branches that have been grafted on graphite surface. The efficiency of prepared nanocatalysts towards reduction of nitro aromatics has been examined. It has been demonstrated that our third generation catalyst shows the reduction rate constant of  $21.7 \times 10^{-3} \text{ s}^{-1}$ , which is the highest among reported values. Further, the selectivity of the nanocatalyst towards the selective reduction of nitro groups in presence of halo- and imine-substituents has been verified.

### 2. Experimental

## 2.1. Chemicals

Graphite, fine powder of particle size 50 µm was purchased from Loba Chemie Pvt. Ltd., India. Sulfuric acid, potassium permanganate, hydrogen peroxide, sodium nitrate, thionyl chloride, hydrazine monohydrate, ethylene diamine (EDA), methacrylate (MA), silver nitrate, sodium borohydride, 4-nitrophenol, nitrobenzene, 4-nitrotoluene, 2-hydroxynitrobenzene, 2-chloronitrobenzene, 4-bromonitrobenzene, 4-iodonitrobenzene, 2aminonitrobenzene, 4-aminonitrobenzene, 4-nitrobenzylalcohol, 4-chloro-3,4-dinitrobenzene were obtained from Merck, India. All chemicals were used without further purification. Double distilled water was used through out the experiment.

# 2.2. Systematic preparation of novel AgNPs/GR-G<sub>1.0</sub>PAMAM, AgNPs/GR-G<sub>2.0</sub>PAMAM and AgNPs/GR-G<sub>3.0</sub>PAMAM

# 2.2.1. Preparation of graphene oxide [GR-COOH] from graphite

Graphene oxide (GO) was prepared using a reported procedure of Hummers and Offeman's method [10] with minor modifications. In a typical reaction, 1 g of graphite, 1 g of NaNO<sub>2</sub>, and 50 mL of H<sub>2</sub>SO<sub>4</sub> were stirred together in an ice bath. KMnO<sub>4</sub> (3 g) was slowly added to the stirring mixture, and the rate of addition was controlled to prevent the temperature of reaction vessel from exceeding 20 °C. The mixture was then transferred in to a 35 °C water bath and stirred for 1 h, resulting in the formation of a thick paste. Subsequently, 50 mL of de-ionized water was added gradually, resulting in an increase in temperature to 98 °C. After 15 min, the mixture was further treated with 150 mL de-ionized water and 10 mL 30% H<sub>2</sub>O<sub>2</sub> solution. The warm solution was filtered and then washed with de-ionized water until a pH of 7 is obtained and the GR-COOH was dried at 65 °C under vacuum.

# 2.2.2. Preparation of acylated graphene [GR-COCI] from graphene oxide [GR-COCI]

GR-COOH (0.5 g) was suspended in SOCl<sub>2</sub> (30 mL) and stirred for 24 h at 70  $^{\circ}$ C. This solution was filtered and then washed with

anhydrous tetrahydrofuran (THF), and dried under vacuum for 24 h at room temperature, generating acylated graphene (GR-COCl) (0.4953 g).

# 2.2.3. Preparation of GR-NH<sub>2</sub> initiator from GR-COCl

GR-COCl (0.4953 g) was mixed with ethylenediamine (20 mL) and placed in an ultrasonic bath (40 kHz) for 5 h at 60 °C. The mixture was stirred for another 24 h at the same temperature and the resulting solid was separated by vacuum filtration using 0.22  $\mu$ m Millipore polycarbonate membrane filter and subsequently washed with anhydrous methanol. After repeated washing and filtration, the resulting solid was dried overnight under vacuum, generating GR-NH<sub>2</sub> (0.5020 g).

# 2.2.4. Growth of PAMAM dendrimers on the GR surface initiated by GR-NH<sub>2</sub>

The mixture of methylacrylate (20 mL) and methanol (50 mL) was added to a 250 mL three-necked round-bottom flask. The prepared GR-NH<sub>2</sub> initiator (0.1 g) in 20 mL methanol was carefully dropped in to methylacrylate solution within 20 min with continuous stirring. The solution was placed in an ultrasonic bath (40 kHz) for 7 h at 50 °C and the mixture was stirred for another 24 h. In order to ensure that no ungrafted polymer or free reagents were present in the product, the filtered solid was dispersed in methanol, filtered, and washed three times with methanol. The product was dried overnight to give the dendritic polymer grafted graphite generation 0.5 (GR-G<sub>0.5</sub>PAMAM, 0.1011 g).

After rinsing,  $GR-G_{0.5}PAMAM$  in 20 mL methanol was dropped into 40 mL of 1:1 methanol/ethylenediamine solution. The solution was placed in an ultrasonic bath (40 kHz) for 5 h at 50 °C, and the mixture was stirred for another 24 h at the same temperature. The solid was then filtered and washed three times with methanol to give generation 1.0 dendrimer modified graphite (GR-G<sub>1.0</sub>PAMAM). Stepwise growth using methylacrylate and ethylenediamine was repeated until the desired number of generations (up to generation 3.0) were achieved (Scheme 1). The dendrimer-modified GR was then washed thrice with methanol (25 mL), and water (25 mL) respectively.

# 2.2.5. Dispersion of AgNPs on the hyperbranched GR-G<sub>1.0</sub>, GR-G<sub>2.0</sub>, GR-G<sub>3.0</sub>PAMAM dendrimer grafted graphite [AgNPs/GR-G<sub>1.0, 2.0, 3.0</sub>PAMAM]

A 100 mL two-neck round bottom flask with 50 mg of hyperbranched dendrimer grafted graphite ( $GR-G_{1.0}PAMAM$ ,  $GR-G_{2.0}PAMAM$ , and  $GR-G_{3.0}PAMAM$ ) were dispersed with 10 mL of de-ionized water and then sonicated for 30 min. To this dispersion, 10 mL of 0.01 M of AgNO<sub>3</sub> solution was added drop wise into each of the generation dendrimer grafted graphite and the mixture was stirred for 1 h and then finally reduced with 0.01 M NaBH<sub>4</sub> (10 mL). The filtered solid was washed three times with water. The product was dried overnight under vacuum (AgNPs/GR-G<sub>1.0</sub>PAMAM, AgNPs/GR-G<sub>2.0</sub>PAMAM, AgNPs/GR-G<sub>3.0</sub>PAMAM) (46 mg, 43 mg, 40 mg) respectively.

# 2.3. Characterizations

The PAMAM dendrimer functionalizations on the graphite surface were confirmed by micro Raman spectrometer (Witec Confocal Raman instrument (CRM200) with Ar ion laser 514.5 nm). The crystalline nature of the AgNPs/GR-G<sub>1.0</sub>PAMAM, AgNPs/GR-G<sub>2.0</sub>PAMAM, AgNPs/GR-G<sub>3.0</sub>PAMAM samples were studied by powder XRD using X-pertPRO Pananalytical X-ray diffractometer employing Cu K $\alpha$  radiation. The IR spectra of the samples were recorded on Nicolet 6700 FT-IR spectrometer using KBr method. Surface morphology and elemental composition of the catalyst



Graphite

Scheme 1. AgNPs/GR-G<sub>3.0</sub>PAMAM dendrimer.

were determined by SEM (HITACHI S-3400N Scanning Electron Microscope) along with EDX Energy dispersive-X-ray spectroscopy (Thermo SuperDry II attached with SEM). Tecnai F-30 field emission Transmission Electron Microscope (TEM) has been used to capture the TEM images of AgNPs. The additional information of PAMAM dendrimer grafting was also obtained from thermal gravimetric analyzer (TG-DTA-Q 600 SDT) from room temperature to 800 °C. Optical absorption spectra of the prepared nano catalyst were recorded at room temperature with Ocean optics (HR4000) spectrophotometer.

## 3. Results and discussion

# 3.1. Grafting of PAMAM dendrimer on graphite surface

The grafted content of the PAMAM dendrimer modified graphite can be determined by measuring the weight loss between 200 °C and 800 °C [29,30]. TGA curves in Fig. 1 demonstrate no weight loss for pure graphite whereas the graphene oxide shows weight loss of ~11% between 100 and 150 °C corresponding to the pyrolysis of -OH and -COOH groups [31-34]. In case of PAMAM dendrimers



**Fig. 1.** TGA thermograms of: (a) pure graphite, (b) GR-COOH, (c) GR-G<sub>1.0</sub>PAMAM, (d) GR-G<sub>2.0</sub>PAMAM, and (e) GR-G<sub>3.0</sub>PAMAM dendrimer grafted graphite.



**Fig. 2.** Raman spectra of: (a) pure graphite, (b) GR-G<sub>1.0</sub>PAMAM, (c) GR-G<sub>2.0</sub>PAMAM, (d) GR-G<sub>3.0</sub>PAMAM and dendrimer grafted graphite.



**Fig. 3.** FT-IR spectra of: (a) pure graphite, (b) GR-COOH, (c) GR-COCI, (d) GR-CONH<sub>2</sub>, (e) GR-methylacrylate, and (f) GR-G<sub>1.0</sub>PAMAM dendrimer respectively.



**Fig. 4.** X-ray diffraction patterns of: (a) pure graphite, (b) GR-G<sub>3.0</sub>PAMAM, (c) AgNPs/GR-G<sub>1.0</sub>PAMAM, (d) AgNPs/GR-G<sub>2.0</sub>PAMAM, and (e) AgNPs/GR-G<sub>3.0</sub>PAMAM.

grafted graphite, additional weight losses from organic moieties were also seen and the weight losses were estimated as 16%, 20%, 34%, for GR-G<sub>1.0</sub>PAMAM, GR-G<sub>2.0</sub>PAMAM, GR-G<sub>3.0</sub>PAMAM in the temperature range 200–800 °C. The gradual increase in weight loss from  $G_{1.0}$ PAMAM to  $G_{3.0}$ PAMAM indicates the expansion of dendrimer network and thus the TGA analysis supports our synthetic approach depicted in Scheme 1.

The linkage between graphite and PAMAM dendrimer was investigated by recording the Raman spectra of dry samples of graphite powder using the laser excitation of 514.5 nm. Fig. 2 represents the Raman spectra of pure graphite, GR-G<sub>1.0</sub>PAMAM, GR-G<sub>2.0</sub>PAMAM and GR-G<sub>3.0</sub>PAMAM dendrimer (curves a-d respectively) and all the samples were found to show two predominant peaks corresponding to D and G bands respectively [35–38]. The D and G bands for pure graphite are observed around 1357 and 1568 cm<sup>-1</sup> respectively which arise from the activation in the first order scattering process of sp<sup>3</sup> and sp<sup>2</sup> carbon in graphite sheets respectively. The intensity ratio of D and G bands expresses the sp<sup>2</sup>/sp<sup>3</sup> carbon ratio manifesting the measure of disorder [39]. Generally, the D band is relatively weak or nearly invisible in perfect graphite lattice and can arise from symmetry breaking at the edge. The D bands appeared at 1357 cm<sup>-1</sup> for all the samples without any shift in absorption energy and



**Fig. 5.** UV-visible spectra of: (a) GR-COOH, (b) GR-G $_{3,0}$ PAMAM, and (c) AgNPs/GR-G $_{3,0}$ PAMAM nanocatalysts.



Fig. 6. SEM images of: (A and B) pure graphite, (C and D) GR-G<sub>3.0</sub>PAMAM, (F-H) TEM images of AgNPs/GR-G<sub>3.0</sub>PAMAM.

the peak intensity was found to increase gradually upon the substitution of PAMAM dendrimer. The D/G ratios were found to be 0.730, 0.987, 1.018, 1.03 for pure graphite,  $GR-G_{1.0}PAMAM$ ,  $GRG_{2.0}-PAMAM$ ,  $GR-G_{3.0}PAMAM$  respectively, due to increase in the number of sp<sup>3</sup> carbon atom reflecting the successful functionalization of the PAMAM dendrimer on the graphite surfaces. Furthermore, the G band of the pure graphite appears at 1568 cm<sup>-1</sup> which gets shifted to 1580 cm<sup>-1</sup>, 1583 cm<sup>-1</sup> and 1588 cm<sup>-1</sup> in the case of GR-G<sub>1.0</sub>PAMAM, GR-G<sub>2.0</sub>PAMAM, and GR-G<sub>3.0</sub>PAMAM dendrimers respectively. This observed red shift and increase in the intensity of G band again confirms the substitution induced defect on the sp<sup>2</sup> carbon atom of graphite sheets. These observations are in line with the reports Kudin et al. [37]. Henceforth, the Raman spectral analysis affirms that the PAMAM dendrimers have been profoundly exfoliated on the graphite surface.

Further evidence of PAMAM dendrimer exfoliation on the graphite surface has been probed by FT-IR spectroscopy studies (Fig. 3). The FT-IR spectra of pure graphite (Fig. 3, curve a) shows the stretching vibrations of C=C and C–C groups around 1650 and 1380 cm<sup>-1</sup> to the respectively [25,40]. The spectra of GR-COOH (Fig. 3, curve b) shows broad and intense peaks at 3436, 1734, and 1258 cm<sup>-1</sup> corresponding to the stretching vibration of O–H, C=O, and C–O groups respectively [41]. As observed from the spectrum of acylated graphite GR-COCI in Fig. 3 (curve c), the peak corresponding to O–H stretching vibration at 3436 cm<sup>-1</sup> disappeared and the –C=O stretching vibration shifted from 1734 cm<sup>-1</sup> to 1694 cm<sup>-1</sup> along with the introduction of a new peak at 694 cm<sup>-1</sup> confirms the formation of C–CI bond. The anchoring of ethylene

diamine (Fig. 3, curve d) on to the graphite surface was confirmed by the appearance of an amide band, -CONH- at 1645 cm<sup>-1</sup> and  $-NH_2$ band at 3435 cm<sup>-1</sup>. The formation of GR-methylacrylate (Fig. 3, curve e) was ensured through the vanishing of 3435 cm<sup>-1</sup> signal and introduction of ester peak at 1670 cm<sup>-1</sup>. The confirmation of GR-G<sub>1.0</sub>-PAMAM dendrimer (Fig. 3, curve f) could be seen via the appearance of  $-NH_2$  peak at 3435 cm<sup>-1</sup> and C=O peak at 1722 cm<sup>-1</sup> [28]. Other PAMAM dendrimer grafted samples exhibited similar behavior.

# 3.2. Encapsulation of AgNPs into the graphite grafted PAMAM dendrimer

X-ray diffraction was carried out in order to compare the crystallinity of the grafting PAMAM dendrimer network on the graphite surface and the encapsulated silver nano particles. The powder XRD spectra (Fig. 4, curves c–e) reveals that all the three generation of PAMAM dendrimers supported silver nanoparticle with sizes about 20 nm calculated through Scherrer's equation  $(L=0.9\lambda/\beta(2\theta)\times\cos\theta_{\rm max})$ . The diffraction patterns suggest that AgNPs exist in hcp and shows reflections at  $2\theta = 38.2^{\circ}$ ,  $44.2^{\circ}$ ,  $64.6^{\circ}$  and  $77.4^{\circ}$  corresponding to  $\{1\,1\,1\}$ ,  $\{2\,0\,0\}$ ,  $\{2\,2\,0\}$ , and  $\{3\,1\,1\}$  lattice planes respectively [42,43]. Moreover the damage to graphite layer structure can be seen from complete collapse of diffraction pattern at 26.45° implying that the PAMAM grafted graphite samples are composed of mostly single or few layers.

Systematic changes were observed in UV-visible spectra while grafting the dendrimer and also during the encapsulation of AgNPs



Fig. 7. Energy dispersive-X-ray spectrum (EDX) of AgNPs/GR-G<sub>3.0</sub>PAMAM.



**Fig. 8.** (A) UV-visible spectra for the reduction of 4-nitrophenol measured at 15 s intervals using AgNPs/GR-G<sub>3.0</sub>PAMAM nanocatalyst and (B) plot of ln *A* vs time (s) for the reduction 4-nitrophenol using AgNPs/GR-G<sub>3.0</sub>PAMAM nanocatalyst.

(Fig. 5, curves a–c). In Fig. 5 (curve a) an absorption band at 240 nm, indicative of  $\pi$ – $\pi$ \* transition of graphene oxide appeared and this band shifted to 300 nm upon grafting the PAMAM dendrimer. This red shift is ascribed to the n– $\pi$ \* transition of PAMAM dendrimer (Fig. 5, curve b) and this confirms the successful grafting. Encapsulation of AgNPs can be seen in Fig. 5 (curve c) through the strong surface plasmon resonance absorption at 417 nm [44,45].

The scanning electron microscope images demonstrate a clear preview of the surface of graphite samples before and after functionalization with PAMAM dendrimer. Fig. 6A and B shows the SEM images of pure graphite which shows flakes like structures indicating multilayered morphology. In the case of PAMAM substituted graphite (Fig. 6C and D), the detectable layers have been replaced by diffused snow like features which could be ascribed to the distraction of graphite layers by dendrimer substitutions. Fig. 6E represents the SEM images of third generation PAMAM dendrimer encapsulated with AgNPs which indicates that the AgNPs are uniformly anchored dispersed within the PAMAM dendrimer network. TEM images shown in Fig. 6F-H also demonstrate the successful encapsulation of AgNPs within PAMAM dendrimer. AgNPs are buried inside the dendrimer network cavities and hence the clear crystalline morphology of AgNPs could not be visualized clearly and they appear as black mass.

Further the catalyst was also characterized by EDX analysis (Fig. 7). The EDX analysis demonstrates the AgNPs accumulation



Fig. 9. Catalytic dosage of AgNPs/GR-G<sub>3.0</sub>PAMAM.

with in the PAMAM dendrimer cavity. In the EDX spectrum, the signals of C, O, and N are present besides the Ag signal, indicating the AgNPs distribution with the PAMAM dendrimer structure.

Table 1

Systematic literature survey of the reduction of 4-nitrophenol and corresponding rate constant at room temperature.<sup>a</sup>

Entry	Sample	Carrier system	Metal	Particle size (nm) <sup>b</sup>	k (s <sup>-1</sup> ) <sup>c</sup>	Ref.
1	AgNPs/GR-G <sub>3.0</sub> PAMAM <sup>d</sup>	PAMAM dendrimer	Ag	20 nm	$21.7 \times 10^{-3} \ s^{-1}$	This work
2	AgNPs/GR-G <sub>2.0</sub> PAMAM <sup>d</sup>	PAMAM dendrimer	Ag	20 nm	$10.7  imes 10^{-3}  s^{-1}$	This work
3	AgNPs/GR-G <sub>1.0</sub> PAMAM <sup>d</sup>	PAMAM dendrimer	Ag	20 nm	$2.4  imes 10^{-3} \ s^{-1}$	This work
4	Au-PF <sup>e</sup>	Gel	Au	8 nm	$7.4  imes 10^{-3}  s^{-1}$	13
5	Au-PAMAM/PPI <sup>f</sup>	Dendrimer	Au	8.3 nm	$1.78{-}13.2\times10^{-3}s^{-1}$	14
6	Au-resin <sup>g</sup>	Ion-exchange resin	Au	17 nm	$0.16  imes 10^{-3}  s^{-1}$	15
7	Ag-PS-PEGMA <sup>h</sup>	Polymer brush	Ag	7.5 nm	$0.33 \times 10^{-3} \ s^{-1}$	16

<sup>a</sup> Reactions were catalyzed by AgNPs/GR-G<sub>1.0</sub>PAMAM, AgNPs/GR-G<sub>2.0</sub>PAMAM, AgNPs/GR-G<sub>3.0</sub>PAMAM.

<sup>b</sup> Nanoparticles size (observed by TEM).

<sup>c</sup> Apparent rate constant (k) s<sup>-1</sup>.

<sup>d</sup> Graphite grafted G<sub>3.0, 2.0, 1.0</sub> PAMAM dendrimer encapsulated AgNPs respectively.

<sup>e</sup> Polymeric phloroglucinol carboxylic acid-formaldehyde supported Au nanoparticles.

<sup>f</sup> Polypropyleneimine dendrimer supported AuNPs.

<sup>g</sup> Polystyrene anion resin supported AuNPs.

<sup>h</sup> Polystyrene grafted poly(ethyleneglycol) methylacrylate supported AgNPs.

# Table 2

Catalytic reduction of various nitro aromatics over AgNPs/GR<sub>3.0</sub>-PAMAM.<sup>a,b</sup>

Entry	Substrate	Product	Time (min)	Yield <sup>c</sup> (%)
1	NO <sub>2</sub>	NH <sub>2</sub>	20	100
2	NO <sub>2</sub> OH	NH <sub>2</sub> OH	25	100
3		NH <sub>2</sub> OH	25	100
4	NO <sub>2</sub> NH <sub>2</sub>	NH <sub>2</sub> NH <sub>2</sub>	20	100
5	NO <sub>2</sub>	NH <sub>2</sub>	20	100
6	NO <sub>2</sub> HO	NH <sub>2</sub> OH	25	100
7	NO <sub>2</sub> NH <sub>2</sub>	NH <sub>2</sub> NH <sub>2</sub>	25	100
8		NH <sub>2</sub> NH <sub>2</sub> Cl	40	64
9	NO <sub>2</sub> Cl	NH <sub>2</sub> Cl	10	100
10	NO <sub>2</sub> Br	NH <sub>2</sub> Br	20	100
11	NO <sub>2</sub>	NH <sub>2</sub>	20	100
12		NH2 N NH2	40	61

<sup>a</sup> Reactions conditions: 50 mg of catalyst, 1 mmol of substrate 10 mmol of NaBH<sub>4</sub>, 50 mL of water stirring at room temperature.

<sup>c</sup> Conversion yield was monitored through GC.

<sup>&</sup>lt;sup>b</sup> Reused of the catalyst after separation from the reaction mixture.

# 3.3. Catalytic activity

#### 3.3.1. Catalytic reduction of nitro arenes

The catalytic performance of the AgNPs/GR-G<sub>1.0</sub>PAMAM, AgNPs/GR-G<sub>2.0</sub>PAMAM, AgNPs/GR-G<sub>3.0</sub>PAMAM, was studied through model reduction kinetic experiment using 0.01 M aqueous solution of 4-nitrophenol and 0.1 M NaBH<sub>4</sub> and 5 mg catalyst [13–16]. The reduction was monitored through the absorbance recorded at 400 nm (Fig. 8) and the pseudo first order rate constant was estimated to be  $21.7 \times 10^{-3} \text{ s}^{-1}$  (Table 1), for AgNPs/GR- $G_{3,0}$ PAMAM which is the highest achieved so far to the best of our knowledge in catalytic reduction of aromatic nitro compounds. The enhanced catalytic activity observed with our nanocatalyst is attributed to the hydrophobic environment created by the dendrimer backbone which stabilizes the aryl nitro substrates adjacent to the catalytic sites which in turn facilitates the reduction of nitro groups [46]. The maximum catalytic activity obtained at AgNPs/GR-G<sub>30</sub>PAMAM (Table 1) could be the consequence of more number of encapsulated AgNPs catalysts in the highly expanded network of third generation PAMAM than the others. The reduction was found to occur only in the presence of our nanocatalyst and no reduction occurred at pure graphite powder or third generation dendrimer graphite in the absence of AgNPs which shows that the catalytic reduction occurs at the surface of our nanocatalyst. Furthermore, the catalyst could be regenerated successfully after the reduction reaction and could be reused for at least 10 more times under same conditions without any change in the reduction rate.

## 3.3.2. Influence of catalytic dosage

Fig. 9 shows the influence of catalytic dosage with various amount of AgNPs/GR-G<sub>3.0</sub>PAMAM catalyst. As expected with an increasing amount of catalyst, the rate of the reduction of 4-nitrophenol increases. The individual kinetic reactions for each dosage are shown in Figs. S1–S5 (see electronic supplementary material).

# 3.3.3. Eco-friendly procedure for selective reduction of nitro groups of various halo and imine containing nitro aromatics

In a typical reduction, 50 mg of AgNPs/GR-G<sub>3.0</sub>PAMAM catalyst was added to 50 mL of aqueous solution containing 1 mmol of halonitro compound and 10 mmol of NaBH<sub>4</sub>. The mixture was vigorously stirred at room temperature. The reaction was monitored through TLC and reaction mixture was quenched by extracting the organic derivatives with ethyl acetate. The solvent was evaporated under vacuum to give crude product of corresponding amine compound. Further purification was done through column chromatography. Then the final products were confirmed by the melting point, IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR. The conversion yield was monitored through GC [8,47].

The efficiency of AgNPs/GR-G<sub>3.0</sub>PAMAM catalyst in reducing different nitro derivatives is presented in Table 2. The striking feature of our catalyst is the quantitative reduction of halo-substituted nitro benzenes without any dehalogenations (Table 2, entries 8–11). To the best of our knowledge, this is the first report showing halonitro-derivative reduction at mild conditions without any dehalogenations. All mononitro derivatives resulted in 100% amine formation. However, dinitro derivative result in about 60–65% conversion. The remaining 35–40% have yielded monoamine derivative which can be further reduced to diamine derivatives through a separate reduction step. Another interesting feature is the selective reduction of nitro groups in the presence of imine groups (Table 2, entry 12). No imine reduction occurs under these mild experimental conditions. However, when the reaction solution was brought to reflux, imine reduction occurred.

#### 4. Conclusions

In conclusion, we have demonstrated low cost alternative procedure for systematic grafting of hyperbranched PAMAM dendrimer on graphite surface using Michael addition of methacrylate and ethylenediamine which can encapsulate and stabilize AgNPs. The third generation graphite grafted PAMAM dendrimer encapsulated AgNPs shows excellent catalytic activity towards the reduction of 4-nitrophenol under mild conditions. The versatility of our system has been demonstrated through speed of the reaction and selective nitro reduction without dehalogenation in halonitroarene and Schiff's base ligands containing imine groups. Further investigation on the encapsulation of other noble metal nanoparticles into our graphite grafted PAMAM dendrimer and their application in photocatalysis and electrocatalysis are underway.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2012.04.001.

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