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Reduction of nitroarenes catalyzed by microgel-stabilized silver nanoparticles

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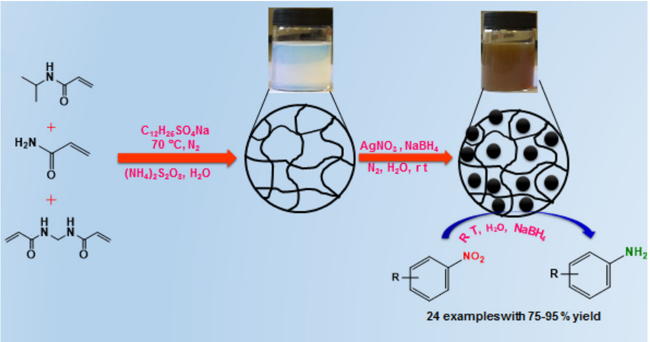
GRAPHICAL ABSTRACT



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ABSTRACT

Poly(N-isopropylacrylamide-co-acrylamide) (PNA-BIS-2) microgels were synthesized by free radical precipitation polymerization in aqueous medium. Spherical Ag nanoparticles with diameter of 10–20 nm were fabricated inside the PNA-BIS-2 microgels by in-situ reduction of silver nitrate using sodium borohydride as reducing agent. The Ag nanoparticles- loaded hybrid microgels were characterized by Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Energy dispersive X-ray (EDX), Scanning transmission electron microscopy (STEM), Ultraviolet visible spectroscopy (UV Visible), Thermogravimetric analysis (TGA) and X-ray diffraction (XRD). Ag contents in the hybrid system were determined by inductively coupled plasma - optical emission spectrometry (ICP-OES). Various nitroarenes were successfully converted into their respective aromatic amines with good to excellent yields (ranging from 75% to 97%) under mild reaction conditions. The catalyst has ability to successfully convert substituted nitroarenes into desired products keeping many functionalities intact.

Abbreviations: NiPAM, N-isopropylacrylamide; AAm, acrylamide; SDS, sodium dodecyl sulfate; APS, ammonium per sulfate; BIS, N, N-methylenebisacrylamide; SEM, scanning electron microscopy; PNA-BIS-2, poly(N-isopropylacrylamide-co-acrylamide) microgel; Ag-PNA-BIS-2, silver nanoparticles loaded poly(N-isopropylacrylamide-co-acrylamide) microgel; TEM, transmission electron microscopy; STEM, scanning transmission electron microscopy; XRD, X-ray diffraction; TGA, thermogravimetric analysis; EDX, energy dispersive X-ray; ICP-OEC, inductively coupled plasma - optical emission spectrometry; TLC, Thin layer chromatography; TMS, tetramethylsilane; ^{1}H NMR, proton NMR; ^{13}C NMR, carbon; HRMS, high resolution mass spectrometer; EtOAC, ethyl acetate; GC-QTOF-MS, gas chromatography time-of-flight mass spectrometer; ESI, electronic supplementary information; λ_{spr}, surface plasmon resonance wavelength

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The catalyst can be stored for long time without any sign of aggregation and can be used multiple times without any significant loss in its catalytic activity.

1. Introduction

Synthesis of aryl amines is an important process in laboratory and chemical industry because aromatic amines are important intermediates in synthesis of biochemicals, polymers, antioxidants, dyes, pharmaceuticals and fine chemicals [1–3]. Amines are generally synthesized from chemical reduction of their corresponding easily available and in-expensive nitro compounds in the presence of a catalyst [[4–7]]. Reduction of nitroarenes has been reported in the presence of both homogeneous [4–7] and heterogeneous catalysts [8]. Homogeneous catalysts are expensive, toxic and generally commercially unavailable. They cannot be recycled easily. Difficulty in separating them from final reaction product is still a challenge for researchers dealing homogeneous catalysis [9,10]. Recycling and separation problems can be overcome by replacing homogeneous catalysts by heterogeneous catalysts. But the use of heterogeneous catalysis is limited due to catalytic poisoning and low contact of reactant molecules with catalyst [11]. Nanocatalysis is a bridge between homogeneous and heterogeneous catalysis which can be used to overcome aforementioned problems associated to both homogeneous and heterogeneous catalysis [12]. Therefore metal nanoparticles catalyzed reduction of nitroarenes into their corresponding aryl amines has gained a considerable attention in the last decade [13]. Pt, Pd, Au and their bimetallic nanoparticles are generally used as catalysts for such kind of transformations [14–23]. These metals are highly expensive, due to which their scope as catalyst for such kind of reactions may be limited particularly on industrial scale. Moreover hydrogenation of nitroarenes in the presence of precious expensive nanocatalysts is generally carried out using highly explosive molecular hydrogen as reductant under high pressure [24,25]. It also requires specialized laboratory equipment to supply high pressure molecular hydrogen to carry out reduction process. Transfer hydrogenation may be an alternate methodology to avoid the use of H_2 [26] but it is carried out in organic solvent or combination of solvents at high temperature which are not mostly environmentally benign and catalyst cannot be recovered and reused.

Although reduction of nitro group of nitroaromatics has been reported in the presence of nanoparticles of relatively cheap metals [27–29] but such metal nanoparticles are highly unstable and non-recoverable for their multiple use as catalysts. Additionally, reduction of a nitroarene may get stopped during reaction due to accumulation of reaction intermediates on the surface of nanoparticles or due to aggregation and oxidation of nanoparticles. Catalytic reduction of nitroarenes in the presence of Ag nanoparticles using sodium borohydride as reducing agent in aqueous medium offers a solution of aforementioned problems [30] but naked Ag nanoparticles are not highly stable and may aggregate due to their high surface free energy. As a result, they may lose their catalytic activity. To increase their shelf-life and to avoid poisoning and deactivation on exposure to air, they are stabilized by surfactants [31,32], ionic liquids [33], dendrimers [34], block copolymers [35] and microgels [36–41].

Smart polymer microgels are ideal candidates for stabilization of Ag nanoparticles particularly for their use in catalysis [42]. Ag nanoparticles can be easily synthesized by reduction of silver ions within polymeric network. Size and size distribution of Ag nanoparticles can be controlled by controlling cross linking density of polymer microgel particles. Ag nanoparticles are highly stable due to donor-acceptor interaction between functional units of polymer system and metal nanoparticles [41]. Reactant molecules can access surface of nanoparticles loaded into microgels easily due to open polymer network. Hybrid catalyst can be recovered by decantation and centrifugation. Ag nanoparticles loaded into polymer hydrogels have good dispersibility in water which makes them effective catalysts for reactions occurring in aqueous medium [42]. Another important feature of polymer microgels loaded with Ag nanoparticles is their externally tunable catalytic activity [23,43,44]. Synthesis and stabilization of Ag nanoparticles in N-isopropylacrylamide (NiPAM) based polymer microgels for catalytic reduction of nitroarenes has been extensively reported in the literature [45–57]. However, silver nanoparticles-loaded polymer microgels have been generally used as catalysts for catalytic reduction of only one substrate (4-nitrophenol) in aqueous medium using sodium borohydride as hydrogen source [45–57]. Some of us have reported fabrication and stabilization of Ag nanoparticles in poly(N-isopropylacrylamide-co-acrylamide) microgels for the first time and tested their catalytic activity using reduction of 4-nitrophenol into 4-aminophenol as a model reaction in the presence of sodium borohydride [47]. All of the above mentioned publications just deal with reduction of model nitroarenes (generally 4-nitrophenol) with limited scope of substrate, without separation, purification and characterization of resulting amines. Moreover, in most of the nitroarenes reduction reactions reported in the literature, sodium borohydride has been used in excess as compared to substrate concentration ($[NaBH_4]/[substrate]$ ratio ≥ 100). It is time to move towards the catalytic applications of Ag nanoparticles-loaded hybrid microgels in practical synthetic chemistry. To the best of our knowledge, we are pioneer who are going to report synthesis of a variety of aryl amines (separated and purified) from catalytic reduction of their corresponding nitroarenes with good yields and excellent conversions in the presence of silver-poly(N-isopropylacrylamide-co-acrylic acid) hybrid microgels under mild reaction conditions using relatively small amount of sodium borohydride (only 6–8 times of substrate).

In the present work, we report synthesis and characterization of Ag nanoparticles stabilized in poly(N-isopropylacrylamide-co-acrylamide) microgels for catalytic reduction of a broad scope of nitro compounds into the corresponding amines with good to excellent yields in environmentally benign solvent, water, under mild reaction conditions. The resulting products have been separated, purified and characterized.

2. Experimental section

2.1. Materials

N-isopropropylacrylamide (NiPAM) (97%), acrylamide (AAm) (99%), ammonium per sulfate (APS) (99%), N, N′-methylenebisacrylamide (BIS) (98%), sodium dodecyl sulfate (SDS) (99%), sodium borohydride ($NaBH_4$) (96%), silver nitrate ($AgNO_3$) (98%) were purchased from Sigma Aldrich and used as received. All nitroarenes with high purity were used as received. All processes including synthesis and catalysis were carried out in deionized water. Macromolecular porous dialysis membrane tubing with molecular weight cut off value of 12000–14000 g/mol used for purification of microgels and hybrid microgels was obtained from Sigma-Aldrich.

2.2. Synthesis of microgels

Poly(N-isopropylacrylamide-co-acrylamide) microgel particles with slight modification of feed composition were synthesized by free radical precipitation polymerization as reported by our group previously [48]. The feed composition of polymer was taken in a two neck round bottom flask with a magnetic stirrer bar and dissolved in 95 mL deionized water. The flask was fitted with a condenser and temperature measuring device and was put on stirring at a rotation rate of 500 rpm. The feed composition of microgels is given in Table 1. For synthesis of PNA-BIS-2 polymer microgels, SDS (0.08 g), NiPAM (2.15 g), AAm (0.04 g) and BIS (0.06 g) were dissolved in 95 mL deionized water in a two neck round bottom flask fitted with a magnetic stirrer bar. The flask was fitted with condenser and temperature measuring device and was put on stirring at a rotation rate of 500 rpm. The solution was purged with N_2 for 30 min at room temperature and then temperature was raised to 70 °C. The reaction mixture was kept as such at 70 °C under N_2 purging for 20 min. The process of polymerization was initiated with addition of 5 mL APS solution (0.05 M). The reaction was carried on for 4.50 h under aforementioned conditions. The resulted dispersion was cooled down, centrifuged and re-dispersed in the same volume of deionized water. The dispersion was dialyzed against distilled water for 5 days to remove un-reacted moieties from polymer dispersion.

2.3. Ag nanoparticles synthesis

The fabrication of silver nanoparticles was carried out within polymer microgels by using the methodology reported by some of us with a modification in contents of precursor and microgels [48]. More precisely, the microgel dispersion (36 mL) and de-ionized water (12 mL) were mixed and stirred under N_2 purging at room temperature for 30 min. $AgNO_3$ aqueous solution (6 mL, 2 mM) was added into the dispersion and stirring was carried out for 1 h at room temperature under N_2 atmosphere before performing the dialysis of Ag^+ ions loaded microgels against distilled water for 30 min to remove the free silver ions. The reduction of Ag^+ ions was then initiated by dropwise addition of freshly prepared sodium borohydride solution (6 mL, 8 mM) into the reaction mixture at room temperature. The reaction was allowed to carry on for one hour before dialysis against distilled water.

2.4. Characterization

The surface morphologies of Ag-PNA-BIS-2 hybrid microgel particles were obtained by scanning electron microscopy (SEM) using S-4800 instrument (Hitachi Co., Japan). Imaging was made on working voltage of 10–20 kV and working distance of 7.2 mm. Small drops of dilute microgel and hybrid microgel dispersions (with dispersion to water ratio of 1/5) were dispersed onto a carbon coated copper grid for transmission electron microscopic (TEM) measurements which were performed on a JEM-2100 F electron microscope equipped with Energy Dispersive X-ray (EDX) detector (JEOL Ltd., Japan). UV–vis spectra of both pure and hybrid microgels were scanned on UVD-3500 (Labomed Inc., USA) spectrophotometer in the wavelength range of 220–700 nm. UVD-3500 was also used to monitor the progress of catalytic reduction of nitrobenzene by scanning reaction mixture in the wavelength range of 205–355 nm. Thermogravimetric analysis (TGA) of PNA-BIS-2 microgels and Ag-PNA-BIS-2 hybrid microgels was performed on TA instrument TGA-Q 500 using N_2 flow on the rate of 40 mL/minute. Approximately 3.93 mg oven dried sample was heated by varying the temperature from 25 °C to 700 °C on the heating rate of 10 °C /minute. Powder X-ray diffraction (XRD) analysis of PNA-BIS-2 microgels and Ag-PNA-BIS-2 hybrid microgels were carried out on PANalytical Xpert diffractometer with Cu-Kα radiation (k =1.54 Å) in the diffraction angle (2θ) range of 10-80° at ambient temperature. Ag contents in Ag-PNA-BIS-2 sample were measured by inductively coupled plasma (ICP) on the instrument, MY16270003. Nuclear magnetic resonance (both ^1H and ^{13}C NMR) and Mass spectrometric measurements were made on Bruker 400 MHz NMR Spectrometer and gas chromatography time-of-flight mass spectrometer (GC-QTOF-MS) respectively.

2.5. Procedure of Catalytic reduction of nitroarenes

Required amount of a nitroarene (0.25 mmol), $NaBH_4$ (1.5–2.0 mmol) and water (3 mL) were taken in Schlenk tube and then hybrid microgel dispersion (3 mL, 0.26 mol% Ag) was added. The resulting mixture was stirred at the rotation speed of 500 rpm at room temperature. The progress of the reaction was monitored by thin layer chromatography (TLC). The crude mixture was extracted using ethyl acetate (EtOAC) and solvent was removed under vaccum. The resulting crude product was loaded on silica gel column to yield final product. NMR spectra of the products were collected on a Bruker 400 MHz NMR spectrometer using tetramethylsilane (TMS) as internal standard.

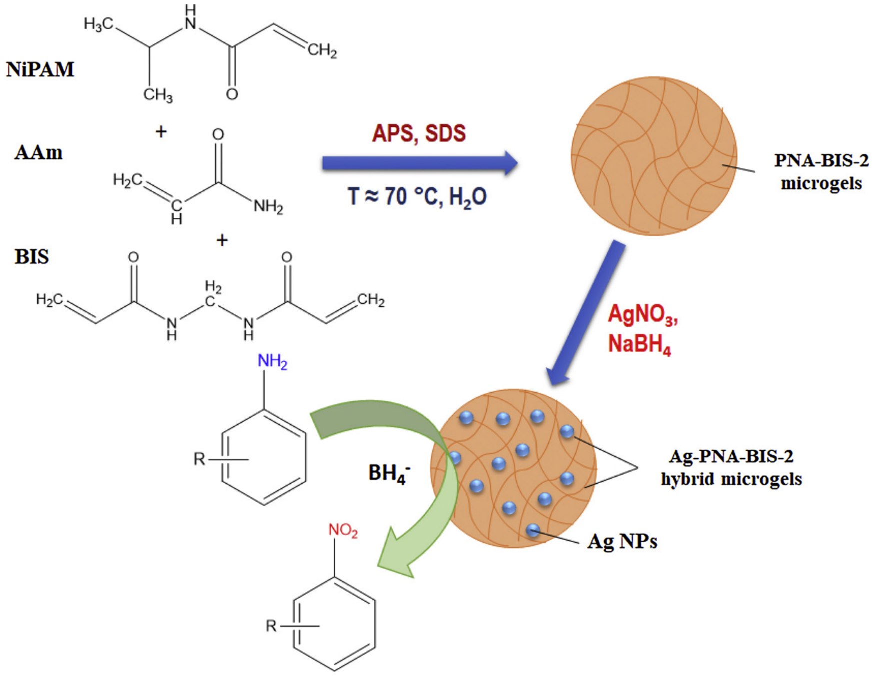
3. Results and discussion

3.1. Synthesis of pure and hybrid microgels

Poly(N-isopropylacrylamide-co-acrylamide) (PNA-BIS-2) microgel particles were synthesized by a widely used technique, free radical precipitation polymerization in aqueous medium, and used as micro-reactors for fabrication and stabilization of Ag nanoparticles via in-situ reduction of Ag^+ ions using sodium borohydride as reducing agent (Scheme 1) and has been discussed in detail by some of us previously [48]. The resulting microgels were to be expected to have good water dispersibility due to addition of hydrophilic acrylamide into NiPAM. The acrylamide functional group in the polymeric network is the least reactive due to which PNA-BIS-2 microgels can be treated as inert microgel systems. The inertness of these microgel systems makes them a potential candidate for the carrier of inorganic nanoparticles to be used as catalysts in various organic reactions. In particular, the PNA-BIS-2 microgels have a potential to be used in catalysis due to their inertness, thermal stability, open network, ligand characteristics of their functionalities, high water dispersibility, non-ionic nature and hydrophilicity in a wide temperature range. In-situ reduction of Ag^+ ions was carried out in PNA-BIS-2 microgels to obtain silver nanoparticles loaded poly(N-isopropylacrylamide-co-acrylamide) (Ag-PNA-BIS-2) microgels. The colour change of reaction mixture from milky white to brownish yellow upon addition of sodium borohydride was an indication of fabrication of Ag nanoparticles in polymer microgels as shown in Fig. S1 and supplementary movie (SM1) of electronic supplementary information (ESI). The colour change in reaction mixture upon in situ fabrication of Ag nanoparticles has been already reported by us and others [46–49,56,57]. Ag-PNA-BIS-2 microgel particles with average diameter of 400 nm were successfully obtained as reflected in SEM images shown in Fig. 1(A—D). Microgel particle loaded with spherical Ag nanoparticles of diameter of 10–20 nm is indicated with in a green circle in Fig. 1(C). The bright spots within microgel particle encircled by red color are Ag nanoparticles formed inside the polymer network by in-situ reduction using sodium borohydride as reducing agent. Fig. 1(A) reveals that Ag nanoparticles are predominantly present inside/on the polymer network rather than outside of the microgel particles. We were interested in determination of size and morphologies of silver nanoparticles loaded into polymer network, because catalytic activity of silver nanoparticles depends upon size, shape and number of silver nanoparticles [58,59]. For this purpose, TEM and STEM images of hybrid system were obtained at various magnifications (Fig. 2A–H). Presence of small spherical dark dots in TEM image (Fig. 2A) and spherical small bright dots in STEM image (Fig. 2E) indicated the loading of Ag nanoparticles into polymer network. The polymeric network is invisible in the TEM image due to high contrast between Ag nanoparticles and polymer network in the electron beam [36]. Moreover polymer burning

Table 1
Feed composition of poly (N-isopropylacrylamide-co-acrylamide) (PNA-BIS-2) microgels.

BIS			NiPAM			AAm		
mol%	mmol	gram	mol%	Mmol	Gram	mol%	mmol	Gram
2.00	4.00	0.06	95	19	2.15	3.00	0.60	0.04



Scheme 1. Synthesis of poly(N-isopropylacrylamide-co-acrylamide) (PNA-BIS-2) microgels and silver nanoparticles loaded poly(N-isopropylacrylamide-co-acrylamide) (Ag-PNA-BIS-2) hybrid microgels for catalytic reduction of nitroarenes.

during TEM measurements may be another possible reason of invisibility of polymer microgel particles in TEM image (Fig. S2 and Fig. S3). High resolution TEM and STEM analysis was also performed to investigate the crystalline nature of silver nanoparticles loaded into polymer microgels as shown in Fig. 2(D and H) respectively. The high resolution TEM image of a single Ag nanoparticle shown in Fig. 2(D) indicates that nature of the particle is crystalline with regular lattice spacing of 0.24 nm which can be attributed to (111) lattice planes of face centered cubic silver nano structure [60]. In addition, the energy-dispersive X-ray (EDX) spectra (Fig. S4) confirmed the presence of metallic silver on nanoscale without any impurity. The spectra exhibited the peaks for Ag nanoparticles at 2.99 and 3.16 keV which provides supportive evidence for the existence of Ag nanoparticles immobilized in polymer microgels [30]. The diameter of Ag nanoparticles estimated by TEM was found to be the same as that measured by SEM analysis. The Formation of Ag nanoparticles was further confirmed by UV Visible analysis of pure and hybrid microgel dispersions as shown in Fig. S5 (A) in ESI. The presence of a single peak at

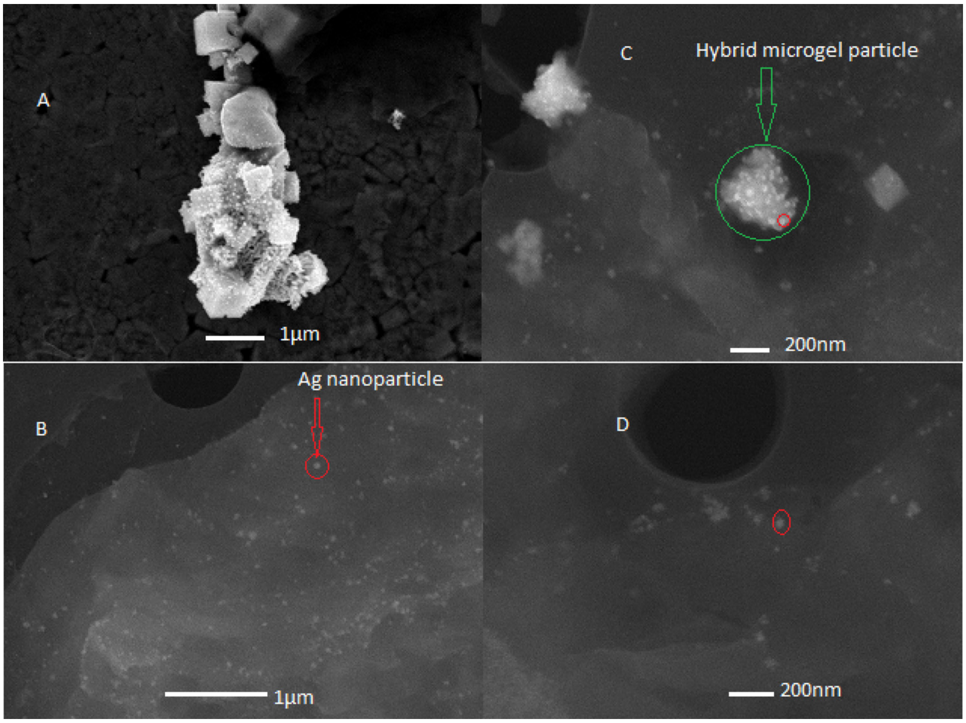


Fig. 1. SEM images of dilute aqueous dispersion of silver nanoparticles loaded poly(N-isopropylacrylamide-co-acrylamide) (Ag-PNA-BIS-2) microgels at different magnifications.

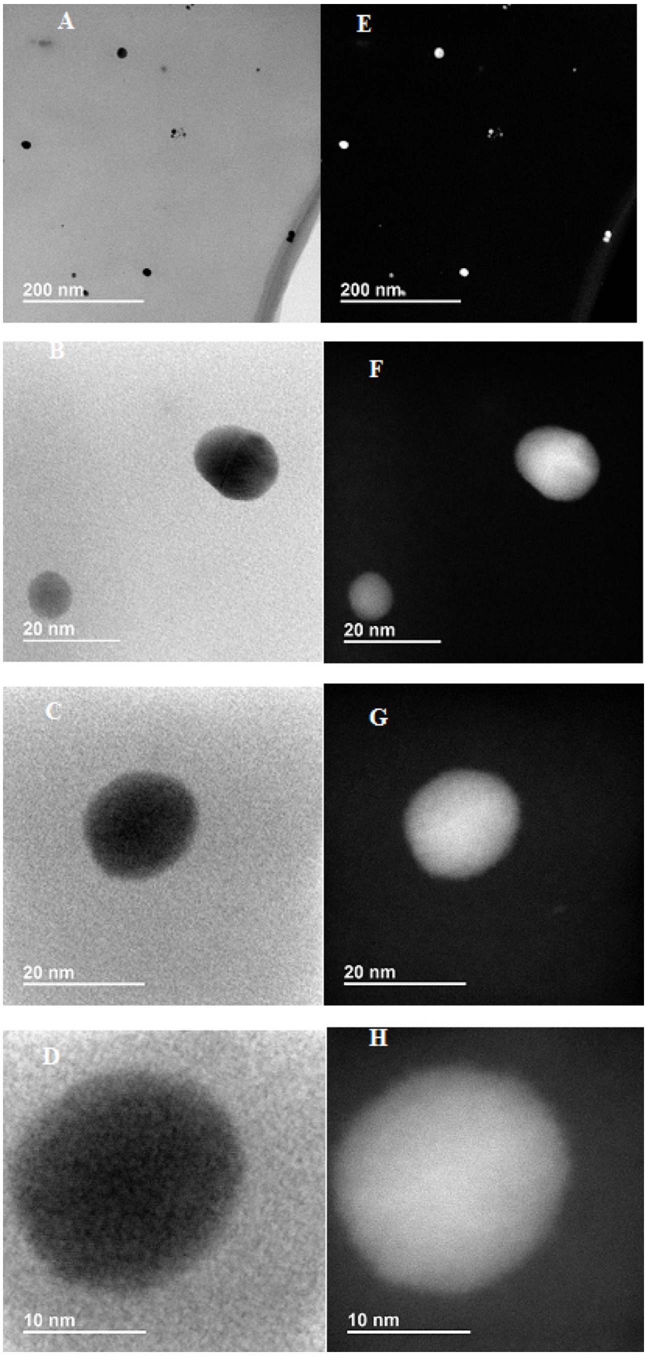


Fig. 2. TEM (A–C) and STEM (D–H) images of dilute aqueous dispersion of Ag nanoparticles fabricated in poly(N-isopropylacrylamide-co-acrylamide) (PNA-BIS-2) microgels at different resolutions.

wavelength of 410 nm in case of hybrid microgel sample is attributed to surface plasmon resonance property of spherical monodisperse Ag nanoparticles and has been reported in various publications [52,57]. Dilute dispersion of Ag-NA-BIS-2 sample was stored in dark and its UV visible spectra were scanned as a function of time of storage as shown Fig. S5 (B) in ESI. No significant change in value of λ_{spr} was observed which indicated the stability of Ag nanoparticles in microgels. Monitoring of stability of Ag nanoparticles in different microgel systems on the basis of value of λ_{spr} using UV Visible spectrophotometry has been reported in recent literature [61]. TGA analysis of NA-BIS-2 microgels (Fig. 3, dotted line) and Ag-NA-BIS-2 hybrid microgels (Fig. 3, solid line) was performed to investigate the stability of hybrid microgels at a wide range of temperature for determination of working temperature range of the catalyst. Moreover TGA was also used for determination of weight percentage of metal content in hybrid microgels which is an important parameter in catalysis. TGA curve for both pure and hybrid microgels shown in Fig. 3 indicates initial weight loss (about 10 wt%) in the temperature range of 24–90 °C in case of Ag-NA-BIS-2 hybrid microgels and 24–170 °C which can be attributed to water loss. Then both PNA-BIS-2 microgels and Ag-NA-BIS-2 hybrid microgel systems become stable up to about 300 °C after which a significant weight loss occurs around 310–410 °C (62.73 wt% in case of Ag-NA-BIS-2) which is probably due to decomposition of polymer network. 3rd weight loss in the temperature range of 410–600 °C may be caused by further decomposition of organic materials. TGA analysis reveals that Ag-NA-BIS-2 hybrid polymer microgels is stable in a wide range of temperature (T ≤ 300 °C). So this hybrid system can be used as catalyst for even those reactions where high temperature is needed. No residue was practically found in case of PNA-BIS-2 sample while a significant amount of inorganic residue was found at the end (see Fig. 4) in case of Ag-PNA-BIS-2 sample which off course is associated to Ag nanoparticles loaded into polymer microgels [62,63]. The weight percentage of Ag in hybrid polymer microgels determined by TGA analysis was found to be 3.84%. XRD analysis of PNA-BIS-2 microgels and Ag-PNA-BIS-2 hybrid microgels is presented in Fig. 4. The peaks at 2θ values of 38.37, 44.8, 64.72 and 77.38° appeared in XRD pattern of Ag-PNA-BIS-2 hybrid microgels are associated to (111), (200), (220) and (311) crystal planes of Ag nanoparticles cubic lattice and confirm crystalline state of silver nanoparticles. The peak intensities and 2θ values are consistent with standard XRD patterns of Ag (JCPDS 4–783). XRD pattern of PNA-BIS-2 microgels did not show such peaks. However both PNA-BIS-2 microgels and Ag-PNA-BIS-2 hybrid microgels samples have two broad peaks at 2θ values ranging from 15° to 20° and from 36° to 40° which may be attributed to polymeric network [60]. The XRD analysis confirm that Ag nanoparticles were successfully loaded to PNA-BIS-2 microgels.

3.2. Catalytic reduction of nitroarenes

The catalytic activity of Ag-PNA-BIS-2 hybrid microgels towards reduction of 4-nitrophenol (4-NP) under different concentrations of sodium borohydride, substrate and catalyst in aqueous medium has been already reported by some of our group [48]. More over catalytic reduction of 4-NP by sodium borohydride in aqueous medium has

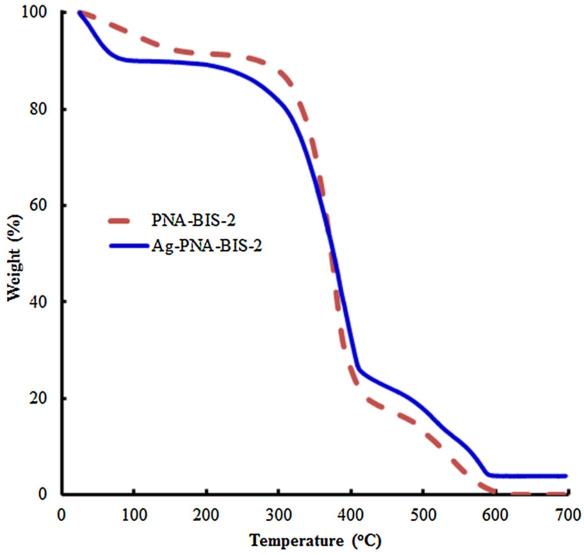


Fig. 3. TGA curves for poly(N-isopropylacrylamide-co-acrylamide) (PNA-BIS-2) microgels and silver nanoparticles loaded poly(N-isopropylacrylamide-co-acrylamide) (Ag-PNA-BIS-2) microgels at the heating rate of 10 °C per minute in temperature range of.24 °C–700 °C.

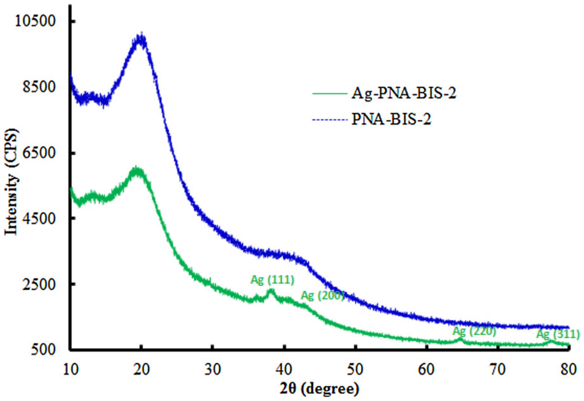


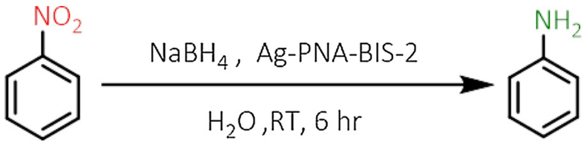
Fig. 4. Powder XRD pattern of oven dried samples of poly(N-isopropylacrylamide-co-acrylamide) (PNA-BIS-2) microgels and silver nanoparticles loaded poly(N-isopropylacrylamide-co-acrylamide) (Ag-PNA-BIS-2) microgels.

become a bench mark reaction to test the catalytic activity of Ag nanoparticles stabilized in polymer microgels [42–57]. However the scope of the substrate has been rarely reported in literature. So the purpose of this study was to synthesize a wide variety of aryl amines from reduction of nitroarenes in the presence of Ag-PNA-BIS-2 hybrid microgels using sodium borohydride as hydrogen source in aqueous medium under mild reaction conditions. Therefore we started our work with the scope of substrate in this project without screening of solvent, hydrogen source and catalyst. However a few controlled primary experiments were conducted to identify the true active catalytic species. The reduction of nitrobenzene was tried in the presence of PNA-BIS-2 pure microgels using sodium borohydride as hydrogen source, but only 2% conversion was observed even in 6 h which indicated that polymer microgel particles are not true catalysts and reduction reaction is thermodynamically feasible but kinetically unfavourable. The similar observation was noted in case of reduction of nitrobenzene by $NaBH_4$ without polymer microgels and hybrid microgels. No conversion was observed in the presence of polymer microgels or hybrid microgels without sodium borohydride which indicated that polymeric system was not hydrogen source. It is sodium borohydride which acts hydrogen source in this reduction reaction. Complete conversion of nitrobenzene into respective aniline within 6 h was observed in the presence of sodium borohydride and Ag-PNA-BIS-2 hybrid microgels (Scheme 2) which indicated that Ag nanoparticles loaded into polymer microgels are true catalysts. Reactants diffuse through polymeric network towards the catalyst surface, and react with each other on catalyst surface to form product which ultimately diffuses out from polymeric network as reported in literature [56]. To probe the kinetics of the reaction, 2.5 mL of mixture containing 0.07 mM nitrobenzene, 7 mM sodium borohydride and 0.5 mL Ag-PNA-BIS-2 hybrid microgels was taken in a cuvette and was subjected to UV Visible scan at 20 °C, which is shown in Fig. 5. The value of absorbance at wavelength of 265 nm was found to decrease with corresponding increase in absorbance at wavelength of 230 nm with the passage of time, which indicated the conversion of nitrobenzene into aniline in the presence of Ag-PNA-BIS-2 hybrid microgels [64]. The value of apparent rate constant (k_{app}) determined from the slope of plot of $\ln(A_t/A_o)$ vs time using pseudo first order kinetic equation was found to be $0.09\ min^{-1}$ that is higher than previously reported value under similar conditions [64]. A controlled experiment under similar conditions was also carried out without the Ag-PNA-BIS-2 hybrid microgels, no significant change in absorbance at wavelength of 265 nm was observed even after one hour which proved that reduction of nitrobenzene into aniline occurred on the surface of Ag nanoparticles loaded into microgels. Moreover spectra of catalytic reduction of nitrobenzene signified that reaction intermediates formed during the catalytic reduction of nitrobenzene are not UV visible detectable.

The catalytic reduction of various nitroarenes with sodium borohydride in the presence of hybrid microgels was carried out in aqueous medium at room temperature and a summary of the results is presented in Table 2. The catalytic system has ability to successfully convert nitroarenes with electron withdrawing and electron donating groups as substituents to their corresponding amines. The product of each catalytic reaction was separated and purified. The purified product was characterized by ^{1}H NMR, ^{13}C NMR and HRMS (Data S1 and spectra S1). The catalytic system was found to be effective and selective for reduction of nitroarenes having halogen functionalities (I, Br, Cl) and halogenated anilines with good to excellent yields were successfully obtained (Table 2, entries 1–4). The hybrid microgels catalyzed reduction of nitroarenes with CN, OH and NH_2 functionalities (Table 2, entries 5–12) gives yields in the range of 89–95% depending upon the nature and position of the functional group on aromatic ring with respect to NO_2 group to be reduced. The catalytic reduction of 2-nitrophenol (Table 2, entry 7) gives relatively low yield and takes more time to be completed, which may be attributed to steric hindrance and intra-molecular hydrogen bonding among NO_2 and OH groups which are close to each other on the benzene ring. Sahiner and co-workers have reported catalytic reduction of 2-nitrophenol and 4-nitrophenol in the presence of nickel nanoparticles loaded in polymer hydrogels and found that catalytic reduction of 2-nitrophenol is sluggish than that of 4-nitrophenol under similar reaction conditions [65]. The catalytic reduction of o-,m-, and p-nitro toluene gives excellent yields of corresponding amines and reaction was found to be completed within 5–6 hrs. The yield of p-product was found to be higher than m- and o-products (Table 2, entries 13–15) because of the aforementioned reasons. In order to investigate the catalytic activity of our system towards a wide variety of substrates, we studied catalytic reduction of nitroarenes with other functional groups in the same system. For this purpose, reduction of nitro group of nitroarenes substituted with $-CH_2OH$, $-CH_2COOH$, $-COOCH_3$, $-OCH_3$, $-CHO$, $-COOH$, $-COOMe$ *etc* was performed in aqueous medium (Table 2, 16–23). In case of reduction of nitroarenes with $-COOMe$ group, only reduction of nitro group was observed. (Table 2, entry 18). The catalytic system has poor selectivity in case of reduction of nitroarenes with ketone and aldehyde functional groups. Reduction of both carbonyl and nitro groups was observed in such cases (Table 2, entries 20–23). Moreover in case of nitroarenes with ketone and aldehyde functionalities, 8 equivalents sodium borohydride was used to complete their conversion into amines because sodium borohydride is used to reduce both nitro and carbonyl groups present on benzene ring of nitroarenes.

3.3. Proposed mechanism of reduction of nitroarenes

The Langmuir-Hinshelwood mechanism is a widely accepted mechanistic scenario for catalytic reduction of nitroarenes in the presence of Ag nanoparticles loaded into polymer microgels [46–48,66–71]. According to this scenario, both reacting species diffuse from polymer network to the surface of Ag nanoparticles, get adsorbed and interact with each other to form product which desorbs from catalyst surface and diffuses out to bulk solution from polymer network. This story has been narrated for catalytic reduction of nitroarenes using metal nanoparticles in polymeric stabilizers in various publications [46–48,66–71] but insight covering all possible steps of the reduction mechanism has



Scheme 2. Synthesis of aniline from reduction of nitrobenzene in the presence of hybrid microgels in aqueous medium at room temperature.

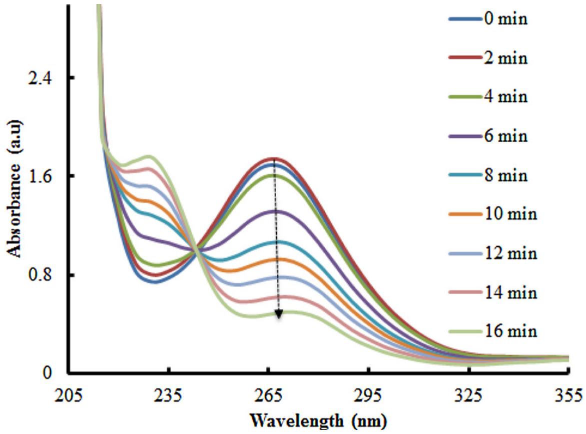


Fig. 5. UV Visible spectra of catalytic reduction of nitrobenzene into aniline using 0.07 mM nitrobenzene, 7.5 mM sodium borohydride in the presence of silver nanoparticles loaded poly(N-isopropylacrylamide-co-acrylamide) (Ag-PNA-BIS-2) microgels at 20 °C.

not been provided. Herein, we assumed that sodium borohydride (B–H) got hydrolyzed to produce $NaB(OH)_4$ and molecular hydrogen. Hydrogen got attached with the surface of Ag nanoparticles as a result of dissociative adsorption of H_2 as reported in literature. [13,72]. Hydrogen adsorbed on Ag nanoparticles represented as [Ag]-H is responsible for reduction of nitroarenes in a suitable solvent (H_2O) as shown in Scheme 3. Proton (H^+) coming from solvent gets attached on negatively charged oxygen of nitro group of substituted nitroarene following donation of hydride from [Ag]-H to positively charged nitrogen of nitro group to produce specie **a**. Further protonation of specie **a** due to attack of solvent proton on the other negatively charged oxygen of nitro group of nitroarene gives specie **b** which upon its rearrangement produces specie **c**. Specie **c** generates a water molecules following hydride gain from [Ag]-H to give specie **d** which is a reaction intermediate already identified by Lykakis et al. who reported mechanistic studies of nitroarenes by sodium borohydride using Au nanoparticles supported on TiO_2 as catalyst [73]. They reported that nitroarenes are converted into aryl amines through the formation of only one reaction intermediate (hydroxylamine). Specie **d** produces water molecule following hydride gain from [Ag]-H to give aryl amine as shown in Scheme 3.

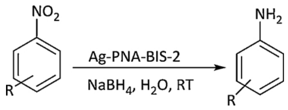
3.4. Gram scale experiment

Based on good results of catalytic activity of Ag-PNA-BIS-2 hybrid microgels for successful conversion of nitroarenes into corresponding aryl amines on small scale, we extended our work to carry out synthesis of a model aryl amine on gram scale. Catalytic conversion of nitrobenzene into aniline was chosen as model reaction for this purpose because resulting product (aniline) is one of the most useful chemicals and reaction intermediates in industrial production of pesticides, polymers, pigments, dyes and pharmaceuticals [74,75]. More precisely, gram scale synthesis of aniline from reduction of nitrobenzene (1.10 g) in the presence of Ag hybrid catalyst using 8 equivalents of sodium borohydride (2.07 g) was performed in aqueous medium. The desired product (aniline) with yield of 95% was successfully synthesized, separated and purified.

3.5. Catalyst recycling experiment

Recyclability of the hybrid microgel catalysts was examined using reduction of nitrobenzene as a model reaction. Hybrid polymer microgel catalyst was separated out after completion of each cycle, washed, dried and re-dispersed in 3 mL deionized water for the next cycle. Each cycle was performed under similar conditions (0.25 mmol

Table 2
Substrate scope for the reduction of Nitroarenes with reaction completion time and percentage yield of corresponding aryl amine.



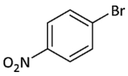
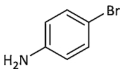
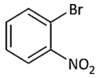
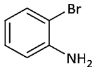
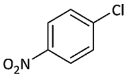
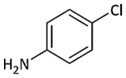
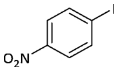
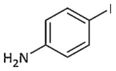
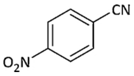
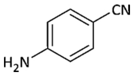
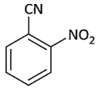
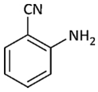
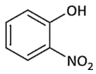
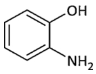
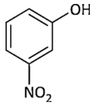
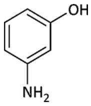
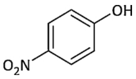
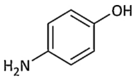
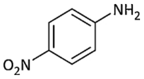
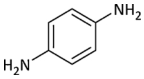
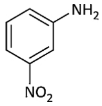
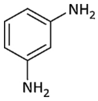
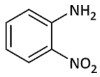
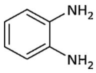
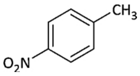
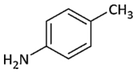
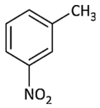
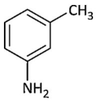
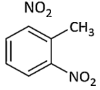
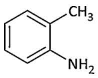
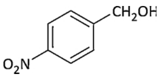
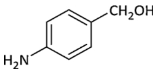
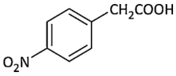
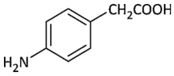
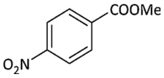
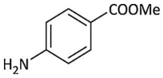
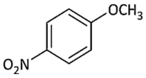
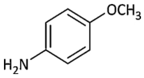
Entry	Substrate	Product	Yield (%)	Time (h)
1			90	6.5
2			75	8
3			88	7
4			85	7.5
5			90	4
6			97	3
7			89	9
8			93	5
9			90	9
10			92	8
11			87	7
12			90	8
13			95	5
14			86	6
15			84	5
16			94	6
17			87	6
18			89	6.5
19			85	7

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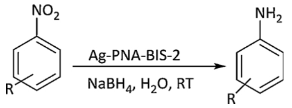
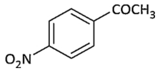
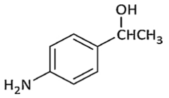
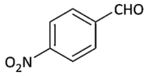
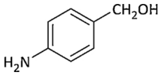
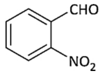
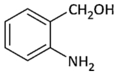
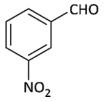
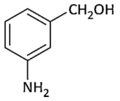
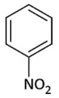
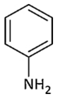
Table 2 (*continued*)



20			90	6
21			90	6
22			90	6
23			91	5
24			88	6

nitrobenzene, 6 equivalent sodium borohydride, 3 mL hybrid microgel dispersion, 1.5 mL water, 6 h) at 25 °C. No significant decrease in percentage yield of nitrobenzene into aniline was observed as shown in Fig. 6(A). The slight decrease in yield with recycle number can be attributed to loss of catalyst during its washing, drying and re-dispersing process for the next cycle. It is worth mentioning that percentage yield obtained in first cycle can be achieved even in fourth cycle by increasing reaction time or temperature of the medium. TEM analysis of the hybrid microgel dispersion was also performed after catalysis to investigate any change in morphology of Ag nanoparticles during catalysis. The typical TEM image of the hybrid microgel sample taken after catalysis is shown Fig.6(B) which reflects that morphologies of Ag nanoparticles are not significantly affected during catalysis. Filtrate of reaction mixture was subjected to ICP analysis to determine the metal content in it. No significant silver contents were detected in filtrate which indicates that Ag nanoparticles are tightly bound within polymer network and do not leach out during catalysis. To observe the shelf-life of the catalyst, hybrid microgels dispersion was stored in dark for one month and no change in colour was observed. Furthermore TEM analysis of stored sample was also performed again and no aggregation of Ag nanoparticles was observed in TEM image shown in Fig. 6(C). No Change in value of surface plasmon resonance wavelength after one month (Fig. S5) is also a proof of stability of Ag nanoparticles in polymer microgels.

4. Conclusions

Spherical Ag nanoparticles with diameter of 10–20 nm were successfully fabricated in nearly chemically inert PNA-BIS-2 microgels via a simple and facile in-situ reduction methodology. They were used as an effective catalyst for transformation of a wide variety of nitroarenes into their corresponding aryl amines with good to excellent yields without any side product in aqueous medium under mild reaction conditions. The catalyst can covert substituted nitroarenes to desired products keeping many functionalities like –X, -CN, −OH, −COOH, $-OCH_3$ and −COOMe intact. The protocol is simple and safe because no high pressure equipment is needed for reduction and the product can be easily separated out from reaction mixture by simple centrifugation. The catalyst is recoverable and reuse-able without any significant loss of catalytic activity and selectivity up to 4 cycles. Ag nanoparticles are tightly bound in the polymeric network due to their donor-acceptor interaction with microgel functionalities and do not leach out during catalysis. This strategy can be applied for synthesis and stabilization of other metal nanoparticles to catalyse other organic transformations in future. Following this approach, a variety of aryl amines can be successfully synthesized from nitroarenes at room temperature with simple catalyst preparation, good activity, high conversion ability and recoverability of the catalyst. The investigation of catalytic activity of this particular hybrid catalytic system towards other reduction and oxidation reactions is in progress in our lab.

Acknowledgements

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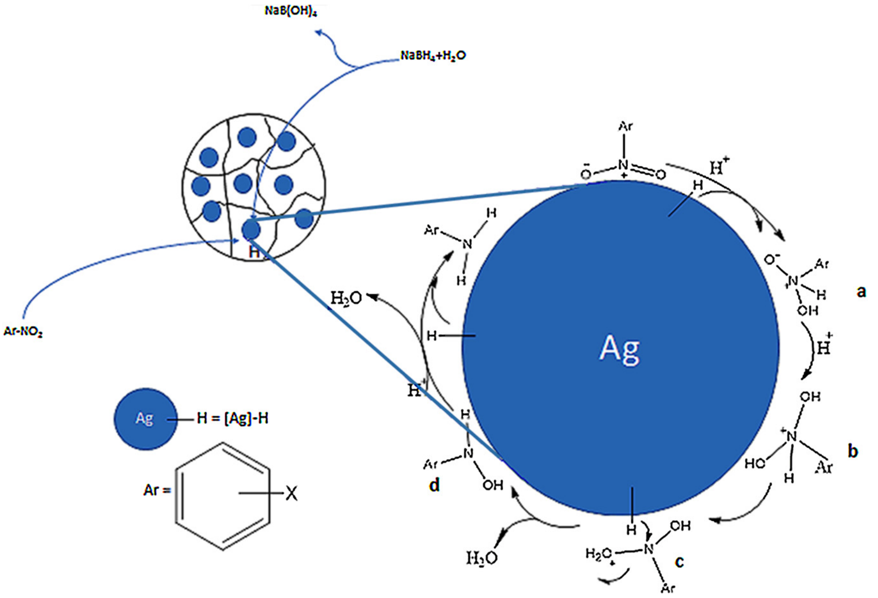

Scheme 3. Plausible mechanism of catalytic reduction of nitroarenes by sodium borohydride (B–H) in the presence of Ag nanoparticles in aqueous medium.

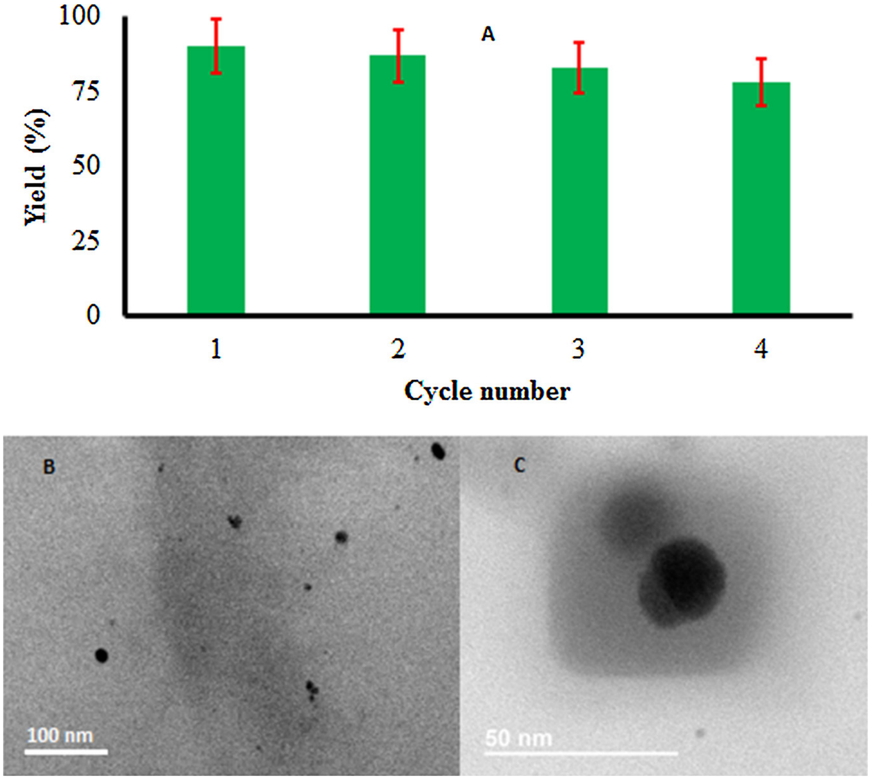

Fig. 6. The percentage yield of nitrobenzene as a function of recycling number (A), TEM image of silver nanoparticles loaded poly(N-isopropylacrylamide-co-acrylamide) (Ag-PNA-BIS-2) microgels catalyst after recycling (B) and after one month of their storage in dark.

Matthew, Alex, Troy and Jackson for doing help in microscopic, TGA, XRD and ICP-OES analysis respectively.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jhazmat.2019.05.080.

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