Designed synthesis of silver nanoparticles in responsive polymeric system for their thermally tailored catalytic activity towards hydrogenation reaction

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Abstract−Poly(N-isopropylacrylamide-acrylamide-methacrylic acid) [p(NIPa-AAm-Ma)] polymer microgels were prepared by free radical precipitation polymerization method. AgNPs were fabricated in the sieves of polymer network by chemical reduction using $AgNO_3$ salt as a precursor of silver ions. Various techniques like dynamic light scattering (DLS), transmission electron microscopy (TEM), Fourier transform infrared microscopy (FTIR), and UV-Visible spectroscopy were used for characterization of pure and composite microgels. The diameter of AgNPs fabricated in polymeric network was found to be in the range of 10-15 nm. Stimuli responsive behavior of hybrid microgels was same as that of pure microgels. Catalytic efficiency of the hybrid microgels was investigated by reducing 4-Nitroaniline (4-NA) into 4-Aminoaniline (4-AA) using $NaBH_4$ as reducing agent under different conditions of temperature of the medium, concentration of reducing agent, 4-Nitroaniline and hybrid microgels to explore the catalysis process. Kinetic and thermodynamic aspects of reduction of 4-Nitroaniline in the presence of catalyst were also discussed on the basis of values of Arrhenius and Eyring parameters like pre-exponential factor, activation energy, enthalpy of activation and entropy of activation. Catalytic activity of the hybrid microgels was found to be thermally tunable in the temperature range of 25-70 °C. The value of rate constant (k_{app}) for reduction of 4-NA was minimum at 55 °C, which can be attributed to volume phase transition of the hybrid microgels.

Keywords: Microgels, Nanoparticles, Catalysis, Kinetics, Thermodynamics

INTRODUCTION

Microgels show sensitivity to various triggers such as temperature [1], pH [2] and ionic strength of the medium [3] due to specific functionalities present in their network. They show sudden increase or decrease in their size upon variation in certain external parameters. For example, at 32 °C, size of poly(N-isopropylacrylamide) [p(NIPa)] microgel particles is decreased abruptly in aqueous medium due to their thermo-sensitivity [4]. N-isopropylacrylamide is copolymerized with some comonomers to obtain multiresponsive polymer microgels along with their temperature sensitivity [5].

Due to this responsive behavior, microgels find application in different fields such as drug delivery [6-8], sensing [9], photonics [10,11], purification [12], separation [13-15] and nanotechnology [16,17]. Use of microgels for preparation of metal nanoparticles has gained much importance over other conventional methods adopted for synthesis of metal nanoparticles due to some specific advantages. For example, easy preparation, tunable size, functionaliza-

tion of various groups, porous network with controlled degree of crosslinking, high stability and stimuli responsive behavior of microgels make them more appropriate template for fabrication of metal nanoparticles and their use in different fields. Microgels have been reported as an effective micro-reactor for synthesis of different inorganic nanoparticles [18-21]. Size and shape of nanoparticles can be controlled by controlling the feed content of microgels and hybrid microgels [22,23]. The nanoparticles immobilized inside the microgels can be stabilized for long time without their aggregation [24, 25]. Metal nanoparticle fabricated hybrid microgels with porous structure have potential as an excellent catalyst for various organic reactions [24,26,27]. The catalytic activity of hybrid microgels can be tuned by varying external stimuli. For example, when temperature of the medium is increased, NIPa based hybrid microgel particles shrink at a certain temperature called volume phase transition temperature (VPTT) that makes the diffusion of reactants to the surface of metal nanoparticles difficult due to which catalytic activity of the hybrid catalytic system decreases [26]. This feature of thermo-responsive hybrid microgels makes them a potential candidate as catalyst for highly explosive exothermic catalytic reactions at controlled rate to avoid any explosion [28,29].

Hybrid microgels are used as catalyst for various organic reactions such as hydrogenation [30], reduction of nitroarenes [31] and

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various other reactions [32]. Begum et al. prepared silver-poly(N-isopropylacrylamide-acrylamide) [Ag-p(NIPa-AAm)] composite microgels as catalyst for reduction of 4-Nitrophenol (4-NP) using NaBH$_4$ as reducing agent [33]. Lu and coworkers prepared core-shell microgel particles with polystyrene (Pst) core and p(NIPa) shell for in-situ fabrication of Ag NPs in their shell region [29]. Synthesized Ag-Pst-p(NIPa) core-shell composite microgel catalysts were used for degradation of 4-Nitrophenol (4-NP) in aqueous medium. They reported that catalytic activity of Ag-Pst-p(NIPa) core-shell hybrid microgels can be tuned by varying temperature of the medium, but synthesis of core-shell microgels involves more than one step, and relatively more difficult procedure was adopted for synthesis of these hybrid microgels. Moreover, content of AgNPs per unit microgel particles was found to be very low and a large amount of catalyst was needed to carry out catalytic reduction of 4-NP at industrial scale. Thermally tunable hybrid microgel catalytic systems have been tested only for catalytic reduction of 4-NP. Thermally tunable catalytic reduction of other nitroarenes like 4-NA in the presence of such kind of catalytic systems has not been reported in literature, yet. However, few reports on catalytic reduction of 4-NA in the presence of metal nanoparticles stabilized in non-responsive systems are available in literature [34-36]. For example, Chiu and coworkers used gold nanocubes, octahedral and dodecahedral crystals as catalysts for reduction of 4-Nitroaniline (4-NA) into 4-Aminoaniline (4-AA) in aqueous medium [37]. Reddy et al. prepared and stabilized AuNPs using Sapindus Mukorossi Gaertn fruit pericarp [38]. They applied these biosynthesized AuNPs for reduction of 4-NA. But synthesis of AuNPs and their application as catalyst for degradation of 4-NA is not a cost effective way and cannot be employed at industrial level. According to best of our knowledge, no one has reported the reduction of 4-NA into 4-AA in the presence of silver nanoparticles loaded p(NIPa-AAm-Ma) microgels using NaBH$_4$ as reducing agent to elaborate the catalysis process under various conditions.

In this work, we prepared p(NIPa-AAm-Ma) microgels by precipitation polymerization and used this dispersion as micro-reactor for fabrication of AgNPs in aqueous medium. Different techniques such as FTIR, DLS, TEM and UV-Visible spectroscopy were employed to characterize the pure and composite microgel particles. Catalytic efficiency of thermo-sensitive Ag-p(NIPa-AAm-Ma) composite microgels was investigated by adopting the reduction of 4-NA as benchmark reaction. Catalytic activity of hybrid microgels was also investigated under different reaction conditions like temperature of the medium, catalyst dose, concentration of NaBH$_4$ and 4-NA. Kinetic and thermodynamic parameters for catalytic reduction of 4-NA using NaBH$_4$ reducing agent were also calculated before and after VPTT of the hybrid microgels to elaborate the reduction process.

EXPERIMENTAL PART

1. Chemicals

N-isopropylacrylamide (NIPa, 99%), ammonium per sulfate (APs, 99%), acrylamide (AAm, 98%) and sodium borohydride (NaBH$_4$, 99%) were imported from Sigma Aldrich, Germany, while sodium dodecyl sulfate (SDs, 98%) and methacrylic acid (Ma) were pur-

chased from Merck. 4-NA was purchased from Alfa Aesar while N, N-methylene bis acrylamide (BiS, 99%) was obtained from Amresco. All chemicals were used as such and were not further processed for purification. Deionized water was used during experimental work.

2. Preparation of Polymer Microgels

p(NIPa-AAm-Ma) microgel particles were prepared by precipitation polymerization method as reported earlier [39]. For this purpose, 1.03 g NIPa (91 mol%), 0.0213 g AAm (3 mol%), 0.046 g BiS (3 mol%) and 0.05 g SDs were dissolved in 95 mL deionized water in a 250 mL three-necked round bottom flask. Reaction mixture was stirred for 20 minutes to dissolve solid reagents properly. Then 26 µL Ma (3 mol%) was added into the reaction mixture at room temperature. Temperature of the reaction mixture was raised to 76 °C. Heating and stirring was continued under nitrogen supply for 30 minutes to remove dissolved oxygen while temperature of reaction mixture was maintained at 76 °C. 5 mL aqueous solution of APs (0.1 M) was added in reaction mixture to initiate the process of polymerization. Clear solution of reaction mixture turned turbid after few minutes of addition of APs. Reaction was further continued under constant N$_2$ supply for 4 hours to complete the polymerization process. Prepared microgels dispersion was cooled at room temperature and purified by dialysis for one week using spectra pore macromolecular porous membrane tubing having a cut off value of 12,000-14,000 at room temperature to remove initiator, surfactant and un-reacted monomers.

3. Synthesis of Hybrid Polymer Microgels

Hybrid microgels were prepared by reducing silver ions within p(NIPa-AAm-Ma) polymer network at room temperature using in-situ reduction method reported previously by us and others [3,25]. 14 mL microgels dispersion was mixed with 36 mL ultrapure water in a three-necked round bottom flask and stirred for 20 minutes under gentle N$_2$ supply to remove dissolved oxygen from aqueous dispersion. Then, 0.4 mL aqueous solution of AgNO$_3$ (0.1 M) was added into the reaction mixture under nitrogen purging. The reaction mixture was stirred for 30 minutes under continuous N$_2$ purging, and 5 mL NaBH$_4$ (0.052 mM) was added in the reaction mixture. Reaction was continued further for 90 minutes. The hybrid microgel dispersion was subjected to dialysis for 1 hour using porous membrane to remove unreacted species as reported previously [3].

4. Characterization

For Fourier transform infrared (FTIR) analysis, powdered samples of pure and composite microgels were scanned on RXI FT-IR spectrometer (Perkin Elmer) in wavenumber range of 4,000 to 650 cm^{-1}. UV D-3500 (Labomed, Inc., USA) spectrophotometer was used to scan UV-Visible spectra of pure and composite microgels. FESEM JSM-7500F (JEOL limited USA) operating at 60 kV was used to capture TEM images of pure and hybrid microgels. For TEM analysis, dilute dispersion was placed on carbon coated copper grids and air dried before measurements. Dynamic light scattering (DLs) analysis was carried out on BI-200SM, Brookhaven Instrument Corp., USA at 90° using standard He-Ne laser (632.8 nm) as light source.

5. Study of Catalytic Activity of Hybrid System

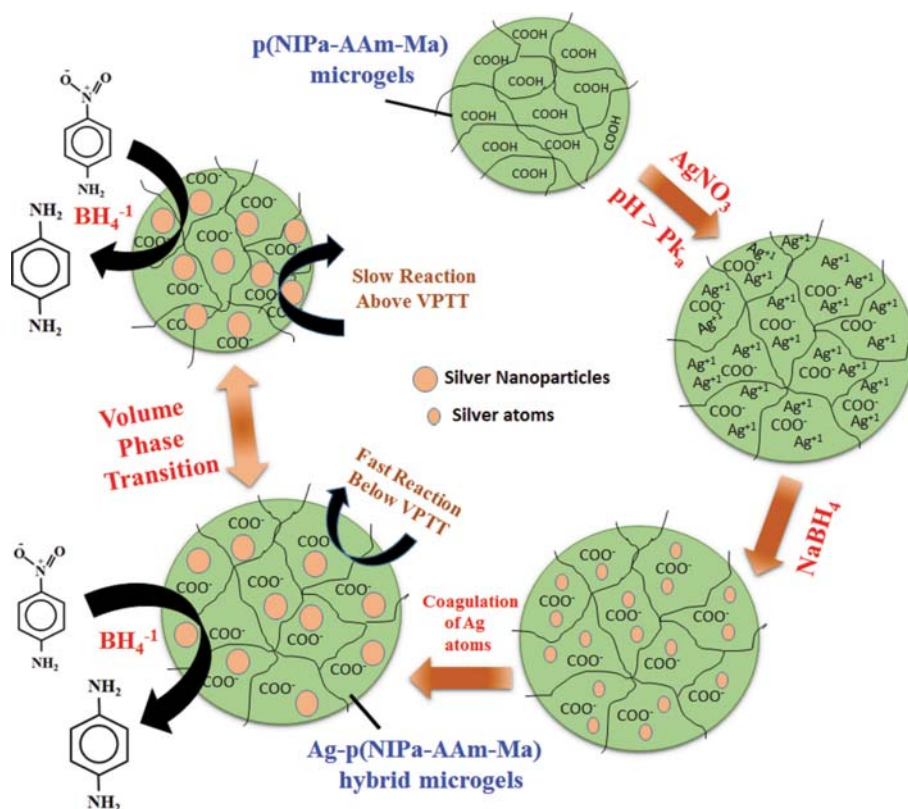Catalytic activity of Ag-p(NIPa-AAm-Ma) composite microgels

Fig. 1. Schematic representation for synthesis of Ag-p(NIPa-AAm-Ma) hybrid microgels for their thermally tunable catalytic reduction of 4-nitroaniline.

was investigated by adopting the catalytic reduction of 4-NA as a model reaction. Effect of reaction conditions like temperature of the medium, catalyst dose, concentration of reducing agent and 4-NA was also studied. To study the effect of concentration of reducing agent, its concentration was changed from 3.35 to 10.06 mM, while amount of catalyst and 4-NA was kept constant at 0.012 mg/mL and 0.067 mM, respectively. Catalyst dose was varied from 0.012 to 0.060 mg/mL to study its effect on the value of apparent rate constant (k_{app}) for reduction of 4-NA using 6.70 mM NaBH$_4$ and 0.067 mM 4-NA. Similarly, concentration of 4-NA was varied from 0.030 to 0.060 mM to study its effect on value of k_{app} for reduction of 4-NA using 6.70 mM NaBH$_4$ and 0.012 mg/mL hybrid microgels at 23 °C. Effect of temperature on catalytic activity of hybrid microgels catalyst was also investigated by varying its value from 25 to 70 °C while all other reaction conditions were kept constant. The required amounts of 4-NA, NaBH$_4$ and catalyst were taken in a quartz cuvette, and progress of reaction was monitored by scanning time dependent UV-Visible spectra of reaction mixture in the wavelength range of 200-500 nm using UV-D3500 spectrophotometer.

RESULTS AND DISCUSSION

1. Synthesis of Microgels and Hybrid Microgels

Poly(N-isopropylacrylamide-acrylamide-methacrylic acid) [p(NIPa-AAm-Ma)] microgel particles were prepared by emulsion polymerization method in aqueous medium [16], while Ag-p(NIPa-AAm-Ma) hybrid microgel particles were prepared by in-situ

chemical reduction method at ambient temperature [17]. Schematic representation for synthesis of Ag-p(NIPa-AAm-Ma) hybrid microgels is shown in Fig. 1. Emulsion polymerization method is the best reported method for synthesis of polymer particles with micro size and avoiding macro gelation. High temperature (70 °C) decomposes the APs into persulfate ($S_2O_8^{-2}$), which alternatively decomposes into sulfate (SO_4^{-}) free radical with negative charge at its one end and free electron at other end. Sulfate (SO_4^{-}) free radical gives electrons to carbon-carbon double bond present in monomers to convert into carbon-carbon single bond and initiates the polymerization [16]. At the start, unstable precursor particles are formed which combine with each other or with other growing polymer chains. Charge induced by initiator is not enough to stabilize the microgel particles. So, emulsifier (SDs) was also used to induce stability as well as to control the size of microgel particles [17]. It has already been reported that the size of microgel particles decreases with increase of concentration of emulsifier [17]. Solution became milky on polymerization due to change in dimensions of microgel particles as well as due to change of refractive index of microgel particles [16].

Diluted microgels dispersion was treated with AgNO$_3$ salt which acted as precursor of silver ions. pH of the microgels dispersion was kept at pH greater than pk$_a$ of methacrylic acid (pH>pk$_a$=4.68) [16]. At this pH, all carboxylic acid (COOH) groups of Ma exist as carboxylate ions (COO$^-$) and microgel particles are present in swelled state. Maximum loading of silver ions in the microgels network was obtained due to its swelled state. NaBH$_4$ acted as reduc-
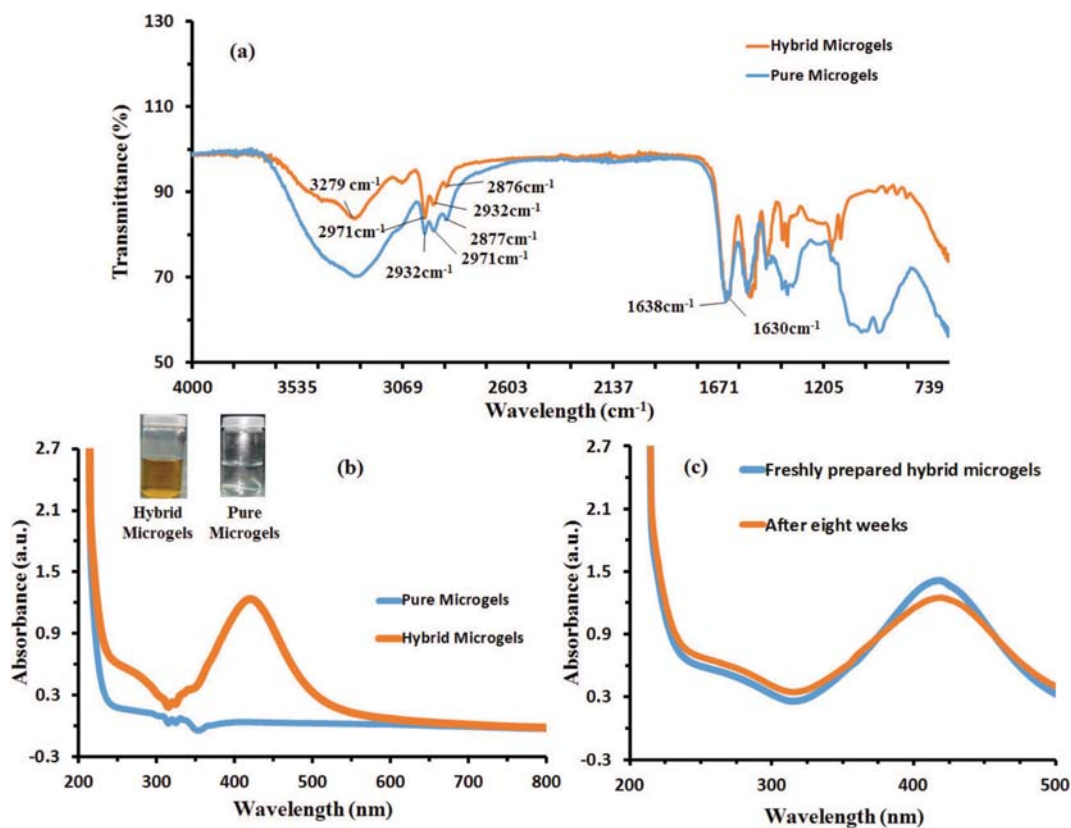
Fig. 2. (a) FTIR spectra of p(NIPa-AAm-Ma) microgels and Ag-p(NIPa-AAm-Ma) composite microgels, (b) UV-visible spectra of p(NIPa-AAm-Ma) polymer microgels and Ag-p(NIPa-AAm-Ma) hybrid polymer microgels (c) UV-visible spectra of freshly prepared Ag-p(NIPa-AAm-Ma) composite microgels and after eight weeks.

ing agent and donated electron to silver ions and reduced them into silver atoms. Silver atoms combined to form AgNPs. The color of microgels dispersion was changed from milky appearance to yellow brown as shown in Fig. 2(b), which also indicates the successful fabrication of AgNPs in microgel network.

2. Characterization

2-1. FTIR Analysis

FTIR analysis of p(NIPa-AAm-Ma) microgels and Ag-p(NIPa-AAm-Ma) composite microgels was performed to identify functional groups of polymeric network and their interaction with metal nanoparticles. FTIR spectra of pure and hybrid microgels are given in Fig. 2(a). The peak at 2,971 cm^{-1} in FTIR spectra of pure microgels can be attributed to asymmetric stretching of C-H bond, while the peak at 2,877 cm^{-1} may be associated with symmetric stretching of C-H bond. Peaks at 1,542 and 1,459 cm^{-1} were observed due to stretching and bending of C-H bond of methylene (CH_2) groups. A peak at 1,389 cm^{-1} associated with methyl group was observed. Peaks associated with amide groups can be seen at wave numbers of 1,638 and 1,630 cm^{-1} in FTIR spectra of both pure and hybrid microgels. Amide groups of polymeric network play a vital role in stabilization of silver nanoparticles by donating electron pair to metal nanoparticles as reported previously [13]. An intense and broad peak at wavenumber of 3,279 cm^{-1} indicates the formation of hydrogen bonding between amide groups of polymer network and molecules of water present inside the network. The de-

crease in intensity and broadness of this peak upon loading of metal nanoparticles into the microgels may be attributed to displacement of some water present in network sieves by metal nanoparticles. No peak relevant to vinyl double bonds was noticed in FTIR spectra of pure and hybrid microgels samples, which indicates the conversion of carbon-carbon double bond into carbon-carbon single bond as a result of polymerization. Small change in position and intensity of various peaks in FTIR spectra of polymer microgels indicates the establishment of interaction between silver nanoparticles and functional groups of microgel particles.

Shift in position of peaks in finger print region of FTIR spectra was also observed upon fabrication of metal nanoparticles inside the network, which also indicates some sort of interaction of various functional groups of polymer microgels with silver nanoparticles. The nature of the interaction of these functional groups with silver nanoparticles has already been explored by Dong et al. [40]. Other researchers also reported the use of FTIR spectroscopy for determination of functional groups of different systems [33,41].

2-2. UV-visible Analysis

UV-Visible analysis of pure and composite microgels was also done and spectra are given in Fig. 2(b). No peak was observed in UV-Visible spectra of p(NIPa-AAm-Ma) pure microgel sample, while a prominent peak was seen at 420 nm in case of Ag-p(NIPa-AAm-Ma) composite microgel sample, which can be attributed to surface plasmon resonance (SPR) phenomenon of AgNPs as a
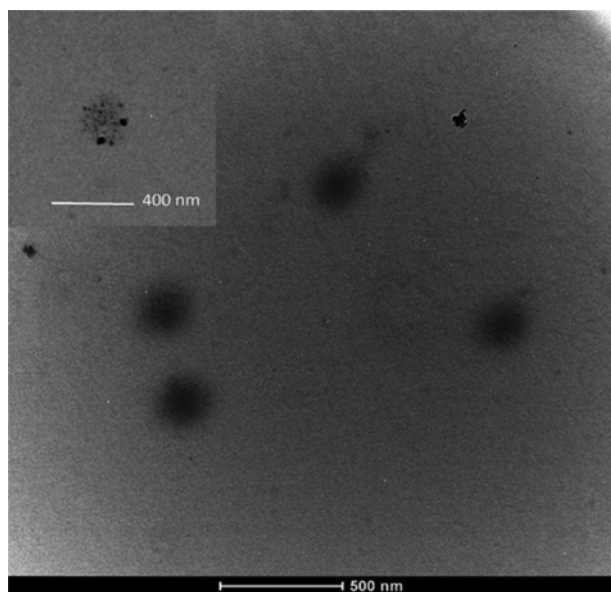
Fig. 3. TEM image of p(NIPa-AAm-Ma) microgels, Inset: TEM image of Ag-p(NIPa-AAm-Ma) composite microgel particles.

Fig. 4. Plot of D_h of p(NIPa-AAm-Ma) microgels and Ag-p(NIPa-AAm-Ma) composite microgels as a function of pH of the medium at 23 °C in aqueous medium.

result of their interaction with electromagnetic radiation. A simple and narrow peak at 420 nm indicates that AgNPs are spherical with narrow size distribution. UV-Visible spectra of Ag-p(NIPa-AAm-Ma) hybrid microgels scanned after eight weeks of synthesis show that no change in position of SPR band occurs as shown in Fig. 2(c), which indicates the high stability of AgNPs in polymer network. One of the causes of high stability of AgNPs in such kind of polymer microgels is strong donor-acceptor interaction between carboxyl and amide groups of microgel particles and silver nanoparticles as reported previously [40].

2-3. TEM Analysis

TEM analysis of p(NIPa-AAm-Ma) microgels and Ag-p(NIPa-AAm-Ma) composite microgels was carried out using dilute dispersions of pure and hybrid microgels, and their images are given in Fig. 3. Inset of Fig. 3 is an image of hybrid microgel particles which shows the successful fabrication of AgNPs in polymer microgels. Dark spots indicate the presence of AgNPs inside light colored microgel particle. TEM analysis indicates that microgel particles and AgNPs fabricated in polymer microgel particles both are spherical. Diameter of microgel particles and that of AgNPs fabricated inside the microgel particles was estimated to be in range of 290-300 nm and 10-15 nm, respectively.

2-4. DLS Analysis

DLS analysis was done to determine the value of hydrodynamic diameter of p(NIPa-AAm-Ma) microgels and Ag-p(NIPa-AAm-Ma) composite microgels at different pH values of the medium at 23 °C. The value of hydrodynamic diameter (D_h) of pure and composite microgel particles as a function of pH of the medium is shown in Fig. 4. Fig. 4 shows the gradual increase in diameter of pure and composite microgel particles with increase in pH of the medium from 2 to 10 due to ionization of carboxylic acid groups of polymer network. The maximum variation in diameter of pure and hybrid microgel particles was observed in the pH range of 3-5
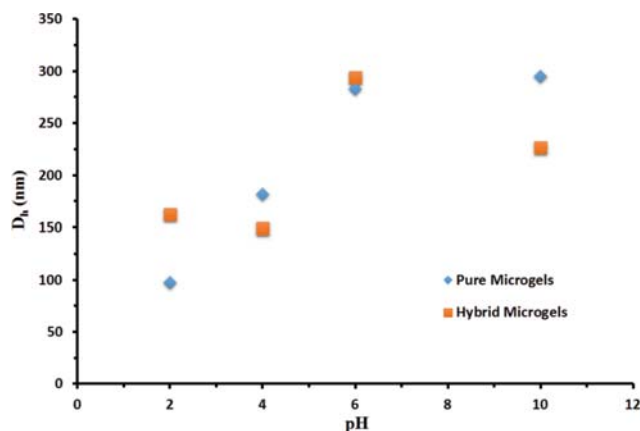
because pk$_a$ value of methacrylic acid (Ma) is 4.68 as reported previously [16]. Similar observations related to size variation in similar microgel particles with pH change have already been reported with detailed reasoning by our group [16,42]. Particle size derived by DLS analysis has also been reported by other researchers [43].

Pure and hybrid polymer microgels showed almost same pH sensitive behavior. Swelling ratio of hybrid polymer microgel particles was found to be smaller than that of pure microgel particles due to presence of AgNPs in the sieves of polymer microgels. Responsive behavior of hybrid microgel particles has great importance for their use as catalyst in various reactions. Swelling of hybrid microgel particles at high pH triggers the movement of reactants in and product out of polymer network during catalytic reaction. Swollen polymer microgel particles not only enhance the diffusion process but also provide hydrophilic micro environment to hydrophilic reactants like 4-NA to move in network. For example, Au-p(NIPa) yolk shell hybrid microgel system is a good catalyst for reduction of 4-NP in its hydrophilic swollen state, but it does not have good catalytic activity for reduction of NB in swollen state because 4-NP is hydrophilic and Nitrobenzene (NB) is hydrophobic [27]. That is why catalytic activity of Ag-p(NIPa-AAm-Ma) hybrid microgels towards reduction of 4-NA was investigated under basic pH conditions.

3. Catalytic Activity

Catalytic efficiency of Ag-p(NIPa-AAm-Ma) composite microgels was investigated by adopting the 4-NA reduction into 4-AA as benchmark reaction in the presence of NaBH$_4$. Catalytic conversion of 4-NA into 4-AA is of great importance academically and technologically because aromatic amionic compounds have many applications in various fields [31]. 4-NA is highly toxic and water soluble compound and has carcinogenic effects on human beings on its exposure. It is difficult to remove from aqueous medium by conventional methods due to its high solubility in water. However, it can be converted into useful product (4-AA) by catalytic reduction method, but previously reported catalysts for catalytic reduction of 4-NA are very expensive [11]. It is an urgent need to design new and cheap but effective catalyst for reduction of 4-NA. Moreover, catalytic conversion of 4-NA into 4-AA can be moni-

tored by UV-Visible spectrophotometry. Due to aforementioned reasons, this reaction was selected as model reaction to test catalytic activity of Ag-p(NIPa-AAm-Ma) hybrid microgels. Catalytic reaction was carried out under different operating conditions to find optimum conditions for its rapid and economical degradation. Here, reduction of 4-NA was monitored by UV-Visible spectrophotometry. Decrease in value of absorbance at 380 nm with passage of time was observed due to decrease in concentration of 4-NA as shown in Fig. 5. No change in color of reaction mixture containing 4-NA and NaBH$_4$ and its value of absorbance at wave-
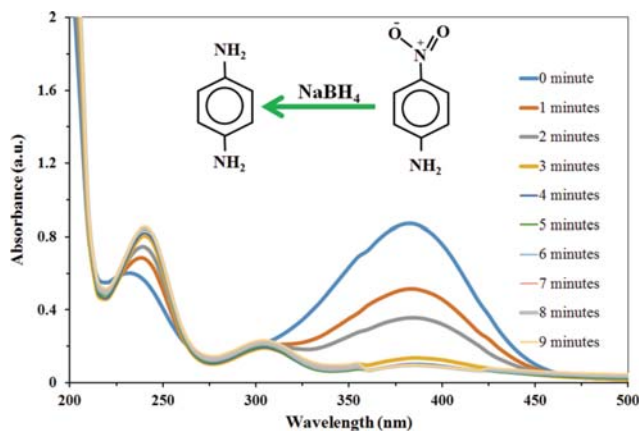
length of 380 nm was noted without catalyst for two hours, which indicated that catalytic reduction of 4-NA is kinetically restricted. However, a quick decrease in the value of absorbance at 380 nm was observed in the presence of catalyst in reaction mixture due to catalytic conversion of 4-NA into 4-AA.

Catalytic reduction of 4-NA was carried out under different concentration of NaBH$_4$, 4-NA, catalyst and temperature of the medium to study their effect on the value of apparent rate constant (k$_{app}$). Moreover, during catalytic reduction of 4-NA, concentration of NaBH$_4$ was kept high as compared to that of 4-NA. Following pseudo-first-order equation was used to calculate the value of k$_{app}$ for 4-NA reduction.

$$-\frac{dC}{dt} = k_{app}C_t \tag{1}$$

In Eq. (1), $-dC_t/dt$ shows the rate of 4-NA reduction in term of its rate of consumption, while C_t indicates the 4-NA concentration at any time 't' during progress of reaction. By integrating Eq. (1) and solving it under conditions of concentration of 4-NA at any time (C_t) and at zero time (C_o), a linear relation is obtained between $\ln(C_t/C_o)$ and time which is used to find the value of k$_{app}$ for reduction of 4-NA.

Ratio of C_t/C_o was found from value of absorbance of 4-NA at 380 nm at any time during progress of reduction reaction and at zero time, respectively.

4. Kinetic Study of Catalytic Reduction of 4-NA under Different Conditions

4-NA was reduced to 4-AA using different Ag-p(NIPa-AAm-

Fig. 5. UV-Visible spectra of reduction of 4-NA [Conditions: Ag-p(NIPa-AAm-Ma) hybrid microgels=0.012 mg/mL, [NaBH$_4$]= 5.03 mM, [4-NA]=0.067 mM and temperature=23 ^{o}C].
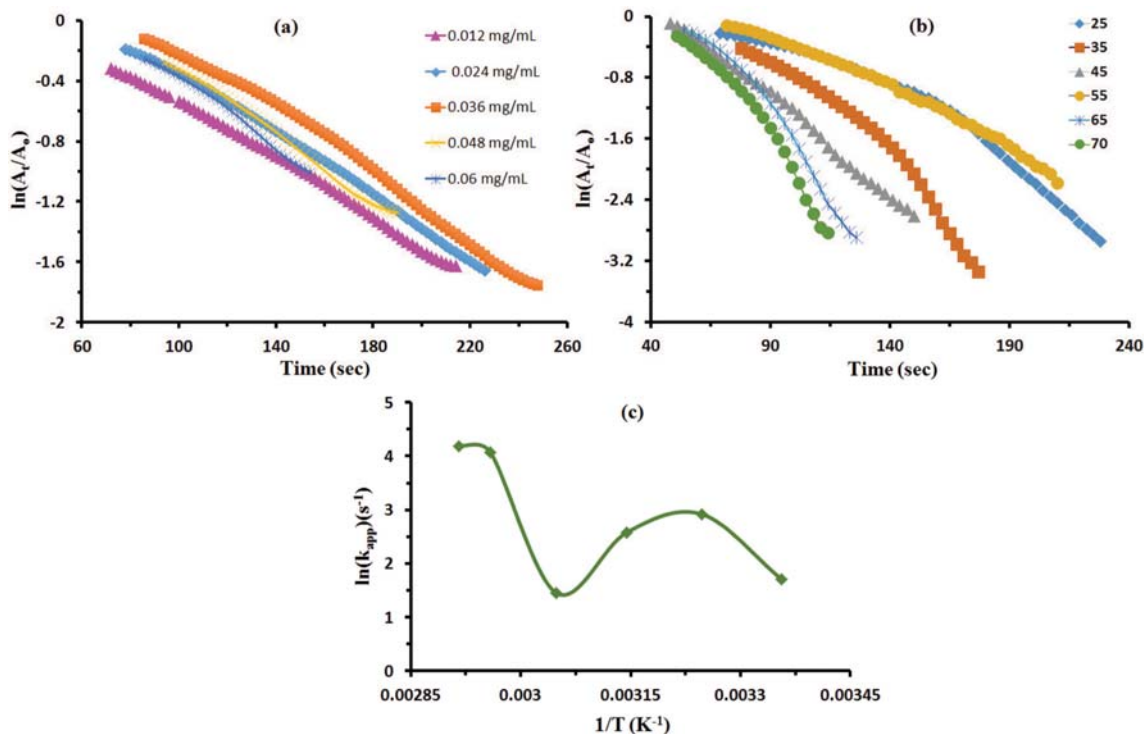

Fig. 6. Linear portion of plots of ln(A$_t$/A$_o$) vs time for reduction of 4-NA at (a) various amounts of Ag-p(NIPa-AAm-Ma) composite microgel catalyst (b) different values of temperature of the medium (c) plot of lnk$_{app}$ vs 1/T for 4-NA reduction in presence of 6.70 mM NaBH$_4$, 0.067 mM 4-NA and 0.012 mg/mL catalyst.

Ma) hybrid microgels catalyst dose in its range of 0.012-0.060 mg/mL, while concentration of 4-NA and NaBH$_4$ was kept constant as 0.067 mM and 6.7 mM, respectively, at 23 °C. ln(A$_t$/A$_o$) was plotted as a function of time to determine the value of apparent rate constant (k$_{app}$) for reduction of 4-NA. Time in which value of ln(A$_t$/A$_o$) was not changed with time at start of reaction for reduction of 4-NA is called the induction period [15]. However, when induction period passed, ln(A$_t$/A$_o$) was found to be decreased linearly with time and become constant. Constant value of ln(A$_t$/A$_o$) with time at the end of reaction shows the completion of reduction of 4-NA. Fig. 6(a) shows the portion of plot of ln(A$_t$/A$_o$) vs t in which value of ln(A$_t$/A$_o$) decreases linearly with time. This plot was used to calculate the value of k$_{app}$ for reduction of 4-NA at various amounts of catalyst. The value of k$_{app}$ for reduction of 4-NA was increased from 0.96×10^{-2} to 1.17×10^{-2} s^{-1} when dose of catalyst was increased from 0.012 to 0.060 mg/mL, respectively, as given in Table 1. At high catalyst dose, more surface area of AgNPs was available for adsorption of reactant molecules and rate of reduction reaction was increased [15]. Thus, value of k$_{app}$ for reduction of 4-NA was found to be increased with increase of catalyst dose.

Effect of concentration of NaBH$_4$ on rate of reduction of 4-NA was investigated by changing its concentration from 3.35 to 10.05 mM, while concentration of 4-NA and catalyst dose was kept constant as 0.067 mM and 0.012 mg/mL, respectively, at 23 °C. The value of k$_{app}$ for reduction of 4-NA was found to be increased with increase of concentration of NaBH$_4$, became constant and then was decreased. Value of k$_{app}$ was found to be changed with change of concentration of reducing agent. At start, k$_{app}$ was increased with increase of amount of NaBH$_4$, approached to maximum value and then decreased at the end. Actually at initial stages, increase in concentration of reactants increased the rate of their diffusion through polymeric network to approach the surface of AgNPs and ultimately

increased their extent of adsorption on the surface of AgNPs, which resulted in increase in the value of k$_{app}$ for reduction reaction. But it was observed that high concentration of NaBH$_4$ causes decrease in value of k$_{app}$ for reduction of 4-NA. This may be due to excessive use of NaBH$_4$ which occupies the whole active sites of AgNPs catalyst present in polymer network and results in decrease in value of k$_{app}$ [38].

Table 1 gives the values of k$_{app}$ for reduction of 4-NA at different amount of NaBH$_4$. 4-NA was reduced to 4-AA using its different concentration in presence of 0.012 mg/mL catalyst dose and 6.7 mM reducing agent at 23 °C. It was observed that value of k$_{app}$ was not changed appreciably with change of concentration of 4-NA in a wide concentration range. The same trend has also been reported previously [44]. However, a slight decrease in the value of k$_{app}$ for reduction of 4-NA with concentration of 4-NA in its high concentration range was observed as shown in Table 1.

These observations support Langmuir-Hinshelwood mechanism of catalysis in which both reactants get adsorbed on the surface of silver nanoparticles, interact with each other and are converted into products [39].

5. Thermodynamic Aspect of Reduction Reaction

Temperature of the medium is an important parameter that can be used to tune the catalytic activity of hybrid microgels towards 4-NA reduction. 4-NA reduction was done under different conditions of temperature by varying its value from 25 to 70 °C while all other reaction conditions as concentration of catalyst and reactants were kept constant. Plot of ln(A$_t$/A$_o$) vs time for linear portion only at different temperature of the medium is shown in Fig. 6(b). Value of k$_{app}$ for 4-NA reduction at various values of temperature was calculated from slope of the plot of ln(A$_t$/A$_o$) vs t as shown in Fig. 6(b). Values of k$_{app}$ for the catalytic reduction of 4-NA at different values of temperature of the medium are given in Table

Table 1. Values of k$_{app}$ for reduction of 4-NA using different amount of catalyst, reducing agent, 4-NA and different temperature

Reaction conditions	NaBH$_4$ (mM)	Catalyst (mg/mL)	4-NA (mM)	T (°C)	k$_{app} \times 10^2$ (s^{-1})
Catalyst	6.70	0.012	0.067	23	0.96
	6.70	0.024	0.067	23	1.02
	6.70	0.036	0.067	23	1.07
	6.70	0.048	0.067	23	1.13
	6.70	0.060	0.067	23	1.17
NaBH$_4$	3.35	0.012	0.067	23	0.61
	5.03	0.012	0.067	23	1.12
	6.70	0.012	0.067	23	1.09
	10.05	0.012	0.067	23	0.66
4-Nitroaniline	6.70	0.012	0.030	23	1.40
	6.70	0.012	0.040	23	1.11
	6.70	0.012	0.050	23	1.40
	6.70	0.012	0.060	23	1.10
Temperature	6.70	0.012	0.067	25	1.71
	6.70	0.012	0.067	35	2.92
	6.70	0.012	0.067	45	2.58
	6.70	0.012	0.067	55	1.45
	6.70	0.012	0.067	65	4.07
	6.70	0.012	0.067	70	4.19

1. Plot of $\ln(k_{app})$ as a function of $1/T$ is shown in Fig. 6(c). It is clear from Fig. 6(c) that catalytic reduction of 4-NA in the presence of Ag-p(NIPa-AAm-Ma) hybrid microgels does not follow typical Arrhenius behavior in temperature range of 25 to 70 °C.

It was observed that k_{app} was changed from 1.71×10^{-2} to 2.92×10^{-2} s^{-1} with variation in temperature from 25 to 35 °C for reduction of 4-NA. Value of k_{app} was increased with increase of temperature of the medium due to increase of number of molecules having kinetic energy greater than activation energy as interpreted by normal Arrhenius behavior for reactions. Further increase of temperature decreased the value of k_{app} for 4-NA reduction. This decrease in k_{app} value was due to temperature induced volume phase transition of microgel particles. We have already studied the temperature sensitive behavior of p(NIPa-AAm-Ma) microgel particles in aqueous medium under different conditions of pH of the medium. It was observed that VPTT changed with changes of pH of the medium [45]. In our previous studies, we found that VPTT of the microgels lies in range of 50 to 58 °C while pH is in range of 6 to 8. Thus, Ag-p(NIPa-AAm-Ma) hybrid microgels are shrunken at 55 °C and decrease the rate of diffusion of reactant molecules into polymer network to get adsorbed on the surface of AgNPs. As a result, value of k_{app} is decreased rapidly. Volume phase transition of microgel particles due to change of temperature and its effect on rate of reaction at temperature below and above of VPTT is diagrammatically represented in Fig. 1. Lowest value of k_{app} for reduction of 4-NA was observed at 55 °C and was found to be 1.45×10^{-2} s^{-1}. Similar observations have been reported by Lu et al. in case of catalytic reduction of 4-NP in aqueous medium using Ag-[Pst-p(NIPa)] core shell composite microgels as catalysts [46]. Carregal-Romere and coworkers prepared Au-p(NIPa) hybrid microgels catalyst and used it as relay center for electron transfer reaction between hexacyanoferrate (III) and borohydride ions [47]. Catalytic activity of Au-p(NIPa) hybrid microgels was found to be affected by change of temperature as well as cross-linking density of shell region. When temperature of the medium was changed from 55 to 70 °C, the value of k_{app} for reduction of 4-NA was increased. Actually, in this temperature range, the number of reactant molecules with kinetic energy greater than activation energy increases and reduction reaction follows the Arrhenius behavior. Thus, the value of activation energy for reduction of 4-NA was calculated in both swollen and collapsed state of microgel particles (at T<VPTT>T) using the following equation:

$$\ln k_{app} = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A \qquad (2)$$

In Eq. (2), E_a is activation energy, while A is pre-exponential factor for 4-NA reduction in presence of hybrid microgels catalyst both below and above VPTT of hybrid microgels. Eyring equation (Eq. (3)) was also employed to find the value of enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) for catalytic reduction of 4-NA.

$$\ln\left(\frac{k_{app}}{T}\right) = -\frac{\Delta H^*}{R}\left(\frac{1}{T}\right) + \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^*}{R} \qquad (3)$$

In Eq. (3), k_B is Boltzmann constant while h is Planck's constant. Their values are 1.38×10^{-23} JK^{-1} and 6.63×10^{-34} Js, respectively. R

Table 2. Activation energy (E$_a$), pre exponential factor (A), enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) for 4-NA reduction at temperature below and above of VPTT of composite polymer microgels catalyst

Kinetics/ Thermodynamic parameters	T<VPTT	T>VPTT
E$_a$ (kJ/mol)	40.83	70.59
A (s^{-1})	2.46×10^5	2.71×10^9
ΔH^* (kJ/mol)	38.77	67.81
ΔS^* (kJ/mol)	-1.61×10^{-1}	-3.96×10^{-2}

represents general gas constant. Table 2 shows the values of E_a, A, ΔH^* and ΔS^* for reduction of 4-NA using hybrid microgels catalyst at temperature above and below of VPTT. E_a at temperature above VPTT was two-times higher than its value below VPTT. This may be due to presence of a barrier faced by reactants for diffusion offered by shrunk polymer network to approach the surface of AgNPs at high temperature. Also, the value of A was found to be 10^4 times higher at temperature above VPTT as compared to temperature below VPTT. Actually, A represents the value of k_{app} for reaction at infinite temperature of the medium. It is assumed that at infinite temperature, AgNPs are exposed due to shrinkage of polymer microgel particles, which induces significant increase in value of A. The values of ΔH^* and ΔS^* are given in Table 2.

Positive value of ΔH^* before and after VPTT of hybrid microgels shows that activation process is endothermic. While value of ΔS^* for reduction of 4-NA was found to be 1.61×10^{-1} and -3.958×10^{-2} kJ/molK before and after VPTT, respectively. These results indicate that reduction of 4-NA in presence of hybrid microgel catalyst is a more favorable process at high temperature. The reason is that at high temperature the value of ΔH^* is high while the value of ΔS^* is less negative. Two factors may be involved in modification of value of entropy during activation process after VPTT of hybrid polymer microgels. Former factor is the involvement of extent of freedom of reactants as well as activated complex. Later factor is rate of diffusion of reactants to approach the surface of AgNPs through microgel network. It may be possible that first factor is prominent before VPTT of hybrid microgels particles. So the magnitude of ΔS^* was found to be higher than that after VPTT of hybrid microgels.

CONCLUSION

Silver nanoparticle loaded poly(N-isopropylacrylamide-acrylamide-methacrylic acid) [Ag-p(NIPa-AAm-Ma)] hybrid microgels were prepared by simple and economical method for their use as an efficient catalyst. Catalytic activity of hybrid microgels was demonstrated by reducing 4-NA into 4-AA. FTIR and UV-Visible analysis showed the successful fabrication of AgNPs inside the polymer network. Hybrid microgels showed high catalytic activity towards 4-NA reduction. Effect of various reaction parameters on the value of k_{app} for 4-NA reduction was also studied systematically. It was observed that activity of composite microgels catalyst is tunable by changing the medium temperature. Temperature (before VPTT) for optimum activity of Ag-p(NIPa-AAm-Ma) composite

microgels for 4-NA reduction was found to be 35 °C. The value of k_{app} was $2.93 \times 10^{-2}\,s^{-1}$ for 4-NA reduction, while half-life was 23.2 s at 35 °C. Ag-p(NIPa-AAm-Ma) hybrid microgels showed minimum catalytic activity at 55 °C due to deswelling of hybrid microgel particles. Value of k_{app} and half life for 4-NA reduction was $1.45 \times 10^{-2}\,s^{-1}$ and 47.8 s, respectively, at 55 °C. Conditions like concentration of reactants, catalyst and temperature of the medium can be set to optimize the rate of reduction of 4-NA. The reported hybrid microgels can be used as catalyst for reduction of other nitro aromatic compounds in aqueous medium in future.

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