Fabrication of Ag and Au nanoparticles in cross-linked polymer microgels for their comparative catalytic study

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Three dimensional cross-linked polymer microgels with temperature responsive N-isopropyl acrylamide (NIPAM) and pH sensitive methacrylic acid (MAA) were successfully synthesized by free radical emulsion polymerization with different amounts of MAA. Silver and gold nanoparticles with the size of 6.5 nm and 3.5 nm (± 0.5 nm), respectively were homogeneously reduced inside these materials by chemical reduction method at pH 2.78 and 8.36 for the preparation of hybrid materials. The samples were characterized by FT-IR, DLS and TEM techniques. The catalytic activity of the hybrid materials was investigated for the reduction of 4-nitrophenol (4-NP) using NaBH₄ as reducing agent by UV-Vis spectroscopy. The hybrid polymer network synthesized at pH 8.36 showed enhanced catalytic efficiency compared to the catalysts synthesized at pH 2.78. In this study, it has been stated that the catalyst activity strongly depends on the amount of MAA, pH value during synthesis and the type of entrapped metal nanoparticles.

Keywords: *cross-linked polymer microgels; free radical polymerization; metal nanoparticles; catalytic activity; comparative study*

1. Introduction

Due to their intelligent and smart behavior, cross-linked polymer microgels received a significant interest in many fields of applications e.g. drug delivery [1], wound dressing [2], sensors [3], artificial mussels [4], optical devices [5], catalysis [6], lithium batteries [7], nanoreactors [8], etc. Polymer microgels are 3D cross-linked network showing reversible responsive behavior with the environmental stimuli such as temperature [9, 10], pH [11], ionic strength [12], enzymes [5], glucose [13], electric current [14], etc. In catalysis, microgel particles are used as a shelter for the fabrication of metal nanoparticles (NPs). As metal NPs received notable attention due to their catalytic performance, their small size and large surface, because of high surface energy the particles, are unstable and undergo aggregation which restricts their catalytic properties. So, to avoid the aggregation process, cross-linked polymer microgel networks have been designed. These microgel

particles not only provide a support for metal NPs, but also change their properties by changing their own structure with the application of external stimuli. The entrapment of metal particles inside the microgel network enables us to produce hybrid systems which can be used anywhere in a controlled fashion for better yield.

The hybrid systems with responsive tunable properties can be used as catalysts for different reactions. The combination of two or more monomers in a polymer chain gives multiresponsive character to the polymer network, which enhances their use for multiple purposes.

Currently, Wu et al. [15] immobilized copper NPs on responsive chitosan based microgels and applied them as a catalyst for a model azide-alkyne [3 + 2]-cycloaddition reaction. They found that the catalyst efficiency can be tuned to some extent with changing swelling and de-swelling transitions of polymer gels. Liu et al. [16] investigated the temperature responsive catalytic activity of Ag NPs loaded in temperature sensitive poly(N-isopropyl acrylamide) microgels. They

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Table 1. Feed ratios, particle size and zeta potentials of the synthesized copolymer microgels at 25 °C.

Sample code	Feed ratio of NIPAM:MAA:BIS	Total moles	pH	Zeta potential [mV]	Mean diameter by DLS [nm]	Mean size by TEM [nm]
p(NIPAM-co-MAA)-1	85:10:5	0.011	2.78	-3.13	148	108
			8.36	-22.3	293	262
p(NIPAM-co-MAA)-2	80:15:5	0.011	2.78	-4.09	170	123
			8.36	-23.9	371	348

showed that the catalytic activity of embedded Ag NPs can be modulated at four stages by variation of temperature from 20 °C to 45 °C, but more efficiently above 35 °C. Contin *et al.* [17] used laponite nanoclay as a cationic exchanger for metal NPs (Pd, Pt and Au) which upon reduction yielded ternary nanocomposites composed both of metal particles and nanoclays. The materials were applied as catalysts for standard cross coupling reactions in aqueous medium. Gema *et al.* [18] prepared PNIPAM/gold hybrid hydrogels by using catechol redox chemistry. The catalytic activity of hybrid materials was studied by using reduction of 4-nitrophenol (4-NP). The results revealed high catalyst efficiency at 25 °C compared to 38 °C due to the shrinkage of PNIPAM structure. Sahiner [19] fabricated Co and Ni NPs inside cationic poly (ethylene imine) microgel particles prepared by microemulsion polymerization. The synthesized species were used as catalysis medium for reduction of 4-NP to 4-aminophenol. Cationic copolymer microgels composed of vinyl imidazole and N-isopropylacrylamide moieties were prepared by us [20] and successfully applied for the fabrication of Ag NPs. The materials showed good catalytic activity with high stability in the entire pH range. Recently, in another study [21], Ag and Au nanoparticles were reduced inside ter-copolymer microgels at 10 °C and 40 °C and their catalytic activities were studied in detail for the degradation of 4-NP, methylene blue and congo red. The catalysts synthesized at 40 °C showed enhanced catalytic activity due to their direct exposure to reactant molecules.

In this work, for the first time, we fabricated Ag and Au NPs at pH 2.78 and 8.36 in copolymer poly(N-isopropylacrylamide-co-methacrylic acid) P(NIPAM-co-MAA) microgels. The effect

of MAA amount, temperature and pH sensitive behavior on the particle size has been investigated in detail and results obtained have been compared with the literature. The hybrid microgels were tested for their comparative catalytic activity towards the reduction of 4-NP as a model reaction.

2. Experimental

2.1. Chemicals

N-isopropylacrylamide (NIPAM, 98 %, TCI) was recrystallized from a mixture of toluene and n-hexane (V:V = 1:3). Methacrylic acid (MAA, 98 %, TCI) was passed through a neutral alumina column to remove inhibitors. N,N-methylene bisacrylamide (BIS, ACROS), silver nitrate (AgNO₃) and chloroauric acid (HAuCl₄·H₂O) were purchased from ALDRICH. Ammonium peroxodisulfate (APS), sodium dodecyl sulfate (SDS) and 4-nitrophenol (4-NP) were all purchased from TCI and were used as received. Double distilled water (DDW) was used during all the experiments.

2.2. Synthesis of p(NIPAM-co-MAA) copolymer microgels

The synthesis of p(NIPAM-co-MAA) copolymer microgels was carried out by free radical emulsion polymerization reported in the literature [22] with slight modification. Typically, the required amount of monomers NIPAM and MAA (listed in Table 1), 84.7 mg of BIS and 57 mg of SDS were dissolved in 100 mL of deionized water and stirred for 1 h. The mixture was purged with nitrogen, heated to 65 °C, and 5 mL aqueous solution of APS (65 mg/5 mL) was added for initiation. After complete polymerization, the mixture was purified by decantation, centrifugation and transferred

to a dialysis bag with a molecular weight cutoff (MWCO) of 14000 for dialysis. The bag was immersed into distilled water for 10 days at constant stirring; water was continuously replaced twice a day. The resultant p(NIPAM-co-MAA) copolymers were lyophilized and collected for further use.

2.3. Synthesis of metal entrapped p(NIPAM-co-MAA)-Ag and p(NIPAM-co-MAA)-Au hybrid microgels

Polymer hybrid microgels p(NIPAM-co-MAA)-Ag and p(NIPAM-co-MAA)-Au, were synthesized at pH 2.78 and 8.36 from pure microgels. 2 mg of synthesized pure copolymer microgels were diluted by adding 35 mL of pure deionized water in two three-necked flasks. After stirring for 3 h, the pH of both solutions was adjusted to 2.78 by adding very dilute HCl solution. Then, one solution was charged with 5 mL of chloroauric acid ($\text{HAuCl}_4 \cdot \text{H}_2\text{O}$, 1 mM) to one flask and the other one with 5 mL of silver nitrate (AgNO_3 , 1 mM) to another flask. The stirring was continued for another 1 h with continuous purging of N_2 for 0.75 h. 4 mL freshly prepared NaBH_4 solution (0.13 g/8 mL of H_2O) was added to each flask. The color of the solutions was changed rapidly. The reactions were conducted for 3 h to completion; the samples were purified by dialysis for 2 h, dried under vacuum and stored for characterization. The same procedure was followed for hybrid microgels synthesized at pH 8.36 using very dilute solution of sodium hydroxide for pH adjustment.

2.4. Catalytic activity of metal entrapped hybrid microgels

To evaluate the catalytic activity of p(NIPAM-co-MAA)-Ag and p(NIPAM-co-MAA)-Au, 0.06 mmol (8.22 mg) of 4-NP was dissolved in 100 mL of deionized water and stirred to get a clear light yellow colored solution. 5.3 mmol (0.20 g) of NaBH_4 was added to this solution. 2.5 mL of the synthesized solution was transferred into a quartz cell with a path length of 1 cm, followed by adding 0.1 mL of 0.2 mM p(NIPAM-co-MAA)-Ag and p(NIPAM-co-MAA)-Au aqueous

solution separately for each reduction process. UV-Vis spectrophotometer was used to monitor the reaction. The reaction rate constant k_{app} could be calculated from the relationship between the absorption at 400 nm and the reaction time.

2.5. Characterization

The FT-IR spectra were recorded on a NEXUS-470 spectrometer to identify different functional groups present in the microgels. The samples were vacuum dried on silicon chip before analysis. The hydrodynamic diameter and Zeta potentials were measured on a Malvern autosizer 4700 instrument; the samples were filtered through hydrophilic Millipore Millex-HV filters with a pore size of 0.45 μm to remove any dust particles. Transmission electron microscopy (TEM) images were obtained on a JEOL JEM 2100 F transmission electron microscope, and samples for TEM measurements were made by casting one drop of the sample solution on a carbon copper grid. The ultraviolet visible absorption analysis was carried out using a PerkinElmer Lambda 750 UV-Vis-NIR spectrometer.

3. Results and discussion

3.1. Synthesis of microgels

The successful copolymerization and microgel formation of NIPAM and MAA were confirmed by FT-IR spectroscopy. The FT-IR spectra for composition 1 (both pure and hybrid) are shown in Fig. 1, the FT-IR spectrum of p(NIPAM-co-MAA) shows a broad N-H stretching vibration peak at 3300 cm^{-1} , a clear C-N stretching vibration peak at 1459 cm^{-1} and an obvious C=O (amide) stretching vibration peak at 1635 cm^{-1} , however, no characteristic peaks of vinyl functionality indicates the complete disappearance of initial monomers. After combination with Ag and Au nanoparticles, the C=O stretching vibration peak of p(NIPAM-co-MAA)-Ag and p(NIPAM-co-MAA)-Au was shifted from 1651 cm^{-1} to 1642 cm^{-1} and 1635 cm^{-1} , respectively, indicating that the Ag and Au nanoparticles were successfully integrated with C=O groups, while all other

peaks of corresponding functional groups appeared at the same position. The entrapment, existence and size of metal particles was also confirmed by transmission electron microscopy.

Fig. 1. FT-IR spectra of pure and metal entrapped hybrid microgels.

3.2. Sensitive behavior of microgels

The presence of pH-responsive MAA and temperature sensitive NIPAM, introduce a remarkable pH and temperature sensitive behavior in p(NIPAM-co-MAA)s polymer microgels, which changes their size in different environmental conditions. It could be seen from Fig. 2 that the size of p(NIPAM-co-MAA)s determined by DLS was increased with the increase in pH of the microgel solution. This was caused by the deprotonation of carboxyl group in the basic media, which induced electrostatic repulsive interactions and caused extension of the polymer chains and size increase [23]. The critical volume phase transition pH of p(NIPAM-co-MAA)s was approximately 4.5; below this value the particles were small in size of about 148 nm and 170 nm for p(NIPAM-co-MAA)-1 and p(NIPAM-co-MAA)-2, respectively. At pH 2.78, above the transition pH, the particles reached the maximum size value shown in Fig. 2.

Furthermore, with the increase of MAA content in p(NIPAM-co-MAA)s, the pH-dependent size change was more distinct due to the increase in surface charge on the particles, which was further

Fig. 2. Particle size of p(NIPAM-co-MAA)s copolymer microgels at different pH values.

confirmed by measuring zeta potentials at pH 2.78 and 8.36. The particles size was also confirmed by TEM analysis (Fig. 3). The size obtained by TEM was less than that of DLS, and this was due to the dry nature of the samples considered for TEM analysis whereas DLS calculated hydrodynamic size of particles in solution. The zeta potentials and particle size values obtained at room temperature for p(NIPAM-co-MAA)-1 and p(NIPAM-co-MAA)-2 are tabulated in Table 1.

Fig. 3. TEM images of metal entrapped microgel particles at pH 2.78 with their size distribution (a) p(NIPAM-co-MAA)-1-Ag (b) p(NIPAM-co-MAA)-2-Ag (c) p(NIPAM-co-MAA)-1-Au (d) p(NIPAM-co-MAA)-2-Au (e) size distribution of Ag nanoparticles in p(NIPAM-co-MAA)-1-Ag and (f) size distribution of Au nanoparticles in p(NIPAM-co-MAA)-1-Au.

The thermal sensitivity of p(NIPAM-co-MAA)s was investigated at pH 2.78 and 8.36. At pH 2.78, both p(NIPAM-co-MAA)s showed obviously pronounced thermal responsibility (Fig. 4a and Fig. 4c), due to the weak electrostatic interactions of MAA segment. A clear volume phase transition temperature (VPTT) was observed which decreased at the high MAA content in the copolymer composition. The VPTT for pure NIPAM is 32 °C, the introduction of 15 % MAA, lowered VPTT to 29 °C. The value of VPTT is determined by the balance between the hydrophilic and hydrophobic interaction of copolymers. Thus, the increase of hydrophobic MAA monomer leads to a shift of VPTT to a lower temperature. No aggregation was observed for both compositions at high temperature up to 50 °C, which was confirmed by the presence of some charge on the surface of particles at low pH calculated from zeta potential values shown in Table 1. However, aggregation of particles at low pH and high temperature was reported for acrylic

acid (AA) in a previous study [22]. At pH 8.36, the strong electrostatic repulsive forces shifted the VPTT to a higher values and only a slight decrease in particle size was observed at 50 °C (Fig. 4b and Fig. 4d). This decrease is due to the expelling of water molecules from polymer network. The VPTT for p(NIPAM-co-MAA)-2 was found again less than for p(NIPAM-co-MAA)-1 at pH 8.36 due to the high amount of MAA.

3.3. Discussion on catalytic tests

The particle size which is a function of charge on the particle surface is responsible for the entrapment of metal nanoparticles inside the polymer network. It was confirmed by synthesizing hybrid microgels at pH 2.78 and 8.36, and studying their comparative catalytic activity. The catalytic activity was examined for all prepared hybrid microgels used as catalysts for the reduction of 4-NP to 4-aminophenol (4-AP) in aqueous solution

Fig. 4. Diameter of polymer microgel at various temperatures for (a) p(NIPAM-co-MAA)-1 at pH 2.78, (b) p(NIPAM-co-MAA)-1 at pH 8.36, (c) p(NIPAM-co-MAA)-2 at pH 2.78 and (d) p(NIPAM-co-MAA)-2 at pH 8.36.

using NaBH_4 as a reducing agent, by UV-Vis spectroscopy. The reduction in absorption peak intensity at 400 nm due to nitrophenolate ion (NP^-) was plotted against time; the apparent rate constant k_{app} was calculated from the slope of the linear curve.

3.3.1. Catalysts synthesized at pH 2.78

The surface charge for pure copolymer p(NIPAM-co-MAA)-2 at any pH value is greater than that of p(NIPAM-co-MAA)-1 microgel. This increase in charge density enhances the particle size due to which p(NIPAM-co-MAA)-2 can accommodate more metal particles in comparison to p(NIPAM-co-MAA)-1 and shows enhanced catalytic efficiency. The catalytic efficiency was examined at various stages of reaction by noting the reduction in the peak intensity at 400 nm caused by π - π^* allowed transition in NP^- versus reaction time, indicating the consumption of reactants.

The formation of 4-AP was confirmed by color change and the appearance of a peak with low intensity at 300 nm caused by the n - δ^* forbidden transition of amino groups. In the absence of catalyst or NaBH_4 no reduction in the peak intensity was observed which clearly indicates that the reaction is kinetically restricted, although it is thermodynamically feasible. The UV-Vis spectra obtained for p(NIPAM-co-MAA)-2-Ag and p(NIPAM-co-MAA)-2-Au synthesized at pH 2.78 are shown in Fig. 5.

The comparative catalytic activity was evaluated from the apparent rate constant k_{app} value, which was calculated from the slope of $\ln A$ against time, where $A = A_0/A_t$, (A_0 is the initial absorbance and A_t is the absorbance at any time t of 4- NP^-). The k_{app} obtained for p(NIPAM-co-MAA)-1-Ag was 0.16134 min^{-1} which is less than

Fig. 5. UV-Vis spectra for the catalysts synthesized at pH 2.78 (a) p(NIPAM-co-MAA)-2-Ag and (b) p(NIPAM-co-MAA)-2-Au.

the k_{app} value obtained for p(NIPAM-co-MAA)-2-Ag, 0.20656 min^{-1} shown in Fig. 6. This increase in catalytic property is caused by the large size of microgel particles, which can be explained in two ways: first, the large size particles accommodate more metal particles, and second, the diffusion of reactants to the catalyst surface and removal of products from polymer network is facilitated. An induction time was observed for all prepared catalysts at pH 2.78, which was due to the small size of microgel particles, restricting the penetration of reactants inside the polymer network and took some time to come in contact with the metal surface (Fig. 6a).

Fig. 6. Plot of $\ln A$ vs. time for the conversion of 4-NP by p(NIPAM-co-MAA)-1-Ag synthesized at (a) pH 2.78 and (b) pH 8.36.

The catalytic efficiency depends also on the type of metal nanoparticles entrapped in cross-linked polymer network. In this study, we have stabilized Ag and Au nanoparticles in cross-linked polymer network for comparative study. The size of Au nanoparticles was $3.5 \text{ nm} (\pm 0.5 \text{ nm})$ and

Table 2. Obtained k_{app} values for all catalysts synthesized at different pH values used for reduction process.

Sample code	Synthesis pH	k_{app} [min^{-1}]
p(NIPAM-co-MAA)-1-Ag	2.78	0.16134
	8.36	0.24314
p(NIPAM-co-MAA)-2-Ag	2.78	0.20656
	8.36	0.30259
p(NIPAM-co-MAA)-1-Au	2.78	0.19634
	8.36	0.34112
p(NIPAM-co-MAA)-2-Au	2.78	0.23388
	8.36	0.5556

that of Ag nanoparticles was 6.5 nm (± 0.5 nm) as shown in Fig. 3. This small size makes Au based catalysts more efficient as compared to Ag particles containing catalysts, which is demonstrated by their greater k_{app} values tabulated in Table 2.

Fig. 7. UV-Vis spectra for p(NIPAM-co-MAA)-1-Ag synthesized at pH 8.36.

3.3.2. Catalysts synthesized at pH 8.36

The charge density at pH 8.36 is large due to ionization of carboxyl groups in polymer chains. The particles changed to swollen state, due to which they were able to provide more space and attraction for metal ions to come inside the polymer network. The UV-Vis spectra obtained for p(NIPAM-co-MAA)-1-Ag synthesized at pH 8.36 are presented in Fig. 7. Again k_{app} for p(NIPAM-co-MAA)-1-Ag (0.24314 min^{-1}) is

less than the k_{app} for p(NIPAM-co-MAA)-2-Ag (0.30259 min^{-1}). The linear trend for p(NIPAM-co-MAA)-1-Ag synthesized at pH 8.36 is shown in Fig. 6b. No induction time was observed in this case, because the reactants take negligible time to come in contact with metal surface and quickly change into products due to the large size of the polymer network. The k_{app} values obtained for the catalysts synthesized at pH 8.36 were found greater than those for the catalysts synthesized at pH 2.78, which confirms the dependence of catalyst efficiency on the size of polymer microgel network. Due to the large size of polymer network, the reactant molecules easily penetrate inside it forming a colloid with the entrapped metal particles, and a chemical change occurs. After the formation of the products, the formed materials come out easily from the network.

At pH 8.36, Au based catalysts were found again more efficient than other Ag particles containing catalysts. The highest k_{app} (0.5556 min^{-1}) was obtained for p(NIPAM-co-MAA)-2-Au, due to the large size of pure microgel particles and small size of entrapped Au NPs. The pure microgel particles leave enough space for Au particles, and small size of Au NPs provides a large surface area for the reactants to undergo a chemical change. The k_{app} values for all catalysts synthesized at pH 2.78 and 8.36 are given in Table 2.

4. Conclusions

The responsive cross-linked polymer microgels p(NIPAM-co-MAA)s have been synthesized

successfully by free radical emulsion polymerization with varying amount of MAA. Small size Ag and Au nanoparticles were successfully incorporated into the polymer network at pH 2.78 and 8.36. The synthesized doped materials were used as catalysts for the reduction of 4-NP successfully. The results revealed that the catalysts synthesized at pH 8.36 show enhanced catalytic activity compared to the catalysts prepared at pH 2.78. Also it was confirmed that hybrid microgels composed of gold nanoparticles were more efficient than silver based hybrid microgels. Most importantly, it was proven in this study that p(NIPAM-co-MAA)s cross-linked polymer microgels can be used at different pH values for the immobilization of different metal nanoparticles and then can be applied as a catalyst for various organic reactions.

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