RESPONSIVE POLYMER HYBRID GEL CROSS-LINKED BY N,N-(1,2-DIHYDROXYETHYLENE) BISACRYLAMIDE FOR CATALYTIC APPLICATION

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ABSTRACT

Copolymer microgel composed of N-isopropyl acrylamide and methacrylic acid, poly(NIPAM-MAA), was synthesized by free radical emulsion polymerization using N,N-(1,2-dihydroxyethylene) bisacrylamide as cross-linking agent. The hybrid microgels poly(NIPAM-MAA)-Au and poly(NIPAM-MAA)-Ag, were synthesized by in-situ reduction of metal ions using sodium borohydride (NaBH₄) as reducing agent. The temperature and pH sensitivity of pure and hybrid microgels were studied by dynamic light scattering (DLS) and UV-Visible spectroscopy. The existence of gold and silver nanoparticles inside the microgel network was confirmed by transmission electron microscopy (TEM). Poly(NIPAM-MAA)-Au and poly(NIPAM-MAA)-Ag hybrid microgels were tested for the comparative catalytic activity towards the reduction of 4-nitrophenol to 4-aminophenol. The apparent rate constant (kₐp) for poly(NIPAM-MAA)-Au was found superior than poly(NIPAM-MAA)-Ag.

Keywords: Free radical emulsion polymerization, in-situ reduction method, hybrid microgels, surface plasmon resonance, catalytic activity

1.0 INTRODUCTION

Due to enhanced physical, chemical and biological properties, noble metal nanoparticles (NP’s) have drawn a considerable attention in the field of energy conversion 1, drug delivery 2, sensors 3 and especially in catalysis 4. A number of studies have shown that metal nanoparticles (NP’s) exhibit unexpectedly high catalytic activities toward different types of reactions due to their high surface area to volume ratio 5. However, the enhanced surface energy causes aggregation of these NP’s and hinders their applications in many fields.

In recent decades, many attempts have been made to overcome this problem. It has been proven by various studies that anchoring metal NP’s on supports is an effective approach to solve the aggregation problem. Therefore, many materials have been designed for the stabilization of metal NP’s, such as surfactants 6, micelles 7, microspheres 8, hollow capsules 9, polymer brushes 10, polymer microgels 11 and dendrimers 12. Of the wide range of materials, polymer microgels have attracted considerable interest due to their high surface area and quick responsive behavior towards environmental stimuli. Agrawal et al. 13 prepared N-vinylcaprolactam/acetoacetoxyethyl methacrylate/ acrylic acid microgels for the entrapment of colloidal gold nanostructure and studied their catalytic properties. Zheng et al. 14 synthesized chitosan and acrylic acid based granular hydrogels for the stabilization of silver nanoparticles and used it for the catalytic reduction of organic dyes. We have successfully fabricated silver nanoparticles inside the pure thermo responsive poly(N-isopropyl acrylamide) microgels synthesized with different crosslinking density 15 and dual responsive cationic poly(N-isopropyl acrylamide-co-vinylimidazole) microgels 16. The hybrid microgels were used as a catalyst for the reduction of 4-nitrophenol at different pH and the catalyst was found more efficient at pH < 6. In all these studies N, N-methylene bisacrylamide used as a crosslinking agent. To best of our knowledge very little work has been done using pure N,N-(1,2-Dihydroxyethylene) bisacrylamide (DHEBA) as cross linking moiety for 3D microgel formation and used as a template for immobilization of metal nanoparticles.

In this work we have carried out the synthesis of stable poly(NIPAM-MAA) microgels has been explored by using DHEBA as cross-linker for the fabrication of silver and gold nanoparticles. The effect of metal nanoparticles incorporation on size of microgels at different temperature and pH conditions has been studied. The synthesized materials were then tested for their catalytic activity by reducing 4-nitrophenol to 4-aminophenol using NaBH₄. In this study the efficiency of poly(NIPAM-MAA)-Au catalyst was found more than poly(NIPAM-MAA)-Ag catalyst.

2.0 EXPERIMENTAL

N,N-(1,2-Dihydroxyethylene) bisacrylamide (DHEBA) and sodium dodecyl sulphate (SDS) were obtained from Fluka, ammonium peroxodisulphate (APS) from Scharlau and all other materials were purchased from Sigma Aldrich. N-isopropyl acrylamide (NIPAM) was recrystallized from a mixture (1:1 volume ratio) of n-hexane and toluene. Methacrylic acid (MAA) was purified from inhibitors by distillation under reduced pressure prior to use. The cross-linker N,N-(1,2-Dihydroxyethylene) bisacrylamide (DHEBA), initiator ammonium peroxodisulphate (APS), emulsifying agent sodium dodecyl sulphate (SDS) and all other chemicals were used as received without further treating and purification.

2.1 Synthesis of poly(NIPAM-MAA) microgel

The synthesis of poly(NIPAM-MAA) microgel was carried out by free radical emulsion polymerization. The monomers N-isopropyl acrylamide (NIPAM, 0.952g), methacrylic acid (MAA, 103μL), N,N-(1,2-Dihydroxyethylene) bisacrylamide (DHEBA, 0.077g) as cross linking monomer and 0.05g of sodium dodecyl sulphate (SDS) as an emulsifying agent were mixed in a three necked round bottom flask containing 100mL of deionized water by keeping total concentration of mixture 0.01 moles. A constant stirring at 320 rpm was performed during reaction and continuous nitrogen purging for 45 minutes to create an inert atmosphere by removing oxygen from reaction mixture. After this, when the reaction temperature was 70 °C, 5mL of APS solution with concentration 0.05 M was added, with the addition of APS the colourless reaction mixture was changed to milky white stable colloidal solution. The reaction was continued for 6 hours, after completion of reaction the microgel was cooled and purified by dialysis using semi permeable membrane (MWCO:12000-14000) for the removal of SDS, unreacted monomers, initiator molecules etc. The deionised water was replaced twice a day for 14 days.

2.2 Synthesis of poly(NIPAM-MAA)-Au and poly(NIPAM-MAA)-Ag hybrid microgels

Poly(NIPAM-MAA)-Au and poly(NIPAM-MAA)-Ag hybrid microgels were synthesized by in-situ reduction method, the metal ions were reduced inside the polymer microgel network using NaBH₄ as reducing agent. Poly(NIPAM-MAA)-Au hybrid microgel was synthesized by diluting 15ml of pure microgel to 45ml with deionized water, 5ml of HAuCl₄·4H₂O (1mM) was put in the reaction mixture. The mixture was then stirred for 2 hours with continues N₂ purging at room temperature. 5ml of 1.1M solution of NaBH₄ was added drop wise very slowly to the mixture; colour change was observed indicating the reduction of metal ions, reaction was kept for 4 hours to complete. The solution was dialyzed against frequently changed deionized water for 2 hours to remove the reduced metal particles outside the polymer network. The same process was followed for the synthesis of poly(NIPAM-MAA)-Ag hybrid microgel using 5ml of 1mM solution of AgNO₃.

2.3 Catalytic activity of hybrid microgels

Catalytic activity was investigated for the synthesised hybrid microgels used as a catalyst for the conversion of 4-nitrophenol to 4-aminophenol by NaBH₄ as a model reaction. 80ml of solution was prepared by dissolving 1.5mg of 4-nitrophenol and 0.2g of sodium borohydride. 0.1ml hybrid microgel
having 2 μM metal nanoparticles was used as a catalyst.

2.4 Characterization

The FT-IR spectra of dried microgels were recorded on a NEXUX-470 spectrometer to identify different functional groups present in the microgels. DLLS experiments were performed with a standard laser light scattering spectrometer (Brookhaven Instruments) at an angle of 90°. He-Ne laser (35 mW, 637 nm) was used as a light source. Before performing measurements all the samples were passed through hydrophilic Millipore Millex –HV filters with a pore size of 0.45 μm to remove any dust particles. The UV-Visible absorption spectra were taken with Shimadzu 1601 UV-Vis spectrometer. 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’s solution on a carbon copper grid.

3.0 RESULTS AND DISCUSSION

3.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Polymerization and microgel formation was confirmed by FTIR spectroscopy. The FTIR spectra for pure and hybrid microgels are presented in Fig 1. The strong peaks in the range of 690 to 1000 cm⁻¹ due to vinyl group disappeared, that revealed the polymerization has been taken place. The broadening of –NH stretching peak at 3305 cm⁻¹ indicates the H-bonding and confirms the formation of gel. The two peaks at 2973 and 2933 cm⁻¹ are for asymmetric and symmetric –CH stretching respectively. A peak at 1651 cm⁻¹ shows –C=O of amide and 1544 cm⁻¹ corresponds to N-H bending vibration. –CH₂ and –CH bending vibrations were also observed at 1459 cm⁻¹ and 1387 cm⁻¹ respectively. The FTIR spectra of hybrid microgels show the same peaks like pure microgels but with the clear shifting of the carbonyl peak at 1651 cm⁻¹ due to the interaction of metal nanoparticles with –C=O group. This shift is more pronounced in poly(NIPAM-MAA)-Au compared to poly(NIPAM-MAA)-Ag, because of the small size of Au particles compared to Ag.

![FT-IR spectra of synthesized pure and hybrid microgels](image)

3.2 Dynamic Laser light scattering (DLLS)

Dynamic laser light scattering (DLLS) was used for the determination of hydrodynamic diameter of poly(NIPAM-MAA), poly(NIPAM-MAA)-Ag and poly(NIPAM-MAA)-Au microgels at different pH and temperature. The influence of pH on the hydrodynamic diameter is given in Fig 2. It was found that the increase in pH of the medium cause enhancement in size for both pure and hybrid microgels. At low temperature, water act as a good solvent due to strong hydrophilic interactions between water molecules and hydrophilic part of polymer chains. These interactions enable water molecules to penetrate inside the polymer network and increase the particle size. The increase in temperature causes the disruption of hydrophilic forces and expel water molecules from the polymer network, which causes reduction in particle size. The size of microgel shows a rapid decrease at 30°C which corresponds to the volume phase transition temperature (VPTT), after it the temperature has no effect on particle size as shown in Fig 3a. No aggregation of particles was observed as in the previous study.

![Hydrodynamic diameter as a function of pH](image)

Effect of temperature on SPR for poly(NIPAM-MAA)-Au and poly(NIPAM-MAA)-Ag was studied by UV-Visible spectroscopy. The appearance of characteristic peaks at 525 nm in Fig 4a and at 400 nm in 4b, reveal the presence of Au and Ag NP’s inside the microgel networks respectively. Our results indicate that increase in pH produces a clear blue shift and decrease in intensity in SPR peak. This shift is due to the inter-particle coupling, which changes with the size of polymer microgels. At pH 8.20, the microgel particles are in swollen state and hold the metal NP’s inside the network with high space among them, but with the decrease in pH to 3.20, the microgel particles become shrink and inter-particle coupling of metal NP’s takes place, which shift the SPR peak to high wavelength. The same trend was observed for both poly(NIPAM-MAA)-Au and poly(NIPAM-MAA)-Ag hybrid microgels.

![Effect of pH and temperature on surface plasmon resonance (SPR)](image)

Effect of pH and temperature on surface plasmon resonance (SPR) for poly(NIPAM-MAA)-Ag and poly(NIPAM-MAA)-Au was studied by UV-Visible spectroscopy. The appearance of characteristic peaks at 525 nm in Fig 4a and at 400 nm in 4b, reveal the presence of Au and Ag NP’s inside the microgel networks respectively. Our results indicate that increase in pH produces a clear blue shift and decrease in intensity in SPR peak. This shift is due to the inter-particle coupling, which changes with the size of polymer microgels. At pH 8.20, the microgel particles are in swollen state and hold the metal NP’s inside the network with high space among them, but with the decrease in pH to 3.20, the microgel particles become shrink and inter-particle coupling of metal NP’s takes place, which shift the SPR peak to high wavelength. The same trend was observed for both poly(NIPAM-MAA)-Au and poly(NIPAM-MAA)-Ag hybrid microgels.

Effect of temperature on SPR for poly(NIPAM-MAA)-Au and poly(NIPAM-MAA)-Ag were studied at pH 3.14 and 8.36 in the temperature range from 20 to 50°C. At pH 3.14, it was found that increase in temperature produces red shift in SPR peak; this is due to the shrinkage of microgel particles, which brings the metal particles close to each other. At pH 8.36, no effect of temperature on SPR was observed due to the strong repulsive forces inside the microgel network, which inhibit the metal particles coupling; results obtained for poly(NIPAM-MAA)-Au are explored in Fig 5. The UV-Vis spectroscopic results strongly support the results obtained from DLS study for poly(NIPAM-MAA).
3.4 Transmission Electron Microscopy (TEM)

Typical TEM images of hybrid poly(NIPAM-MAA)-Au and poly(NIPAM-MAA)-Ag microgels are given in Fig 6. It is clear from the TEM results that metal particles are entrapped inside the polymer network successfully. The average size of Au NP’s was found ~12 nm while that of Ag NP’s was ~28 nm by software Gatan Digitalmicrograph. The Ag NP’s were found very close to each other, because the samples pH was kept 3.2 and were dried at high temperature before analysis.

3.5 Catalytic activity of hybrid microgels

The catalytic activity of poly(NIPAM-MAA)-Au and poly(NIPAM-MAA)-Ag was investigated for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) using excess sodium borohydride as a model reaction. The pure light yellow solution of 4-NP gives a characteristic peak at 318 nm, addition of NaBH₄ produced dark yellow solution by the formation of stable p-nitrophenolate ion, which shifted the peak to 400 nm \(^2\). The peak intensity was almost constant for a few days, which clearly indicates that reaction cannot proceed without a catalyst. The addition of small amount of hybrid microgels caused the decrease in peak intensity with the passage of time and the yellow solution change to transparent. The reduction was further confirmed by the appearance of a new peak at 300 nm which is a characteristic peak for 4-AP \(^2\). The kinetics of this reaction was monitored by measuring the UV-Visible spectra as a function of time. Fig 7 shows the UV-Visible spectra obtained for poly(NIPAM-MAA)-Ag.

The reaction followed pseudo first order kinetics, because the concentration of NaBH₄ was very high as compared to 4-NP, and could not affect the rate of reaction. The apparent rate constant \((k_{app})\) was calculated from slope by plotting \(\ln(C_t/C_o)\) vs time, as given in Fig 8. The ratio of concentration of 4-NP \((C_t)\) at any time \(t\), to its initial concentration \((C_o)\) at \(t=0\) \((C_t/C_o)\), can be directly obtained by the ratio of the respective absorbance \((A_t/A_o)\). The \(k_{app}\) for poly(NIPAM-MAA)-Ag was found to be \(1.62 \times 10^{-3}\) sec\(^{-1}\), which is less than for poly(NIPAM-MAA)-Au \(2.1 \times 10^{-3}\) sec\(^{-1}\). This enhanced catalytic activity is due to the small size of Au NP’s as compared to Ag NP’s.

CONCLUSION

The poly(NIPAM-MAA) microgel was synthesized using DHEBA as cross-linker and was used as a microreactor for gold and silver nanoparticles. Temperature and pH sensitivity was checked by DLS and UV-Visible spectroscopy. The size and entrapment of metal NP’s was confirmed by TEM. The hydrodynamic diameter of microgels showed inverse behavior to temperature while directly proportional to pH. The surface plasmon resonance peaks for both poly(NIPAM-MAA)-Au and poly(NIPAM-MAA)-Ag showed red shift with increase in temperature and decrease of pH. The catalytic activity of hybrid microgels were checked for the reduction of 4-nitro phenol to 4-aminophenol. Poly (NIPAM-MAA)-Au was found more efficient than poly(NIPAM-MAA)-Ag. The synthesis process is very convenient and can be used for large scale production. The catalysts can be recycled easily by centrifugation and can be applied for the reduction of other organic compounds.
Fig 5 Temperature effect on SPR for poly(NIPAM-MAA)-Au at (a) pH 3.14 and (b) pH 8.36

Fig 6 TEM images for (a) poly(NIPAM-MAA)-Au and (b) poly(NIPAM-MAA)-Ag

Fig 7 UV-vis spectra for the reduction of p-NP to p-AP by poly(NIPAM-MAA)-Ag

Fig 8 Plot of ln(Ct/C0) vs. time for the conversion of p-nitrophenol by poly(NIPAM-MAA)-Ag

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