

Synthesis and Optical Studies of Silver Nanoparticles (Ag NPs) and their Hybrids of Smart Polymer Microgel

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Summary: Ag NPs were synthesized by the chemical reduction method and were optically characterized. The change in size of the nanoparticles and position of surface Plasmon resonance was studied as a function of concentration of different reactants by using UV-Visible spectroscopy. Red shift was observed in the position of SPR by increasing the concentration of silver nitrate, sodium hydroxide and ascorbic acid whereas the SPR was blue shifted by increasing the concentration of silver seed and Cetyl trimethylammonium bromide (CTAB). The former shift shows increase whereas the latter indicates decrease in the size of the nanoparticles. The crystalline nature and morphology of the silver nanoparticles was studied by using X-ray powder diffraction (XRD) and Atomic Force microscopy (AFM). These Ag NPs were hybridized with multiresponsive micro gel system, poly(N-isopropylacrylamide-co-acrylic acid), synthesized by emulsion polymerization. The hybrid system was subjected to Dynamic Laser Light Scattering (DLS) to determine the hydrodynamic radius (R_h) of the hybrid micro gels at different pH and different temperatures. Under different conditions of pH, variation in VPTT value was observed. Fluorescence study was also carried out at different pH values to observe the swelling behavior of hybrid system. The photoluminescence (PL) emission intensity decreased with increase in pH which showed that the hybrid micro gels were more fluorescence active at low pH.

Key words: Hybrid gels; Deswelling ratios; Dynamic laser light scattering; Volume phase transition temperature.

Introduction

Silver nanoparticles (Ag NPs) are becoming promising system for the last two decades on account of their applications in various fields such as electronics and optics [1]. They have unique chemical, physical and optical properties which differ significantly from the bulk materials. Additionally they have characteristics field enhancement which have direct linkage with surface plasmons [2]. Their optical properties depend strongly on particle size and shape. Thus, control of particle size, shape and structure is a powerful approach to adjust their electronic structure and optical properties [3, 4].

The variation in chemical compositions of reactants involved in the wet chemical synthesis of NPs has strong influence on their optical properties. The reactants mostly contain silver salt, reducing agent, solvent, precursor and a capping agent. Gulrajani *et al.* observed that the morphology and surface chemistry of the synthesized Ag NPs are mainly influenced by the stabilizers, their molar ratio to the silver salt, the stirring speed and the temperature of the synthesis reaction. Of all the mentioned parameters, the concentration of the stabilizer has the highest influence [5].

Kallol K. Ghosh *et al.* synthesized colloidal Ag NPs from AgNO_3 using PBHA and ascorbic acid

as reducing agents. They reported that the rate of the formation of Ag NPs was greatly accelerated by increasing the pH value [6].

Addition of surfactants may control particle growth and stabilize the intermediates. Jian Xu *et al.* successfully prepared uniform Ag NPs in reverse micelles of gemini surfactant. Gemini surfactant displayed excellent properties in the preparation and stabilization of Ag NPs [7]. This technique could be extended to the preparation of a variety of metal nanoparticles under appropriate conditions.

So, a lot of work has been done on the synthesis and characterization of NPs. However, the study of effect of the composition of reactants on their optical properties is of prime importance in the field of nanomaterials.

Like surfactants, polymer microgel can also be used as a stabilizer or capping agent. Dong *et al.* observed that very useful optical, catalytic and conductive properties are achieved when Ag NPs are integrated into polymer matrices to form nanocomposites or when they are combined with other metal nanoparticles acting as a shell or a core to form bimetallic nanoparticles [8].

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Kumacheva *et al.* presented the preparation of Ag NPs inside the poly[(N-isopropylacrylamide)-co-(acrylic acid)-co-(2-hydroxyethyl acrylate)] microgel particles. The use of the microgel particles as templates during Ag NPs synthesis led to the controlled deposition of silver clusters into the polymeric network and formation of hybrid microgels with temperature-sensitive properties [9]. Using thermosensitive unimolecular micelles as templates, Liu and co-workers also reported the in situ preparation of Ag NPs with a controllable spatial distribution [10].

Here in, we report the synthesis and characterization of Ag NPs, the microgel and the hybrid material constituted out of these two. The microgels were hybridized with silver nanoparticles with the aim to enhance their optical properties.

Results and Discussion

UV-Vis absorption studies of Ag NPs

UV-Vis absorption studies were carried out for silver seed, silver colloid and silver nanoparticles (Ag NPs), shown in Fig. 1. For silver seed there appears a strong SPR peak at relatively low

wavelength of 396nm. This absorption peak confirms the reduction of AgNO_3 into Ag particles which are of very small size and not fully developed. UV-Vis spectroscopic studies of Ag NPs carried out before and after centrifugation at 6000rpm, showed that before centrifugation the Ag NPs gave maximum absorption peak at 400 nm but after centrifugation there occurred a red shift and the absorption peak appeared at 404 nm. This is interpreted as that centrifugation washed away small sized nanoparticles, the remaining large sized particles have comparably low band gap or the removal of unused material led to the purity of the nanoparticles which came close to each other and grew by the coalescence or Ostwald ripening [11].

XRD of Ag NPs

Fig 2 shows the x-ray diffraction patterns which reveal that the synthesized Ag NPs have good crystallinity and high purity. A number of Bragg reflections corresponding to the (111), (200), (220), (311) and (222) sets of lattice planes are observed. These peaks are matched with the face centered cubic (fcc) structure of Ag NPs [12].

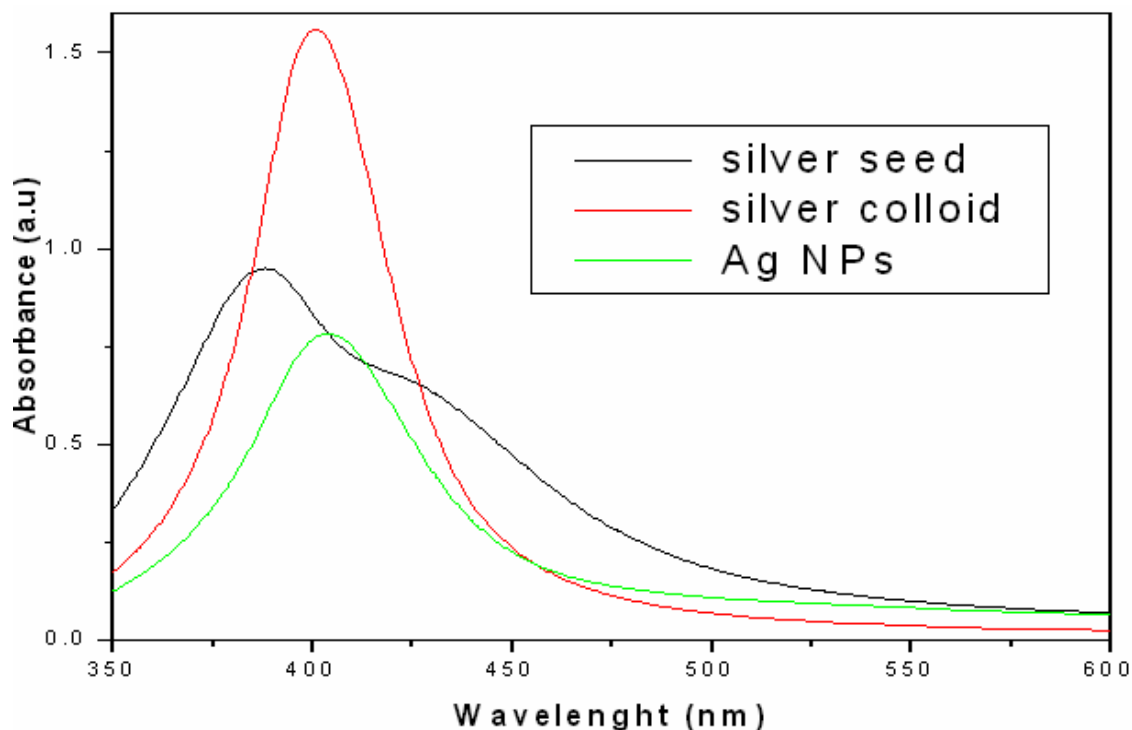


Fig. 1: UV-visible spectra of silver seed, silver colloids and Ag NPs.

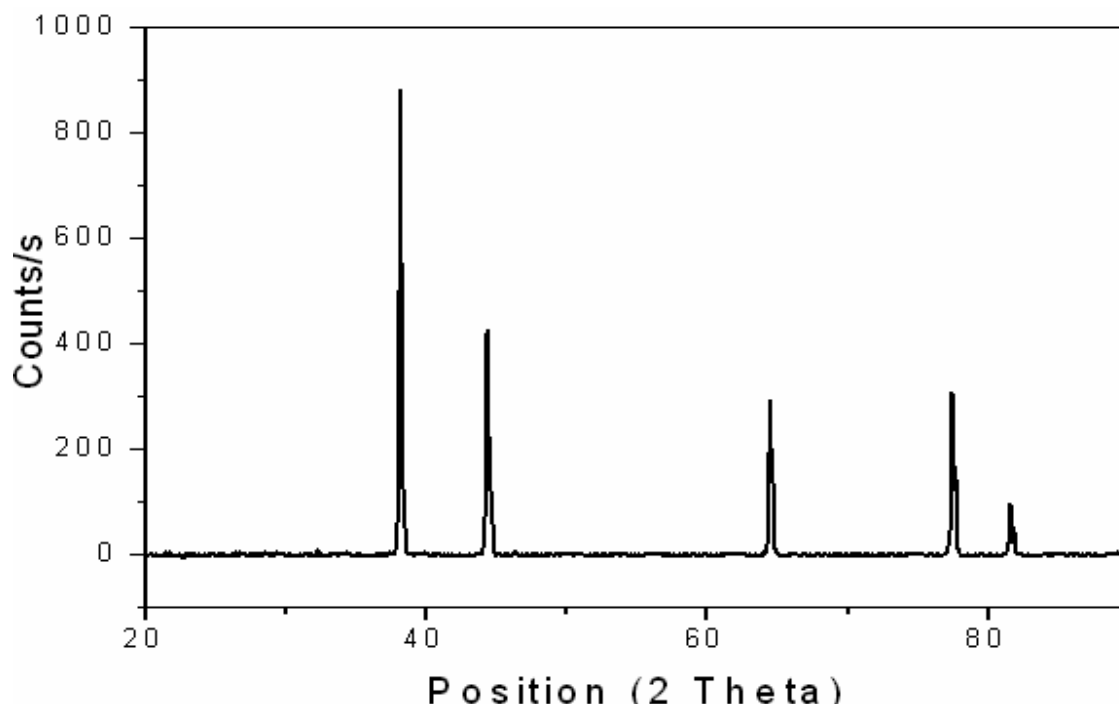


Fig. 2: XRD diffraction patterns of the synthesized Ag NPs.

Intensity, position and width of the peaks in the XRD pattern helped significantly in the characterization of the nanoparticles. Full width at half-maximum (FWHM) was used to determine the mean particle size by employing Debye-Scherrer's formula [13], which was estimated to be 60 nm. Similarly the intensity of peaks indicated high crystalline nature of the Ag NPs.

Effect of Change in Chemical Composition on the Optical Properties of Ag NPs

The optical properties of the Ag NPs, prepared by chemical reduction method, can be tuned by changing the concentration of different reagents used in the synthesis of Ag NPs.

Effect of Change in AgNO₃ Concentration

Fig 3a shows the effect of change in AgNO₃ concentration on the optical properties of Ag NPs. When the initial AgNO₃ concentration is increased, the color of solution changes from yellow to brown. The absorption peak at around 400 nm is attributed to the surface plasmon excitation of silver nanospheres, and hence confirms the formation of Ag NPs [14]. At low initial concentration of AgNO₃, this peak appears at lower wavelength which shows the small size of nanoparticles. With the increase in the concentration of AgNO₃, this characteristic absorption peak is progressively shifted to higher wavelength which

indicates the increase in size of Ag NPs. Similar red shift was observed by Huang *et al.*: when he prepared stable colloidal Ag NPs by reduction of AgNO₃ with 254 nm ultra violet light in presence of Polyvinylpyrrolidone (PVP) [15].

Effect of Change in Silver Seed Concentration

Experiments with different volumes of silver seed were carried out to investigate the influence of seed on the morphology and aspect ratio of Ag NPs while keeping other experimental conditions constant. The experimental results in Fig 3b show that the size of Ag NPs decreases with increase in silver seed concentration. There is a general tendency that Ag NPs get thicker as the volume of silver seeds is on the decline and vice versa. The increase in volume of silver seeds means that there are more nucleation sites for the formation of nanoparticles, thus the Ag NPs undergo decrease in size with the increase in the amount of the metal precursors [16]. Hence the optical properties of Ag NPs can easily be controlled by controlling the amount of silver seed.

Effect of Change in Sodium Hydroxide Concentration

Fig 3c demonstrates that the size of Ag NPs can be efficiently controlled by varying the volume of sodium hydroxide. As we increase the concentration of sodium hydroxide (NaOH), the pH of solution increases which in turn increases the

reducing efficiency of ascorbic acid because ascorbic acid works as a good reducing agent at higher pH values. This leads to the production of a large number of Ag NPs which coalesce or grow by Ostwald's ripening and hence particle size increases. This results in the bathochromic shift of the absorbance peak [17].

Similar increase in particle size was observed by Praharaj *et al.*: but up to a certain concentration of NaOH, above which reduction in the size was noticed due to the formation of Ag₂O [18].

Effect of Change in CTAB Concentration:

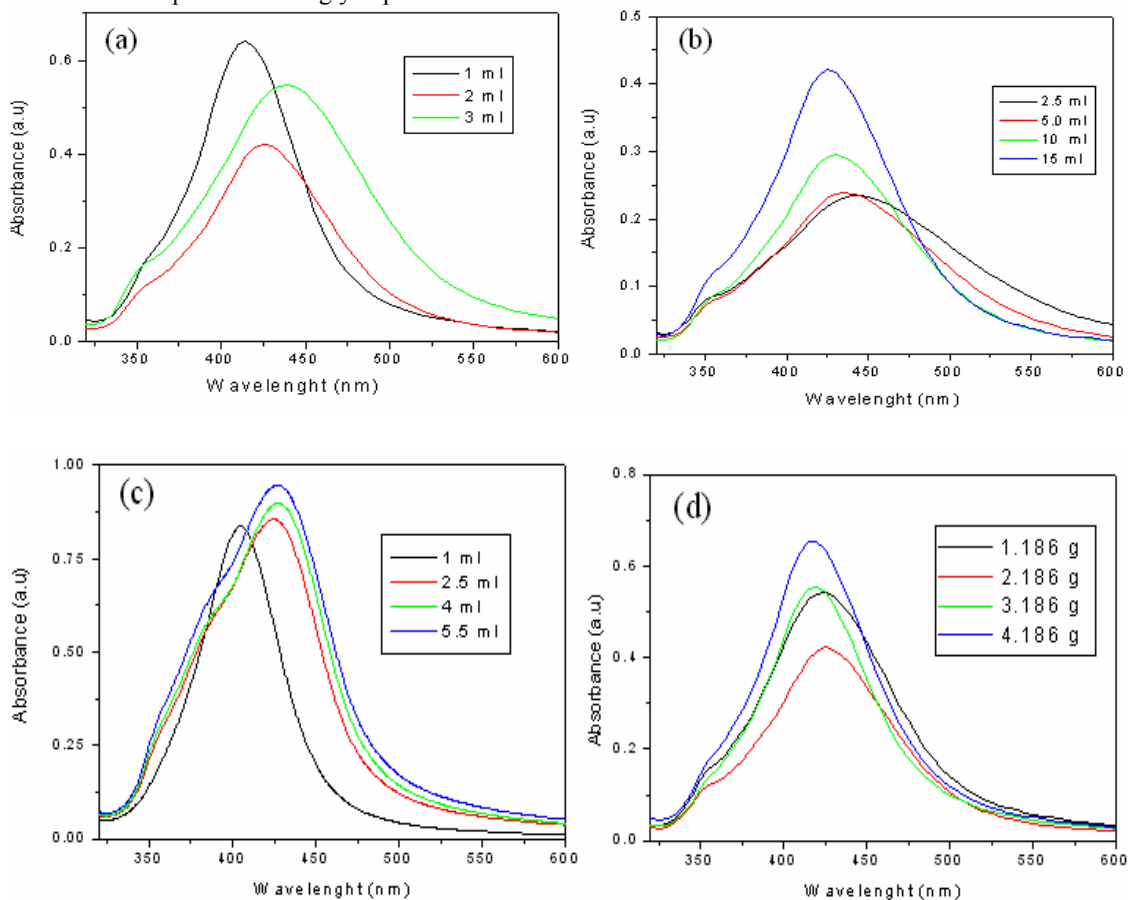
Fig 3d shows the effect of Cetyltrimethylammonium bromide (CTAB) on the size of silver nanoparticle. Cetyltrimethylammonium bromide is a cationic surfactant. It is widely used as a capping agent in the synthesis of stable and monodispersed metal nanoparticles.

While studying the effect of CTAB concentration on the Ag NPs, it was found that the size of the nanoparticles strongly depend on the

concentration of CTAB. Small amount of CTAB is not enough to cape all the Ag NPs properly. As a result, the nanoparticles lose their monodispersity and the uncapped nanoparticles aggregate to form large size particles. As the concentration of CTAB is increased, blue shift is noticed which confirms decrease in the size of nanoparticles and hence blue shift of SPR. So, Ag NPs need enough concentration of CTAB to keep their stability as well as monodispersity [19].

Effect of Change in Ascorbic Acid Concentration:

The effect of concentration of ascorbic acid on the growth of Ag NPs is summarized in Fig 3e. Ascorbic acid is a reducing agent and work very efficiently at high pH. Ag NPs were synthesized with various molar concentrations of ascorbic acid. Results show that the average size of the nanoparticles increases by increasing ascorbic acid concentration. Consequently the wavelength of the surface plasmon resonance (λ_{SPR}) of the nanoparticles solution gets red-shifted. This indicates the growth of nanoparticles [20].



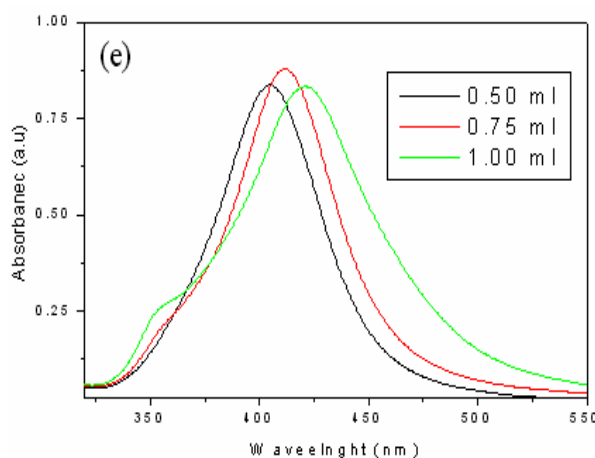


Fig. 3: Effect of change in the quantity of (a) Silver nitrate (b) Silver seed (c) Sodium hydroxide (d) CTAB and (e) Ascorbic acid on the position of surface Plasmon resonance peak of silver nanoparticles. In (a), (c) and (e) λ_{SPR} is red shifted with increasing concentration while the reverse trend is noticed in (b) and (d).

Comparative UV-Vis Absorption Study of Pure Gel, Ag NPs and Hybrid Microgels

UV-Visible spectra of microgel, Ag NPs and hybrid microgels are depicted in Fig 4. The polymer microgels, due to their low refractive index, do not absorb in the visible range of the electromagnetic spectrum. The absorption spectrum of Ag colloids prepared by the reduction of AgNO_3 shows SPR band position at 403 nm.

Upon addition of Ag NPs into the microgel, a slight red shift was observed in the absorbance peak. This is because when we add Ag NPs into microgels, electrostatic attraction between inorganic material and polymer chains develops and this leads to decrease in chain mobility consequently the hybrid particles shrink [21]. This shrinkage of the hybrid microgels brings the nanoparticles close to each other and the red shift most probably originates from end to end aggregation, causing significant size growth.

Atomic Force Microscopy of Ag NPs and Hybrid Microgel

Atomic force microscopy (AFM) was conducted to confirm the morphology, size distribution and arrangement of Ag NPs after introducing them into the microgels. Fig 5 a presents an AFM image of Ag films prepared by the reduction of Ag NPs. When the slides were observed under the AFM, most of the particles were found ranging in size from 60 to 75 nm. By counting 20 particles from

different AFM images, we got the average diameter of the particles on the substrates to be 64 nm [22]. Similarly, AFM image in Fig 5b shows that in hybrid microgels the Ag NPs are not fully visible being trapped in the microgels network. Moreover, in hybrid system the Ag NPs are very close to one another as compared to pure Ag NPs.

Dynamic laser light scattering study of hybrid gels

Fig 6 shows temperature sensitivity of hybrid gels at different pH values. At low pH value when the temperature is increased, there is a collapse followed by aggregation. This is because at high temperature (above VPTT) the hydrophobicity of the hydrogels dominates and interparticle hydrogen bonding between the carboxyl groups of the acrylic acid and the amide group of NIPAM is developed.

It is observed that both the size and VPTT of the hybrid microgel decrease gradually as the pH is lowered which means that the microgel is more temperature sensitive at lower pH. The observed VPTT is higher at high pH because system becomes more pH sensitive at high pH. Under alkaline conditions acrylic acid deprotonates its carboxyl moieties, due to which repulsion between these groups is initiated and consequently size increases. The hydrogen bonding is also strengthened by the increased hydrophilicity. That's why higher temperature is needed for breaking and disruption of these interactions. As a result volume phase transition shifts to higher temperature at higher pH which corresponds to the reported results [23].

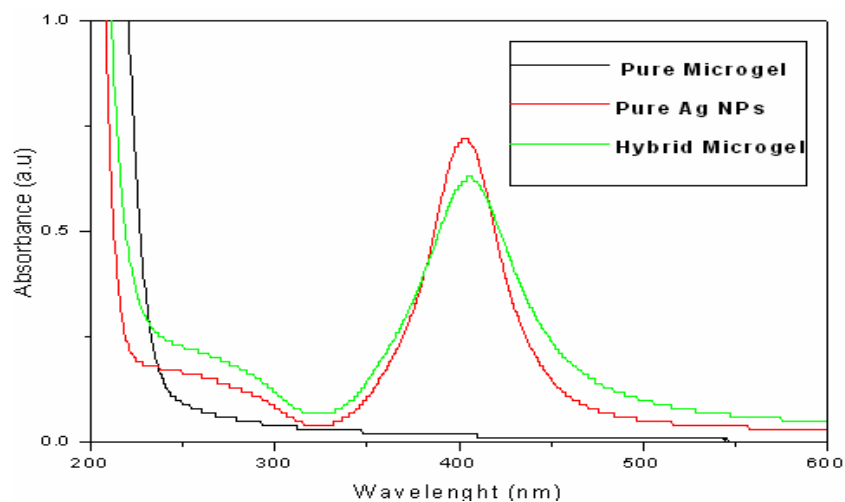


Fig. 4: UV-Visible spectra of microgel gel, pure Ag NPs and hybrid gels.

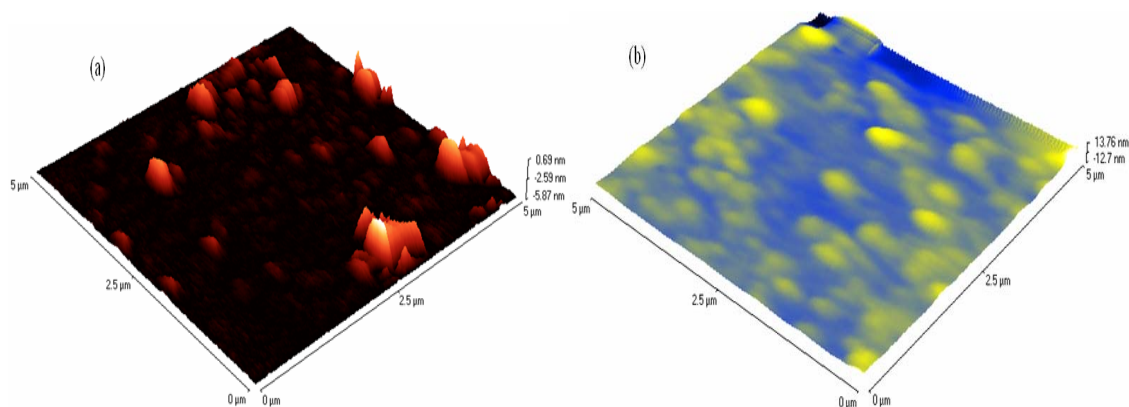


Fig. 5: AFM image of (a) Silver nanoparticles and (b) AgNPs embedded hybrid microgel.

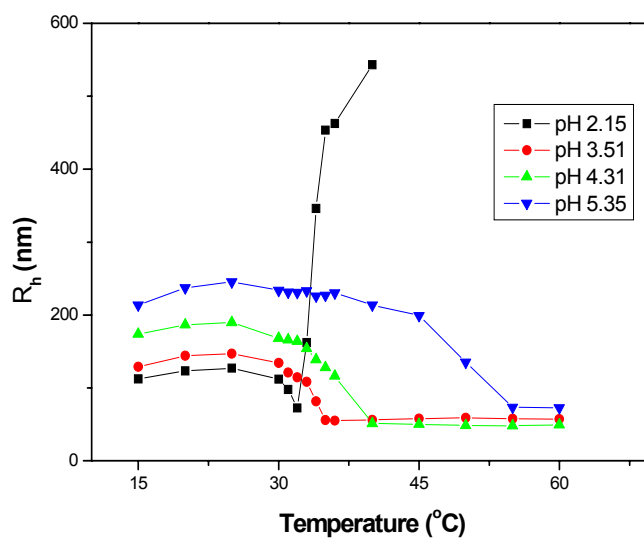


Fig. 6: Plot of Hydrodynamic radius as a function of temperature of hybrid microgels at different pH.

pH sensitive UV-Vis absorption properties of hybrid microgels

Fig 7a shows the pH sensitive UV-Vis absorption properties of poly(NIPAM-co-AAc) hybrid gels at room temperature ($\sim 25^\circ\text{C}$). When pH is decreased from 8.73 (gel shell swollen) to 2.5 (gel shell collapsed) at room temperature, blue shift of the surface plasmon bands is observed [24]. This is because the variation of pH values in the dispersion medium can swell or deswell the polymer gel shell, inducing a local refractive index change on the surface of the Ag NPs, which can further cause a change in the surface plasmon resonance of Ag NPs. The enhancement of the surface plasmon band in the hybrid microgels is attributed to the increase in the refractive index of the collapsed hybrid microgel, which increases the Rayleigh scattering [25].

pH sensitive Photoluminescence properties of Hybrid Microgels

Fig 7b shows the fluorescence active behavior of hybrid microgels at different pH. The results show that the PL quenching of the hybrid microgel can be tuned by changing the degree of swelling of the hybrid system induced by pH. The PL quenching of Ag NPs hybrid gels increased almost linearly with the increase in swelling ratio of the hybrid gels. To explain, how the pH induced swelling of the hybrid microgels trigger the fluorescence quenching, two factors may be held responsible. One is related to the change in local refractive index of the hybrid system around the Ag NPs during its swelling and deswelling transitions [26], and the other is

related to the changes in polymer network. In swollen state at high pH value, the polymer chain tend to dissolve but the cross linking of the polymer chain and binding of polymer chains with Ag NPs hinder the expansion of the polymer network and thus create elastic tension at the cross linking points that could stretch the polymer-Ag NPs interface. Similar phenomenon has also been reported by Wuister's group [27].

Experimental*Materials Used*

N, N-methylenebisacrylamide (BIS) was purchased from Acros chemicals. Silver nitrate, Ascorbic acid and Tri-sodium citrate from Scharlu Spain, Sodium Borohydride from Alfa Aesar Germany whereas N-Isopropylacrylamide (NIPAM), Acrylic acid (AAc), Disodium hydrogen phosphate anhydrous (Na_2HPO_4) and Citric Acid were purchased from Aldrich. NIPAM was recrystallized from hexane-toluene (1:1 volume ratio) mixture and dried in a vacuum. Acrylic acid (AAc) was purified by distillation under reduced pressure to remove hydroquinone inhibitor. All the other chemicals were used without further purification. The pH of the solution was adjusted by using phosphate buffer or dilutes solution of HCl and NaOH. The buffer solutions for experiments were prepared by using disodium hydrogen phosphate anhydrous (Na_2HPO_4) and Citric Acid. Deionozed and distilled water was used for all reactions, preparation of solutions and purification.

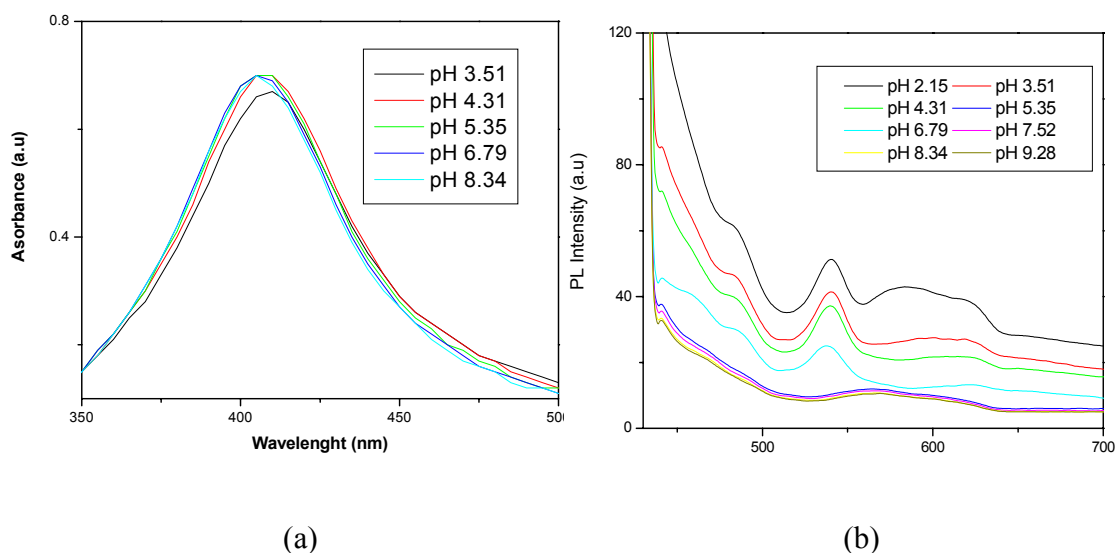
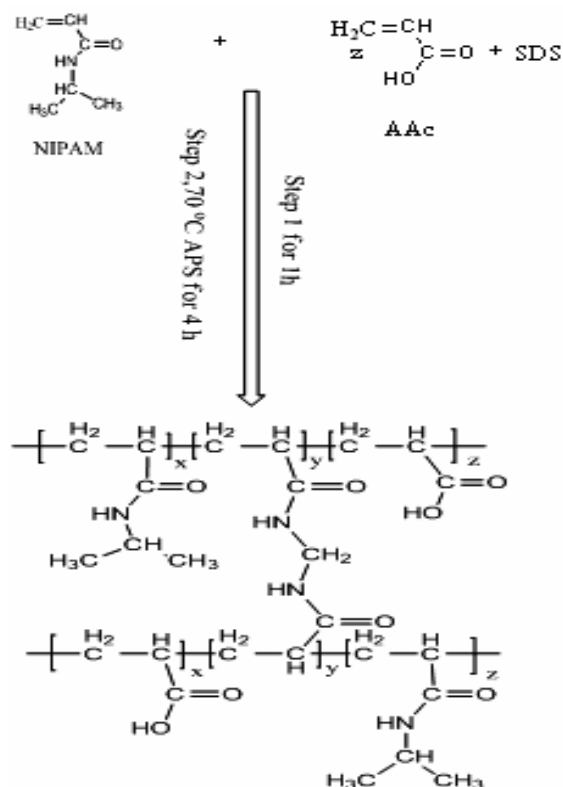


Fig. 7: (a) pH sensitive (a) UV-Vis absorption spectra and (b) photoluminescence spectra of hybrid microgel at 25°C .

Microgels Synthesis

Poly(N-isopropylacrylamide-co-acrylic acid) [poly(NIPAM-co-AA)] was prepared by free-radical microemulsion copolymerization [28]. Microemulsion polymerization was carried out in a three-necked round bottom flask equipped with a stirrer, a reflux condenser and a gas inlet. 1.4 g NIPAM, 0.095 mL AAc, varying amounts of crosslinker BIS 0.0507-0.0861 g and stabilizer SDS (0.057 g) were dissolved in 100 mL deionized water. Ammonium per sulphate (APS) was used as initiator (0.06 g dissolved in 5 mL of aqueous solution). Both the solutions were bubbled in nitrogen atmosphere for an hour. Thereafter the mixture was heated to 70 °C with constant stirring and continuous supply of nitrogen. In the next step initiator was added to start polymerization and reaction was allowed to continue for four hours. The resulting polymer microgel was refined by dialysis followed by centrifugation, decantation and dispersion in 100ml deionized water. The microgel was further purified by dialysis (Molecular porous membrane tubing, cutoff, 12000-14000) for two weeks against very frequently changing deionized water. The chemical reaction for microgels synthesis is shown in scheme-1.



Scheme-1: The chemical reaction for microgels synthesis.

Chemical Reduction Method for Ag NPs Synthesis

Chemical reduction method was used for the synthesis of Ag NPs. Stock solutions of AgNO_3 (0.1mM) and ascorbic acid (100 mM) were prepared separately in volumetric flasks. Initially, 2ml of AgNO_3 (0.1 mM) was added to 198 ml of deionized water. Then 0.0056 g of tri-sodium citrate was added into it and the solution was stirred. After 20 minutes, 2 ml of Sodium Borohydride (0.0303 g/10ml water) solution was added and the stirring was continued for a further duration of 10 minutes. The resulting solution is yellow coloured and is known as silver seed. In the subsequent step, in a separate flask, 2.186 g of CTAB, 2 ml of AgNO_3 (0.1 mM) and 0.5 ml of Ascorbic Acid (0.5 ml) were added into 200 ml of deionized water and allowed to stirrer. After 20 minutes, 15 ml of the already prepared silver seed and 1 ml of 0.01 mM solution of NaOH was also added while stirring. The stirring was continued for 10 minutes. As a result, fully developed Ag NPs were obtained which were centrifuged for 20 minutes at 6000 rpm in order to separate the Ag NPs from the solution.

Hybridization of Microgels

The microgel was hybridized with the Ag NPs. For the hybridization, 1.25 ml of the microgel was added into 23.75 ml deionized water. The solution was stirred for 1 hour in an ice cooled bath. Then centrifuged Ag NPs were added into it and the stirring was further continued for 1 hour. The hybrid microgel was dialysed for an hour in order to remove the uncreative species.

Characterization

The UV-Visible 1601 Shimadzu spectrophotometer with a wavelength range of 190-1100nm was used to confirm the synthesis of Ag-NPs and to study the effect of variation in chemical composition and pH on the hybrid microgel. X-Ray Diffractometer (3040/60 Xpert PRO) was used to ensure the crystalline nature and size of the Ag NPs. For the study of the three dimensional images of Ag NPs and hybrid microgel, Innova atomic force microscope, Model 840-012-711, was employed. The effect of pH on the emission intensity of hybrid microgel was investigated with Perkin elmer LS 55 Fluorometer.

Dynamic laser light scattering (DLS) measurements were performed by means of commercial laser light scattering equipment (Brookhaven) consisting of a BI-200SM motor-driven goniometer and BI-9000AT digital autocorrelator or the BI-9025AT photon counter at scattering angle of 90°. A cylindrical 22 mW uniphase He-Ne laser (wave length 637 nm) with a

pinhole of 100nm and BI-ISTW software was used. Stokes Einstein equation was followed for the calculation of hydrodynamic radius of hybrid microgel particles.

Conclusion

We conclude that by using Chemical Reduction method, the size, shape and optical properties of Ag NPs can be controlled. Ag NPs shows sharp absorption peak at 405 nm due to surface plasmon resonance (SPR) phenomena. Atomic force microscopy (AFM) and X-Ray diffraction (XRD) showed that the particles are highly crystalline and possess face centered cubic (fcc) structure.

The optical properties of Ag NPs can be tuned by changing the concentration of different chemical reagents. Red shift is observed in the surface plasmon resonance (SPR) by increasing the concentration of AgNO₃, NaOH and ascorbic acid which show increase in the size of Ag NPs. Similarly, blue shift is observed by increasing the concentration of Cetyltrimethylammonium bromide (CTAB) and silver seed which show decrease in the particle size.

Polymer microgels are good candidates for the stabilization of metallic nanoparticles. Slight red shift is observed in the SPR peak of Ag NPs inside the microgels as compared to naked Ag NPs because of the interaction among Ag NPs and microgels. This leads to reduction in the size of microgel consequently the nanoparticles come close to each other, and the red shift most probably originates from end to end aggregation of the particles. Dynamic laser light scattering (DLS) results showed decrease in size as well as VPTT of the hybrid microgels with the decrease in pH value. Hybrid microgels show blue shift in the surface plasmon resonance with increase in pH due to swelling of the system.

Photoluminescence (PL) emission intensity of the hybrid microgels is pH dependent and decreases with the increasing swelling of hybrid microgel at higher pH values. The swelling create elastic tension in the bond between Ag NPs and microgel which quenches the emission intensity. These characteristics of the hybrid system make it suitable for applications in optical sensors.

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