

Silver Nanoparticles Fabricated Hybrid Microgels for Optical and Catalytic Study

^{1,2}Luqman Ali Shah, ³Jaweria Ambreen, ⁴Iram Bibi ⁵Murtaza Sayed and ¹Mohammad Siddiq*

¹Department of Chemistry, Quaid-I-Azam University, Islamabad 45320, Pakistan.

²National Centre of Excellence in Physical Chemistry, University of Peshawar, 25120 Pakistan.

³Department of Physics, COMSATS Institute of Information Technology, Islamabad, 45550, Pakistan.

⁴Department of Chemistry, Hazara University, Islamabad 45320, Pakistan.

⁵Department of Chemistry, COMSATS Institute of Information Technology, 22060, Abbottabad, Pakistan.

m_sidiq12@yahoo.com*

(Received on 26th October 2015, accepted in revised form 4th May 2016)

Summary: In this work different compositions of smart poly(N-isopropylacrylamide-vinylacetic acid-acrylamide) poly(NIPAM-VAA-AAm) microgels with different vinyl acetic acid (VAA) contents have been synthesized successfully by conventional free radical emulsion polymerization. Silver metal nanoparticles (NPs) were fabricated inside the microgels network by insitu reduction method using sodium borohydride (NaBH₄) as reducing agent. The confirmation of polymerization and entrapment of metal NPs were carried out by FT-IR spectroscopy. Dynamic laser light scattering (DLS) technique was used for calculating average hydrodynamic diameter of microgel particles. The optical properties of silver NPs were studied by UV-Visible spectroscopy at various conditions of pH and temperature. The hybrid microgels show red shift and increase in intensity of surface plasmon resonance (SPR) band with the increase in temperature and decrease in pH of the medium. The synthesized materials were used as catalysts in the reduction process and it was found that the catalyst composed of high amount of VAA shows enhanced catalytic activity. The apparent rate constant (k_{app}) for catalyst composed of 12% VAA was doubled ($5.6 \times 10^{-3} \text{sec}^{-1}$) as compared to 4% VAA containing catalyst ($2.8 \times 10^{-3} \text{sec}^{-1}$).

Keywords: Free radical emulsion polymerization, in-situ reduction method, responsive polymers, optical properties, catalytic activity.

Introduction

In recent years smart polymers have attracted much interest due to their quick responsive behavior towards environmental factors. The external environmental stimuli that changes the properties of these materials can be classified as temperature, pH [1-3], glucose, enzyme [4, 5], light [6], electric field [7] etc. Smart polymer microgels are the most attractive among varieties of responsive materials because keeping their required behavior offers technical interest for infinite applications in the fields of drug delivery [8, 9], separation [10] and catalysis [11, 12]. These functional materials got a significant interest in the stabilization of metal NPs for optical and catalytic study. The properties of the entrapped NPs can be tuned to their optimum limit by controlling the external conditions. A number of methods have been designed for the fabrication of metal NPs on some supports such as: Rajesh *et al.* [13] used graphene oxide (GO) functionalized with polyamidoamine dendrimers for the stabilization of silver and gold NPs and used these nanocatalysts for the reduction of methyl orange and congo red azo dyes. Yao *et al.* [14] prepared Au@polypyrrole (PPy)/Fe₃O₄ catalysts with Au NPs embedded in PPy/Fe₃O₄ capsule shell. Au NPs were used as a catalyst in the reduction of methylene blue dye with

NaBH₄ as reducing agent. Shi *et al.* [15] synthesized CoMn₂O₄ hierarchiral microspheres catalysts for the reduction of 4-NP to 4-AP. They suggested out that the special morphology of CoMn₂O₄ microspheres and the presence of metal oxide (MO) with d⁷ and d⁵ electronic configurations are favorable to the reduction process. All these catalytic systems show very good results, but the tuning of properties would require the complete synthesis of materials from the start with changing composition. To overcome this problem responsive polymer microgels are suitable carrier for the immobilization of metal NPs. The properties (both optical and catalytic) of the NPs can be controlled by adjusting the environmental conditions. Liu-Sheng Zha *et al.* [16] loaded Ag NPs inside the poly(N-isopropylacrylamide) microgels and studied their temperature controlled catalytic activity. They found that the catalytic activity of hybrid microgels can be tuned in four stages of change in temperature from 20 to 45 °C. Sahiner *et al.* [17] prepared poly(acrylamide-co-vinylsulphonic acid) hydrogels with different mole ratios and used as templet for cobalt and nickle NPs. The hybrid materials were checked for the production of hydrogen in hydrolysis of NaBH₄. In previous study we have synthesized cationic poly(NIPAM-co-VI)

*To whom all correspondence should be addressed.

microgels for loading Ag NPs. The materials were found stable in the entire pH range from 3.0 to 9.3 and used as catalyst for reduction of p-nitrophenol to p-aminophenol [18]. Zhang *et al.*[19] synthesized multiresponsive poly(N-isopropylacrylamide) contain triphenylmethane leucohydroxide microgels for the construction of etalons. The optical properties were investigated by changing the solution pH, temperature, UV/Visible irradiation etc. they observed a red shift in reflectance peaks of etalons by tuning the microgels from swollen to shrunken state. M. Ajmal *et al.* [20] synthesized multiresponsive hybrid microgels for the stabilization of silver NPs. The hybrid materials were used in different amounts and at different temperature conditions as a catalyst for the reduction of 4-NP to 4-AP. They showed that the catalyst was more efficient at 55 °C compared to room temperature.

Silver (Ag) NPs in particular, have received wide attention especially in the field of catalysis and optical sensors. The colloidal Ag NPs are optically active materials, by varying the particle size and shape with some external stimuli allows its surface plasmon resonance (SPR) frequency to be tuned over the UV/Visible range.

In this work we immobilized the silver NPs in the ter-polymer microgel network by insitu reduction method and studied the effect of VAA content on the particle size, their optical behavior towards different pH and temperatures. Importantly, the catalytic properties of the synthesized hybrid microgels are studied in detail.

Experimental

Materials

Thermo-sensitive monomers, N-isopropylacrylamide (NIPAM, ALDRICH) and acrylamide (AAM, ALDRICH) were recrystallized from hexane-toluene (1:1 volume ratio) mixture and dried in a vacuum, pH sensitive moiety, vinyl acetic acid (VAA, ALDRICH) was purified through distillation under reduced pressure. N,N-methylenebisacrylamide (MBA, Alpha Aesar) was used as cross-linking agent without further purification, ammonium persulphate (APS, Scharlau) was used as anionic initiator, sodium dodecyl sulphate (SDS), silver nitrate (AgNO₃), p-nitrophenol and sodium borohydride (NaBH₄) were purchased from ALDRICH and used as received.

Synthesis of poly(NIPAM-VAA-AAM) Microgels

Poly(NIPAM-VAA-AAM) microgel dispersions were prepared by free radical emulsion

polymerization with different compositions of VAA and NIPAM. The amount of materials used for preparation of microgels is given in Table-1. The total number of moles of all the components in each sample was kept at 0.011. The required materials were mixed with 0.057g SDS in 95mL of de-ionized water in a three necked round bottom flask equipped with a condenser, nitrogen inlet and a thermometer. The solution mixtures was continuously stirred and heated at 70°C for one hour with continuous supply of nitrogen gas for the removal of oxygen from the reaction site. After that 5mL initiator APS (0.06M) was added to the mixture to start polymerization reaction. The reaction was carried out for six hours at 70°C with continuous stirring and purging of nitrogen gas. After the completion, microgel dispersions were allowed to cool, purified by centrifugation, decantation, washed with water and dialyzed for one week (Spectra/Por molecular porous membrane tubing, cutoff, 12000-14000) against very frequently pure water at room temperature to remove unreacted monomers, surfactants and other impurities. Finally pure microgels were coded as ML01, ML02 and ML03 and saved.

Table-1: Feed composition of poly(NIPAM-VAA-AAM) terpolymer microgels.

Sample code	Monomer used	Moles percentage	Monomer mass (g)	Total moles of sample	Moles used × 10 ⁴
ML01	NIPAM	87	1.083	0.0110	95.7
	VAA	4	0.0378		4.4
	AAM	4	0.0313		4.4
	BIS	5	0.0847		5.5
ML02	NIPAM	83	1.033	0.0110	90.2
	VAA	8	0.0757		7.7
	AAM	4	0.0313		6.6
	BIS	5	0.0847		5.5
ML03	NIPAM	79	0.983	0.0110	84.7
	VAA	12	0.1136		11.0
	AAM	4	0.0313		8.8
	BIS	5	0.0847		5.5

Synthesis of poly(NIPAM-VAA-AAM)-Ag hybrid microgels

Hybrid microgels with silver nanoparticles (Ag NPs) immobilized inside were synthesized from poly(NIPAM-VAA-AAM) pure microgels. 15mL of prepared microgel was diluted up to 45mL with de-ionized water and stirred for one hour. Then 5mL of 1mM solution of AgNO₃ was added to make the total volume up to 50mL and the solution was stirred continuously for two hours. The sample was then transferred to 100mL of round bottom flask with continuous stirring and purging of nitrogen gas for 30 minutes. After that freshly prepared NaBH₄ solution (0.44g in 5mL of water) was added drop wise, to avoid aggregation of silver nanoparticles to the mixture with continuous stirring at room temperature, color change was observed indicating the formation

of metal nanoparticles from metal ions, reaction was carried out for four hours. The resulting microgels incorporated with Ag NPs were then purified by decantation and dialyzed against frequently changed pure water at room temperature for one hour. Hybrid microgel obtained from ML01 was coded LM01, hybridgel obtained from ML02 was coded LM02 and that obtained from ML03 was coded LM03.

Method for reduction of 4-NP

The reduction of 4-NP was carried out using NaBH_4 as a reducing agent and hybrid microgels as catalysts. 5.4mmol of NaBH_4 and 0.035mmol of 4-NP were dissolved in 80mL of pure deionized water. 2.5mL of the solution was put into quartz cell with 1cm path length. 0.1mL of hybrid microgel was added to the cell and UV-Visible spectra were recorded at regular intervals of time.

Characterization

The FT-IR spectra of dried microgels were recorded with Fourier transform infrared spectrometer in the wavenumber range from 500 to 4000 cm^{-1} . The temperature and pH dependent hydrodynamic diameters were obtained by using DLS experiments in the temperature range from 18 to 55°C and pH range from 2 to 10, with a standard laser light scattering spectrometer (Brookhaven Instruments) at an angle of 90°. He-Ne laser (35mW, 637nm) was used as a light source. All the microgels were passed through Millipore Millex-HV filters with a pore size of 0.45 μm to remove any dust particles before performing measurements. The UV-Visible absorption spectra at varied temperature and pH were taken with Shimadzu 1601 UV-Visible spectrometer.

Results and Discussion

Synthesis and Fourier Transform Infrared (FTIR) study

Free radical emulsion polymerization was used for the synthesis of ter-copolymer poly(NIPAM-VAA-AAm) microgels. At 70°C, persulphate ions ($\text{S}_2\text{O}_8^{2-}$) of initiator (APS) decompose and produce $\text{SO}_4^{\cdot-}$ free radicals which initiate polymerization reaction. The appearance of turbid milky white stable colloidal dispersion after 20 minutes of time indicates the successful synthesis of polymer microgels. The change in dimension of microgel particles produced a change in light scattering which gives white color to the dispersion [21].

FTIR spectroscopy was used to confirm the structure of synthesized polymer microgels and the entrapment of metal nanoparticles (NPs) inside it. The strong peaks in the range of 610-990 cm^{-1} corresponding to stretching mode of vinyl functionality were disappeared in FT-IR spectra of polymer microgels, confirms the polymerization [22]. The peak near 3292 cm^{-1} is the characteristic peak for N-H stretching; the broadness of this peak is due to hydrogen bonding between water molecules and hydrophilic part of polymer chains which confirms gel formation. The peak at 1638 cm^{-1} indicates the presence of carbonyl group of amide. The FT-IR spectra for hybrid microgels were almost same to pure microgels except the peak of amide carbonyl group, which was shifted to higher wavenumber value, this shift is only possible due to interaction of metal NP's with carbonyl group. The FT-IR spectra for ML01 and LM01 are given in Fig. 1.

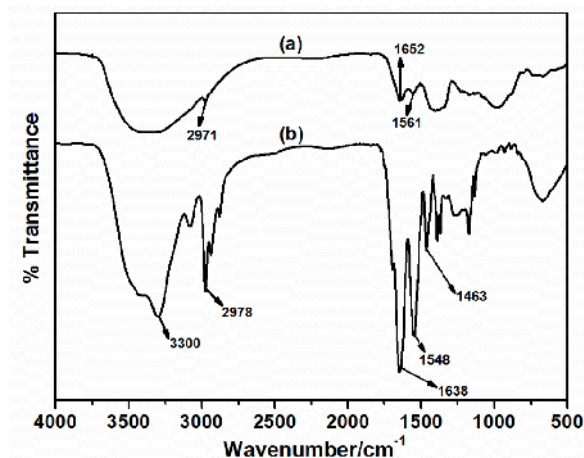


Fig 1: FT-IR spectra for pure (a) ML01 and hybrid (b) LM01 polymer microgels.

Temperature sensitivity of poly(NIPAM-VAA-AAm) terpolymer microgels

The presence of NIPAM moiety in polymer structure introduces the temperature responsive behavior to it. The temperature sensitivity was evaluated at pH 2.84 and 8.54 using DLS by calculating hydrodynamic diameter as a function of temperature at a scattering angle of 90°. The pH adjustment was carried out by using dilute aqueous solutions of hydrochloric acid and sodium hydroxide.

The NIPAM component in the poly(NIPAM-VAA-AAm) microgels network undergoes a volume phase transition from swollen to shrunken (collapsed) state with increasing temperature. The driving force for thermal sensitive

volume phase transition was considered to be a balance between hydrophobic/hydrophilic interactions between network chains and water molecules [23]. The hydrophilicity/hydrophobicity of the pendant groups in the microgels network can be controlled by changing the solution pH [24]. The entropically favored expulsion of water from the polymer network along with hydrophobic and hydrogen bonding interactions between neighboring polymer chains allow the particles to undergo a large-magnitude volume change. This transition is associated with decreasing solvency of water molecules for NIPAM component in the microgels [25].

Fig. 2 shows the temperature induced transition of poly(NIPAM-VAA-AAm) microgels with different VAA content. The pKa value of VAA moiety in poly(NIPAM-VAA-AAm) microgels is 4.3. At low temperature, the degree of H-bonding between solvent (water) molecules and hydrophilic groups of polymer chains is greater, water act as a good solvent and the penetration of water molecules in the polymer network is convenient and size of the particles enhances. The increase in temperature weakens the hydrophilic forces; which expel water molecules from polymer network and produced a reduction in particles size. After collapsing further increase in temperature causes increase in size, this is due to the formation of aggregates by microgel particles. The high temperature at pH 2.84 produced the hydrophobic interactions in polymer network which favor the process of aggregation of the particles [26, 27]. It was found that with the increasing VAA content the size of microgel particles increases but the degree of collapsing decreases, because the addition of VAA produces hydrophobicity in the polymer network. The size of aggregates was totally dependent on the amount of VAA used in the microgels composition, high concentration of VAA will produced larger size of aggregates.

The temperature dependence of average hydrodynamic diameter of poly(NIPAM-VAA-AAm) microgels was also studied at pH 8.54 and results are explored in Fig. 2. At this pH the microgel particles are in swollen state due to the complete ionization of carboxylic groups, which shifted the VPTT to a high value and no phase transition was observed in the studied range (<55 °C). For ML01 a slight reduction in size of the particles occurred, but with the addition of VAA the size becomes almost constant. For ML03, the size of particles was increased slightly at high temperature, this is due to the conversion of amide group of acrylamide (AAm) to carboxyl ions,

which further enhance the repulsions in polymer network and increase its size. Generally, we can say that the temperature effect on microgel particles is almost negligible at pH 8.54.

pH sensitivity of poly(NIPAM-VAA-AAm) terpolymer microgels

pH sensitive behavior of the synthesized terpolymer microgels was evaluated at 20 and 50 °C in terms of change in average hydrodynamic diameter. The pH sensitivity of microgels is consistent to VAA moieties, because it exists in different forms in different pH limits depending on their pKa value. At pH less than the pKa of VAA, the size of microgel particles is small and constant, the increase in pH causes deprotonation of carboxyl groups which results large size for the particles. The pH sensitivity of poly(NIPAM-VAA-AAm) microgels changes environment around the metal particles, which can be employed to elaborate the optical properties of entrapped Ag NPs in microgels network.

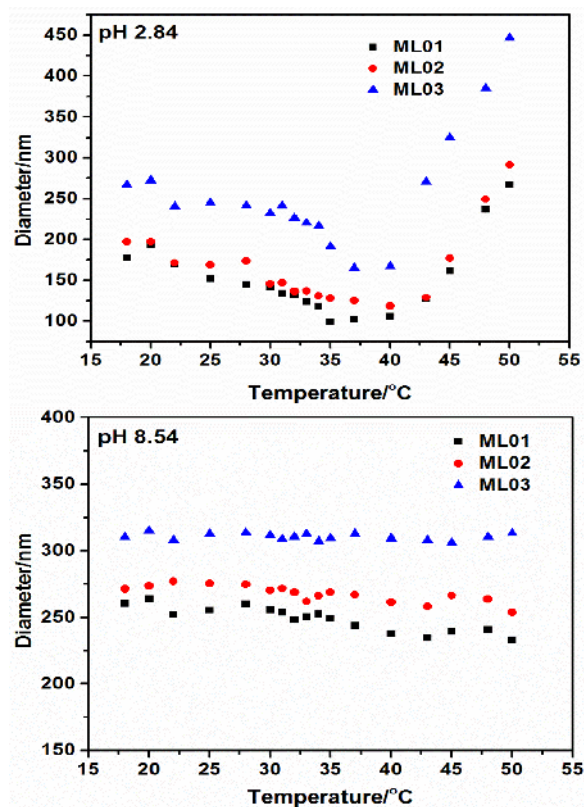


Fig. 2: Temperature effect on average hydrodynamic diameter for poly(NIPAM-VAA-AAm) microgels.

Fig. 3 shows the pH induced volume phase transition of poly(NIPAM-VAA-AAm) polymer microgels at 25 and 50 °C. At 25 °C, a three step transition observed for all the three synthesized microgel samples. First step was associated with pH below the pKa value of VAA i.e <4.3 in which the size of the particles was small, the second step observed at pH~4.3 in which the particles size increased abruptly due to partially deprotonation of carboxyl groups, at pH greater than 6 the carboxyl groups become fully deprotonated and size of the particles increases to maximum value. In our study, all the synthesized samples show three steps pH sensitive volume phase transitions. The size of microgel particles also depend on the amount of VAA used in the composition. The compositions with high amount of VAA enhance the size of particles compared to the compositions having less amount of VAA. However, all the synthesized samples give the same critical transition pH.

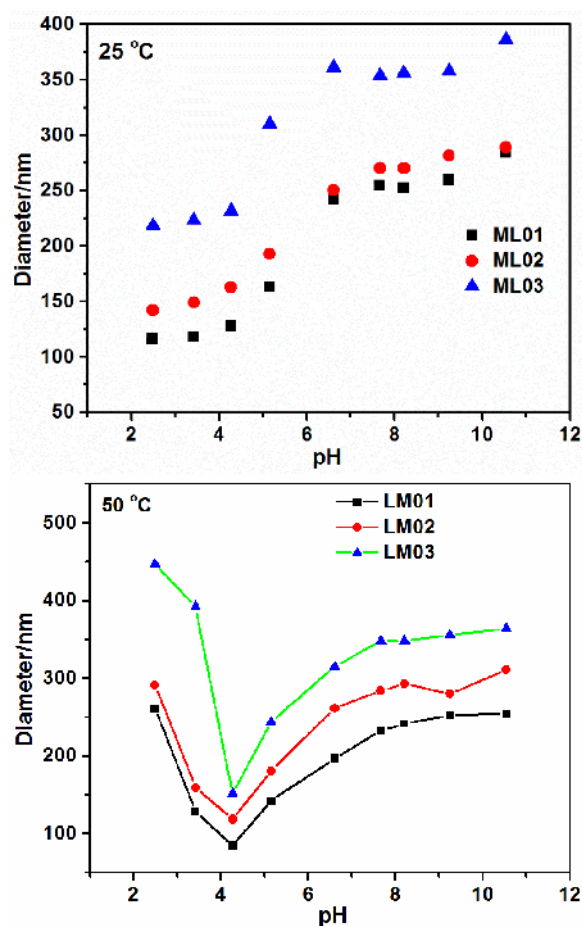


Fig. 3: Temperature effect on average hydrodynamic diameter for poly(NIPAM-VAA-AAm) microgels.

At 50 °C, the increase in pH from 2 to 4.3 produces a reduction in particle size, while increasing from 5 to 10 the particles size enhances again, it shows the reversible behavior of polymer microgels. The reduction in particle size by changing pH from 2 to 4.3 is due to the conversion of aggregates to separate particles, and the increase in particle size by changing pH from 5 to 10 is due to deprotonation of the carboxyl groups. The pH sensitivity of microgels network becomes more significant at high temperature as compared to low temperature. At high temperature the AAm monomers in polymer chains undergo hydrolysis and produced more carboxyl groups which further increase the particles size.

By comparing the size of the particles at 25 and 50 °C at all pH values, it was found that in both acidic and basic mediums the size of particles calculated at 50 °C is larger compared to low temperature, because low pH and high temperature conditions favors the formation of aggregates which carries the size of particle to high value, while basic conditions and high temperature cause the hydrolysis of AAm component of polymer chains into carboxylate groups which further enhances the particle size.

pH-sensitive UV-Visible absorption properties of poly(NIPAM-VAA-AAm)-Ag hybrid microgels

The effect of pH on SPR of hybrid microgels was studied by UV-Visible spectroscopy and the spectra obtained for LM01 are given in Fig. 4. The Ag NPs in the core of hybrid microgels primarily absorb blue light, leaving the red and green light combined to give the dispersions a yellow color.

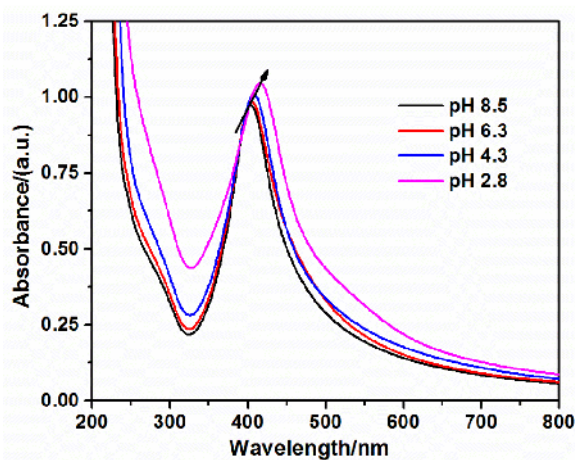


Fig. 4: pH sensitive UV-Visible absorption spectra for LM01.

The swelling and deswelling reversible behavior of polymer microgels with external stimuli produces a change in local refractive index around the NPs which gives a clue to use these smart materials for a number of applications. Ag NPs give a characteristic peak at ~ 400 nm called surface plasmon resonance (SPR) which depends on size and shape of the Ag particles. By entrapping Ag NPs in smart polymer microgels we can easily tune the properties of metal NPs by varying the behavior of smart materials. From Fig. 4 it is clear that by carrying particles from swollen to collapsed state with changing pH, a clear red shift and an increase in absorption intensity of SPR is observed for hybrid microgels. The enhancement of the surface plasmon band is due to two reasons. First one is the increase of refractive index inside the polymer network compared to outside of the particles in collapsed state, which results in an increase of the Rayleigh scattering as predicted by Mie theory [28], because surface polarization is an important factor in determining the intensity of plasmon resonance for metal NPs, it gives very fruitful information about electron oscillation. The second reason is the concentration to volume ratio of the Ag NPs, which increases in the shrunken state. Peak shift occurs due to the coupling of particles, because in shrunken state the Ag particles come close and overlap with each other. The prepared hybrid microgels at low pH were unstable and release the silver nanoparticles within one hour, so the spectra were taken (and should be) quickly after changing the sample pH. However, at high pH these hybrid materials show very good stability for few months.

Temperature sensitive UV-Visible absorption properties of poly(NIPAM-VAA-AAm)-Ag hybrid microgels

Fig. 5 shows the thermo sensitive UV-Visible absorption spectra for LM01 hybrid microgels studied at pH 8.54 and 2.84. At pH 8.54, very little effect on SPR was observed due to the strong repulsive forces inside the polymer network which keep the Ag NPs at a constant distance from each other. At pH 2.84, the increase in temperature produced a red shift and increase in absorption intensity in SPR band due to the transition of polymer microgel from swollen to shrunken state, after VPTT an abnormal increase in absorption band was observed, this indicates the formation of aggregates. These results strongly support the data obtained from DLS analysis. The absorption intensity further depends on the amount of VAA content, the composition having large amount of VAA shows greater absorption intensity because higher the amount of VAA, the greater will be the affinity of

silver ions to diffuse inside the polymer network, and results in an increase in the concentration of Ag NPs in it.

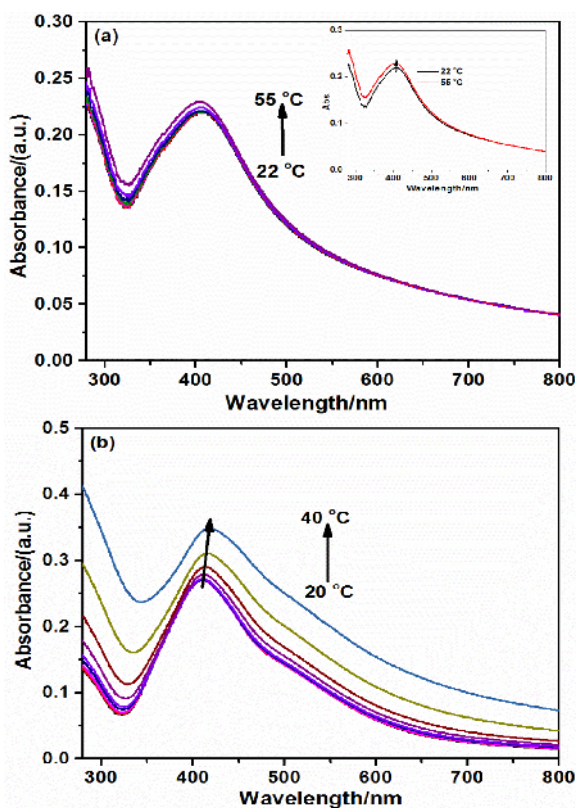


Fig. 5: Temperature sensitive UV-Visible absorption spectra for LM01 at (a) pH 8.54 and (b) 2.84.

Catalytic activity of poly(NIPAM-VAA-AAm)-Ag hybrid microgels

The catalytic activity of poly(NIPAM-VAA-AAm)-Ag hybrid microgels was investigated for the reduction of *p*-nitrophenol (*p*-NP) to *p*-aminophenol (*p*-AP) using NaBH_4 as reducing agent as a model reaction. The pure *p*-NP gives absorption peak at 317 nm and appears light yellow in color, with the addition of NaBH_4 color changed into dark yellow indicating the formation of stable nitrophenolate ion which induced a red shift in absorption peak to 400 nm (shown in inset of Fig. 6(a)). This peak was constant for a long time, and reaction cannot proceed without catalyst. The addition of small amount of catalyst produced gradual reduction in the peak intensity at 400 nm and the appearance of another peak at 300 nm which increased in intensity with the passage of time indicates the formation of *p*-AP. At the end of reaction dark yellow solution was changed into transparent confirms the successful conversion of para-nitrophenolate ion into *p*-AP. The UV-Visible

spectra obtained are given in Fig. 6 (a), (c) and (d) for LM01, LM02 and LM03 respectively.

The reaction follows pseudo first order kinetics because the concentration of NaBH_4 was kept larger compared to p -NP and did not involve in rate of reaction. The apparent rate constant (k_{app}) was calculated for all the three catalysts by plotting $\ln(C_t/C_0)$ against time (C_t is the concentration at any time " t " and C_0 is the initial concentration of p -NP) and the slope of plot gives the k_{app} . In this study it was found that the catalyst composed of high amount of VAA (LM03) shows enhanced catalytic activity

than others (LM01 and LM02). High amount of VAA means more carboxyl groups, which accommodate more silver NPs inside the polymer network and hence enhance the catalytic activity. Also the size of LM03 is large the penetration of reactant molecules inside the reactor is easy and the removal of products from the reactor are quickly. The k_{app} for LM03 ($5.6 \times 10^{-3} \text{sec}^{-1}$) is almost two times compared to LM01 ($2.8 \times 10^{-3} \text{sec}^{-1}$). Fig. 6 (b), (d) and (f) shows the $\ln(C_t/C_0)$ vs time plots for LM01, LM02 and LM03 respectively.

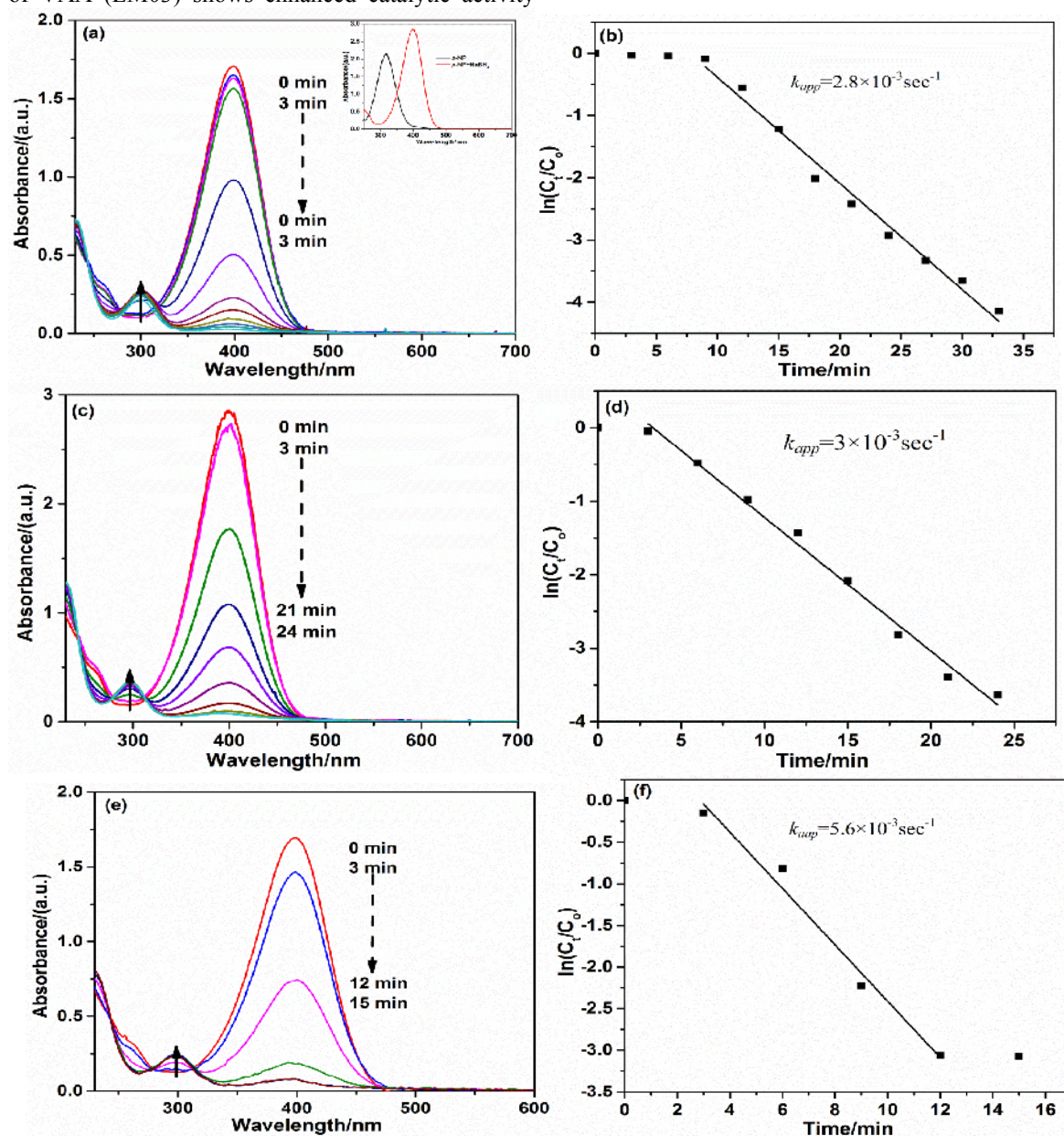


Fig. 6: UV-Vis spectra for the reduction of p -nitrophenol to p -aminophenol by (a) LM01 (c) LM02 and (e) LM03; and plots of $\ln(C_t/C_0)$ vs. time for (b) LM01 (d) LM02 and (f) LM03.

Conclusion

The multiresponsive poly(NIPAM-VAA-AAm) pure and hybrid microgels immobilized by the Ag NPs were successfully prepared by free radical emulsion polymerization. The particles size was found increased with the incremental addition of VAA. UV-visible absorption studied of hybrid microgels showed a clear red shift and increase intensity in SPR band with decreasing pH and increasing temperature of the medium, these smart hybrid microgels with pH and temperature responsive behavior can be used in optical and electronic devices. The hybrid microgels were used as catalyst for the reduction process and the catalyst contains high amount of VAA showed enhanced catalytic activity. This process of synthesis is very convenient and can be applied for large scale production. The catalysts can be recycled by simple centrifugation and used again.

Acknowledgement

Pakistan Higher Education Commission (HEC) is gratefully acknowledged for the financial support.

References

1. R. Pelton, Temperature-Sensitive Aqueous Microgels, *Adv. Colloid. Interfac.*, **85**, 1 (2000).
2. J. Wu, B. Zhou and Z. Hu, Phase Behavior of Thermally Responsive Microgel Colloids, *Phys. Rev. Lett.*, **90**, 048304 (2003).
3. A. Pich, A. Tessier, V. Boyko, Y. Lu and P. H. J. Adler, Synthesis and Characterization of Poly(vinylcaprolactam)-Based Microgels Exhibiting Temperature and pH-Sensitive Properties, *Macromolecules*, **39**, 7701 (2006).
4. R. Yin, K. Wang, S. Du, L. Chen, J. Nie and W. Zhang, Design of Genipin-Crosslinked Microgels from Concanavalin A and Glucosyloxyethyl Acrylated Chitosan for Glucose-Responsive Insulin Delivery, *Carbohydr. Polym.*, **103**, 369 (2014).
5. Z. Gu, T. T. Dang, M. Ma, B. C. Tang, H. Cheng, S. Jiang, Y. Dong, Y. Zhang and D. G. Anderson, Glucose-Responsive Microgels Integrated with Enzyme Nanocapsules for Closed-Loop Insulin Delivery, *ACS nano*, **7**, 6758 (2013).
6. J. Yin, H. Hu, Y. Wu and S. Liu, Thermo-and Light-Regulated Fluorescence Resonance Energy Transfer Processes within Dually Responsive Microgels, *Polym. Chem.*, **2**, 363 (2011).
7. D. R. Snoswell, R. K. Brill and B. Vincent, pH-Responsive Microrods Produced by Electric-Field-Induced Aggregation of Colloidal Particles, *Adv. Mater.*, **19**, 1523 (2007).
8. S. V. Ghugare, P. Mozetic and G. Paradossi, Temperature-Sensitive Poly(vinyl alcohol)/Poly(methacrylate-co-N-isopropyl acrylamide) Microgels for Doxorubicin Delivery, *Biomacromolecules*, **10**, 1589 (2009).
9. D. Teng, J. Hou, X. Zhang, X. Wang, Z. Wang and C. Li, Glucosamine-Carrying Temperature- and pH-Sensitive Microgels: Preparation, Characterization, and in Vitro Drug Release Studies, *J. Colloid Interf. Sci.*, **322**, 333 (2008).
10. H. Nur, M. J. Snowden, V. J. Cornelius, J. C. Mitchell, P. J. Harvey and L. S. Benée, Colloidal Microgel in Removal of Water from Biodiesel, *Colloid. Surface A.*, **335**, 133 (2009).
11. P. Herves, M. Pérez-Lorenzo, L. M. Liz-Marzán, J. Dzubiella, Y. Lu and M. Ballauff, Catalysis by Metallic Nanoparticles in Aqueous Solution: Model Reactions, *Chem. Soc. Rev.*, **41**, 5577 (2012).
12. Y. Lu, S. Proch, M. Schrunner, M. Drechsler, R. Kempe and M. Ballauff, Thermosensitive Core-Shell Microgel as a "Nanoreactor" for Catalytic Active Metal Nanoparticles, *J. Mater. Chem.*, **19**, 3955 (2009).
13. R. Rajesh, S. S. Kumar and R. Venkatesan, Efficient Degradation of Azo Dyes Using Ag and Au Nanoparticles Stabilized on Graphene Oxide Functionalized with PAMAM Dendrimers, *New J. Chem.*, **38**, 1551 (2014).
14. T. Yao, T. Cui, H. Wang, L. Xu, F. Cui and J. Wu, A Simple Way to Prepare Au@ polypyrrole/Fe₃O₄ Hollow Capsules with High Stability and their Application in Catalytic Reduction of Methylene Blue Dye, *Nanoscale*, **6**, 7666 (2014).
15. X. Shi, F. Zheng, N. Yan and Q. Chen, CoMn₂O₄ Hierarchical Microspheres with High Catalytic Activity Towards p-Nitrophenol Reduction, *Dalton Trans.*, **43**, 13865 (2014).
16. Y. Y. Liu, X. Y. Liu, J. M. Yang, D. L. Lin, X. Chen and L. S. Zha, Investigation of Ag Nanoparticles Loading Temperature Responsive Hybrid Microgels and their Temperature Controlled Catalytic Activity, *Colloid. Surface A.*, **393**, 105 (2012).
17. F. Seven and N. Sahiner, Poly (acrylamide-co-vinyl sulfonic acid) p (AAm-co-VSA) hydrogel Templates for Co and Ni Metal Nanoparticle

- Preparation and their Use in Hydrogen Production, *Int. J. Hydrogen Energ.*, **38**, 777 (2013).
18. L. A. Shah, W. Chen, M. Siddiq, J. Hu, A. Dong and D. Yang, Thermal and pH Dual Responsive Copolymer and Silver Nanoparticle Composite for Catalytic Application, *Chinese J. Chem.*, **33**, 467 (2015).
 19. Q. M. Zhang, W. Xu and M. J. Serpe, Optical Devices Constructed from Multiresponsive Microgels, *Angew. Chem. Int. Edit.*, **126**, 4927 (2014).
 20. M. Ajmal, Z. H. Farooqi and M. Siddiq, Silver Nanoparticles Containing Hybrid Polymer Microgels with Tunable Surface Plasmon Resonance and Catalytic Activity, *Korean J. Chem. Eng.*, **30**, 2030 (2013).
 21. J. T. Zhang, X. L. Liu, A. Fahr and K. D. Jandt, A New Strategy to Prepare Temperature-Sensitive poly(N-isopropylacrylamide) Microgels, *Colloid. Polym. Sci.*, **286**, 1209 (2008).
 22. A. Khan, Preparation and Characterization of N-isopropylacrylamide/acrylic Acid Copolymer Core-Shell Microgel Particles, *J. Colloid Interf. Sci.*, **313**, 697 (2007).
 23. S. Zhou and B. Chu, Synthesis and Volume Phase Transition of poly(methacrylic Acid-co-N-isopropylacrylamide) Microgels Particles in Water, *J. Phys. Chem. B.*, **102**, 1364 (1998).
 24. K. Kratz, T. Hellweg and W. Eimer, Influence of Charge Density on the Swelling of Colloidal poly(N-isopropylacrylamide-co-acrylic acid) Microgels, *Colloid. Surface A.*, **170**, 137 (2000).
 25. M. Shibayama, S. Mizutani and S. Nomura, Thermal Properties of Copolymer Gels Containing N-Isopropylacrylamide, *Macromolecules*, **29**, 2019 (1996).
 26. W. Wu, T. Zhou, A. Berliner, P. Banerjee and S. Zhou, Smart Core-Shell Hybrid Nanogels with Ag Nanoparticle Core for Cancer Cell Imaging and Gel Shell for pH-Regulated Drug Delivery, *Chem. Mater.*, **22**, 1966 (2010).
 27. H. Naeem, Z. H. Farooqi, L. A. Shah and M. Siddiq, Synthesis and Characterization of p(NIPAM-AA-AAm) Microgels for Tuning of Optical Properties of Silver Nanoparticles, *J. Polym. Res.*, **19**, 9950 (2012).
 28. P. J. Flory, *Principles of Polymer Chemistry.*, Cornell University Press, London, (1953).