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Synthesis of sensitive hybrid polymer microgels for catalytic reduction of organic pollutants

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ABSTRACT

Multiresponsive tercopolymer microgel poly(*N*-isopropyl acrylamide-*co*-methacrylic acid-*co*-2-hydroxyethyl methacrylate) was synthesized by free radical emulsion polymerization. The silver and gold nanoparticles were homogeneously dispersed in polymer network by in-situ chemical reduction method at 10 and 40 °C using sodium borohydride as reducing agent. FT-IR spectroscopy confirms the microgel synthesis and existing of metal nanoparticles inside the polymer network. Temperature and pH sensitivity on particle size of the microgel particles was investigated by dynamic light scattering. Transmission electron microscopy analysis showed that the size of Ag and Au nanoparticles is 13 and 7 nm, respectively. The catalytic activity of hybrid microgels was studied for the reduction of aqueous solutions of 4-nitrophenol, congo red and methylene blue as model reactions.

1. Introduction

Currently, all over the world, but more specifically in developing countries the control of water pollution is a challenging task for researchers. The major contribution to water pollution is by textile and dyeing industries because of the leaking and discharge of pollutants like organic azo dyes, nitroarenes etc during the utilization and preparation of industrial stuff. Researchers have shown that azo dyes pose serious health issues when come in contact with humans. Therefore new, cheap ways of removing azo dyes and dangerous aromatic species from wastewater is still a challenging task for researcher.

A number of methodologies have been adopted for treatment of waste water containing organic pollutants. These methods include photocatalysis [1,2], adsorption [3], metal nanoparticles (MNPs) catalyzed reduction [4] etc. in all methods used so far, the reduction of azo dyes and nitroarenes to a valuable products in the presence of MNPs is cheap, green and environmental friendly. Organic pollutants can be easily reduced to fruitful products by some reducing agents using MNPs as surface provider. MNPs acquire notable catalytic properties due to their small size and large surface area, however because of their high surface energy as well as vander Waals forces the distinct tendency to aggregate hinders their enhanced catalytic properties. So, the scientists have investigated that anchoring MNPs on some support is a good approach to overcome the far mentioning problem. Therefore, many materials have designed for the stabilization of MNPs such as surfactants [5], solid surface [6], spherical polyelectrolyte brushes [7] hollow capsules [8], dendrimers [9] and polymer hydrogels [10]. Among all mentioned materials, polymer hydrogels gained a significant interest due to their unique properties which include reversible responsive behavior, easy functionalization, quick response time, small size and large surface area. The fabrication of MNPs inside polymer hydrogels produced a composite system, which has interesting perspectives in the development of advanced nanostructured materials for intelligent micro/nano reactors [11], sensors [12], controlled drug release [13], disease diagnosis and catalysis [14]. Zhang et al. [15] stabilized palladium nanoparticles inside the ionic polymer microgels and applied these materials as a catalyst for the hydrogenation of styrene. They found that the catalyst efficiency strongly depends on the size of Pd NPs and 3 nm sized particles were found more active. Cui et al. [8] prepared Au@polypyrrole/Fe_3O_4 hollow capsules for the degradation of methylene blue from waste water. They found that the magnetic properties of the catalysts can be controlled by adjusting the quantity of $FeCl_2.4H_2O$. Sahiner et al. [16,17] used the bulk poly (vinylphosphonic acid) p(VPA) hydrogels as a reactor for metal

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particles. The hydrogels were synthesized by photo polymerization technique using different molar mass of polyethylene glycol as a crosslinker. The prepared composite materials were used as catalyst for the conversion of 4-nitrophenol to 4-aminophenol. Tang et al. [18] synthesized thermo and pH responsive poly(N-isopropylacrylamide-co-2-(dimethylamino)ethyl methacrylate) copolymer hybrid microgels embedded with Ag NPs. The material has good catalytic behavior in the reduction of methylene blue. To the best of our knowledge, all the polymer microgels employed for the stabilization of metal NPs so far composed of mono and di monomeric units and synthesized at room temperature.

Herein, we synthesized ter-copolymer poly(N-isopropylacrylamide-co-methacrylic acid-co-2-hydroxyethyl methacrylic acid) P(NIPAM-MAA-HEMA) microgels for the immobilization of Ag and Au NPs at 10 and 40 °C. The temperature and pH sensitive behavior on the particle size was studied in detail. The hybrid microgels were tested for their catalytic activity towards the reduction of 4-nitrophenol (4-NP), congo red (CR) and methylene blue (MB).

2. Experimental

2.1. Chemicals and materials used

N-Isopropylacrylamide (NIPAM, 98%, TCI) was recrystallized from a mixture of toluene and *n*-hexane (v:v = 1:3). 2-Hydroxyethyl methacralate (HEMA, 98%, TCI) and methacrylic acid (MAA, 99%, Sigma) were purified from inhibitors before used. N,N-methylene bisacrylamide (MBA), Ammonium persulphate (APS), silver nitrate ($AgNO_3$), tetrachloroauric acid ($HAuCl_4$. xH_2O), sodium borohydride ($NaBH_4$) and 4-nitrophenol (4-NP) were purchased from Sigma Aldrich and were used as such, congo red (CR) and methylene blue (MB) dyes were purchased from Merck and used without further purification. Milli Q-grade water was used throughout the experimental work.

2.2. Synthesis of pure microgel

Ter-copolymer, P(NIPAM-MAA-HEMA) was prepared by conventional free radical emulsion polymerization with slight modification compared to previous literature [19]. Typical amount of monomers shown in Table 1 were put in a three necked round bottom flask charged with 84.7 mg MBA, 60 mg SDS and 100 mL of water before, equipped with condenser, thermometer and nitrogen inlet. Inert atmosphere was created by nitrogen purging and heated the reaction mixture upto 70 °C with continuous stirring rate of 500 rpm. APS was added as an anionic initiator for polymerization and reaction was lifted for 6 h. The synthesized milky white colloidal product was cooled to room temperature naturally and then purified by decantation, centrifugation and one week dialysis using Spectra/Por molecular porous membrane, MWCO, 12000-14000. The purified microgel was lyophilized, coded as P01 and stored for further use.

2.3. Synthesis of hybrid microgels

Hybrid microgels composed of silver and gold nanoparticles were prepared from pure microgel at 10 and 40 °C. 13 mg of lyophilized microgel was diluted upto 60 mL by adding pure deionized water and put into two flasks each with 30 mL. The flasks were put in water bath and temperature was maintained at 10 °C. 5 mL of 0.1 mmol $AgNO_3$ solution was added to one flask while the other flask was charged with 5 mL of 0.1 mmol $HAuCl_4.3H_2O$ solution. The reaction mixtures were continuously purged with nitrogen and stirred for 3 h, after that 5 mL freshly prepared $NaBH_4$ solution (0.189 mol) was added dropwise to each flask and lifted the reaction for 4 h. The synthesized hybrid microgels were collected and purified by 2 h dialysis, coded as (P01-Ag10 and P01-Au10) and stored for further use. The same process of synthesis was followed for hybrid microgels synthesized at temperature 40 °C and were coded as P01-Ag40 and P01-Au40.

2.4. Catalytic activity of hybrid microgels

The catalytic activity of P01-Ag's and P01-Au's catalysts, were evaluated for the reduction of 4-NP, CR and MB. Typical amount of each reactant was dissolved in 600 mL of distilled water and every solution was charged with 39.75 mmol of $NaBH_4$ separately. 2.5 mL of the as synthesized solution was transferred into a quartz cell with a path length of 1 cm, followed by adding 0.1 mL of 0.02 mmol/L of the catalyst. The UV–vis spectra were recorded at different time's interval to study the catalytic performance of the catalyst. The colored mixtures changed into colorless solutions indicating the successful reduction of materials.

2.5. Characterization

FT-IR was performed on a NEXUX-470 spectrometer for functional groups determination in synthesized materials. The colloidal particle size interms of average hydrodynamic diameter and Zeta potential values were measured on a Malvern autosizer 4700 instrument. The ultraviolet visible absorption spectra for catalytic reduction of pollutants were obtained from a Perkin Elmer Lambda 750 UV/Vis/NIR spectrometer. Transmission electron microscopy (TEM) images were taken with a 2100 F transmission electron microscope at a voltage of 200 kV. The dilute solution of samples were placed on copper grid which was coated with carbon and dried at room temperature.

3. Results and discussion

3.1. Polymerization and microgel formation

The successful copolymerization of NIPAM, MAA and HEMA, and the existence of metal nanoparticles (MNPs) inside the polymer network were confirmed by FTIR spectroscopy. Fig. 1 shows the FTIR spectra for P01, P01-Ag10 and P01-Au10. The disappearance of strong characteristic peaks for vinyl group in the range of 990–600 cm^{-1} indicates the polymerization, a broad N—H stretching vibration peak at 3300 cm^{-1} shows the hydrogen bonding between water molecules and hydrophilic groups of polymer chains and confirms microgel formation. The peak at 1635 cm^{-1} is due to carbonyl group of amide functionality in FTIR spectrum of P01. The red shift in carbonyl peak occurs in hybrid microgels which indicate the entrapment of metal nanoparticles

Table 1
Feed composition of P(NIPAM-MAA-HEMA) terpolymer microgel particles.

Sample	monomer	moles for monomer × 10^{-3}	total moles used	mass of monomer/g	mole percentage
P01	NIPAM	8.25	0.011	0.93357	75
	MAA	1.65		0.1419	15
	HEMA	0.55		0.0716	5
	MBA	0.55		0.0847	5