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Robust fibrillar nanocatalysts based on silver nanoparticle-entrapped polymeric hydrogels

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ABSTRACT

Robust fibrillar network of hydrogels entrapped with silver nanoparticles were prepared by in situ polymerization of acrylic acid and reduction of silver nitrate using amidodiol as cross-linking cum reducing agent under ambient conditions. Silver nanoparticle-entrapped polyacrylic acid–amidodiol hydrogels (SPAGs) were characterized by UV–visible spectroscopy, SEM, TEM, XRD and rheology. Further, catalytic activities of SPAGs were studied using dyes such as methylene blue, rhodamine 6G and crystal violet. Effects of temperature and pH on the reduction process were studied. The activation energy for the reduction process was calculated and found to be decreased by ~10 kJ/mol in the SPAG-catalysed reaction. In addition, SPAGs showed excellent reusability, easy separation, high rate constant and absence of induction period. All these results suggested SPAGs as a promising catalyst for the reduction of organic molecules.

1. Introduction

In recent years, there has been considerable interest in polymer-dispersed metal nanocomposites, particularly polymeric hydrogel metal nanocomposites which respond to various stimuli in the bulk phase. They were used in responsive artificial muscles, switches, memory devices, catalysis, tissue engineering, etc. [1–5]. Hydrogels are three-dimensional polymeric fibrillar networks which can imbibe large amount of water with stimuli-responsive swelling and de-swelling properties. Covalent and non-covalent interactions such as hydrogen bonding, π–π stacking, and van der Waal's interactions are involved during the organization of these molecules into 3D fibrillar architectures [6–8].

The unique properties of metal nanoparticles are different from their bulk counter parts and they find promising applications in the areas such as nanoelectronic devices, catalysis, sensors, biochemical tagging reagents, optical switches and so forth [9–12]. Among the metal nanoparticles, silver is easily reducible and has high excitation efficiency, surface plasmon resonance energy in the visible region and unique electrical, optical and catalytic properties. They are potential candidates in catalysis because of their high surface area and size and shape-dependent catalytic properties. Silver-catalysed reactions such as Diels Alder reaction, epoxidation, hydrogenation of aldehydes, hydroformylation, carbonylation, reduction of dyes, nitrophenol, etc. have been reported earlier [13–17]. Metal nanoparticles tend to aggregate during the catalytic process due to their van der Waal's forces of attraction and high surface area. A wide range of capping agents such as block copolymers, polysaccharides, latex particles, hydrogels and surfactants have been used to enhance the stability and dispersion of metal nanoparticles [18–20]. Among these stabilizers, polymeric hydrogels with three-dimensional fibrillar networks are receiving importance. The hydrophilic ionic groups present in the hydrogel network can potentially serve as nanoreactors for the synthesis of metal nanoparticles and provide cage effect for its stabilization. Moreover, the fibrillar network can speed up the diffusion of metal ions through the hydrogel networks. Apart from this, the size and shape of metal nanoparticles could be tuned by controlling the amount of monomer, cross-linker and metal ions [21–23].

Polymeric hydrogel metal nanocomposites are viable catalysts because they prevent aggregation of nanoparticles, and the loosely bound dynamic structure will give easy access to the nanoparticles. One of the disadvantages of such systems is their poor mechanical stability. The mechanical and chemical properties of hydrogel can be improved by incorporating inorganic clays, cellulose, carbon nanotubes, etc. [24,25]. Mechanical stability of the hydrogels can be build up by increasing the crosslinking density using rigid rod-like functional molecules as crosslinker. In the present work, we have used amidodiol(1,6-bis(hydroxy butyramido)hexane) as the crosslinking agent which is obtained by the

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aminolysis of γ-butyrolactone with hexamethylene diamine. Amidodiol is endowed with two terminal hydroxyl groups connected through a hexyl linked two amide groups. They are expected to exhibit extensive hydrogen bonding to form intermolecular physical crosslinks with polyacrylic acid. The networks present in the gel may trap silver nanoparticles and also enhance its proximity to reagents. In this context, preparation of robust hydrogel network entrapped with silver nanoparticles with high mechanical stability and catalytic activity is attracting significance. In this paper, we are reporting a novel strategy for the preparation of silver nanoparticle-entrapped robust polymeric hydrogel and demonstrated its efficient catalytic activity for the reduction of dyes. SPAGs were characterized by SEM, TEM, XRD, rheology and UV–visible spectroscopy. Further, efficiency of catalytic activity of these robust hydrogel was studied for the reduction of organic dyes using sodium borohydride as the reducing agent.

2. Experimental

2.1. Materials

Hexamethyelene diamine, rhodamine 6G (Sigma–Aldrich), γ-butyrolactone (Fluka, Germany), isopropanol, acrylic acid, silver nitrate, sodium borohydride, ammonium persulphate (E-Merk, India), methylene blue, crystal violet (Nice Stains, India).

2.2. Preparation of amidodiol(1,6-bis(hydroxy butyramido)hexane)

Amidodiol(1,6-bis(hydroxybutyramido)hexane) was prepared by the aminolysis of γ-butyrolactone using hexamethylene diamine. Typical procedure is as follows: a solution of 0.2 mol (17.2 g) of γ-butyrolactone in 10 mL of isopropanol was taken in a conical flask and cooled in ice bath at 5 °C. A solution of 11.62 g (0.1 mol) of hexamethylene diamine in isopropanol was added dropwise with stirring for 2 h (800 rpm) and kept overnight. Formation of the product was confirmed using TLC in a 7:2:1 benzene, methanol and triethylamine mixture. White crystalline solid formed was filtered and washed several times with isopropanol and then dried in vacuum. Further, it was recrystallized from 150 mL of methanol and acetone mixture. Scheme for the synthesis of amidodiol was shown in the supporting information (Scheme S1).

2.3. Preparation of silver nanocluster-entrapped polyacrylic acid-amidodiol (SPAG)

Acrylic acid (1 mL) and 10% amidodiol (1 mL) in water was mixed with 0.2 mL of 0.02 M silver nitrate. Two drops of 10% ammonium persulphate was added to the mixture. The content was shaken well and kept at room temperature for 10–20 min for gel formation. It was washed several times with distilled water to remove residual monomers and ions. The prepared gel was kept at 70 °C for 12 h to ensure the complete reduction of silver nanoparticles. Experimental details of preparation of SPAGs are given in the supporting information (Table S1). Hydrogel was also prepared in the absence of silver nitrate and is designated as PAG.

2.4. Swelling studies

Definite amount of SPAG hydrogels were accurately dried and transferred into 20 mL of water in a beaker at room temperature for 24 h. Sample was taken out at definite time intervals and the water present on the surface of the swollen hydrogel was removed by soft pressing the sample between the folds of a filter paper before weighing. The uptake of water with respect to time was calculated by periodically weighing the hydrogel. The swelling percentage of SPAGs was calculated using the following equation:

$$S(\%) = \frac{m_t - m_0}{m_0} \times 100$$

Here, m_0 is the initial mass and m_t is the mass of swollen gel at time t.

2.5. Dye reduction studies

Aqueous solutions of cationic dyes such as rhodamine 6G (240 mg/L), methylene blue (160 mg/L) and crystal violet (200 mg/L) were prepared. The dye removal studies were carried out by taking 20 mL of each dye solution, 2 mL of 10 mM sodium borohydride solution and 20 mg of SPAG catalyst. The progress of the reaction was monitored by measuring the periodic decrease in the UV absorbance with small aliquots of solution from the reaction mixture. Effect of silver concentration, pH and temperature on the catalytic reduction was studied.

2.6. Characterization techniques

FT-IR spectroscopic measurements were made with a fully computerized Nicolet Impact 400D FT-IR spectrophotometer. Materials were mixed thoroughly with potassium bromide. All spectra were corrected for the presence of moisture and carbon dioxide in the optical path. The experiments were performed for a scan of 45 times and with a resolution of 4 cm^{-1}. X-ray diffraction studies were done with X-ray diffractometer (Philips X'pert Pro) with Cu Kα radiation ($\lambda \sim 0.154$ nm) employing X'celarator detector and a monochromator at the diffraction beam side. The d-spacing of the nanocomposite was calculated from the angular positions 2θ of the observed d_{001} reflection peaks based on the Bragg's formula $n\lambda = 2d \sin\theta$, where λ is the wavelength of the X-ray beam and θ is the diffraction angle. Averaged 2θ was used with the 2θ resolution of 0.002° from 2° to 70°. For SEM measurements, samples were subjected for thin gold coating using a JEOL JFC-1200 fine coater and the probing side was inserted into JEOL JSM-5600 LV scanning electron microscope. TEM measurements were carried out using FEI (TECNAI G2 30 S-TWIN) with an accelerating voltage of 100 kV. For TEM measurements, the samples were casted on a carbon-coated copper grid and dried in vacuum at room temperature before observation. Optical properties of the gels were studied by absorption spectra in the range 200–700 nm using UV–visible spectrophotometer (Shimadzu model 2100). Rheological measurements of the sample were conducted with Anton Paar Physica MCR 150 rheometer with parallel stainless steel plates of 50 mm diameter, and the gap between parallel plates was set 1 mm.

3. Results and discussion

3.1. Preparation and characterization of silver nanoparticle-entrapped polyacrylic acid-amidodiol hydrogels (SPAGs)

SPAGs were prepared by in situ reduction of Ag^+ ions and polymerization of acrylic acid at room temperature using ammonium per sulphate (APS) as radical initiator and 1,6-bis(hydroxy butyramido)hexane (amidodiol) as reductant cum physical crosslinking agent as shown in Scheme S2. Amidodiol exhibit extensive hydrogen bonding with acrylic acid and increases the crosslinking density and functionality of the hydrogel because of the presence of two terminal hydroxyl groups and two amide groups. The amide group can also interact with metal nanoparticles imparting more stability to the hydrogel nanocomposite. Amidodiol is expected to impart rigidity for the prepared hydrogel and also acting as reducing agent