

Synthesis and characterization of smart acrylamide nanocomposite hydrogel

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Abstract: A poly(acrylamide-co-acrylic acid) [Poly(AAm-co-AAc)] hydrogel was prepared by copolymerising acrylamide (90-100 mol) with acrylic acid (0-10 mol). In this work monomers acrylamide, acrylic acid, N,N'-methylene-bis-acrylamide (cross linker), persulphates (initiator) and N,N,N',N'-tetra methyl ethyl diamine (accelerator) are used to obtain gel at room temperature. Highly stable and uniformly distributed silver nanoparticles have been obtained with hydrogel networks as nanoreactors via in situ reduction of silver nitrate (Ag/TiO₂). The pH value of each solution was obtained by adding either hydrochloric acid or sodium hydroxide. The hydrogels were characterized by using scanning electron microscope (SEM).

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1. Introduction

Hydrogels are three dimensional polymer networks that are highly hydrophilic, yet they are insoluble in water [Tanaka, 1987]. When fully hydrated can contain over 95% water, therefore they are, in effect, parcels of water that can be easily handled.

Hydrogels Intelligent polymers are materials that undergo physical or chemical changes in response to external stimuli, such as stress, temperature or pH. Hydrogels can be formed, that respond to changes in pH by incorporating pH-responsive polymers as pendant groups that can accept or donate protons in response to pH changes [Qiu & Park, 2001].

PH-responsive polymers are polyelectrolytes and have pendant acidic (carboxyl) or basic (amine) groups that ionize just like acid or base groups on monoacids or monobases [McGann, 2009].

The apparent dissociation constant (K_a) for the polyelectrolytes is different from the corresponding monoacids or monobases due to the electrostatic effects from neighboring ionized groups [Qiu & Park, 2001]

Hydrogels sensitive to pH respond to a pH close to the pK_a of the hydrogel [Brondsted & Kopecek, 1992]. The PAAm hydrogel contains amide (-CONH₂) functional groups. The amide functional groups are considered neutral; however, when the gel is placed into a NaOH solution, it swells. In the NaOH solution some of the side chains undergo an alkaline hydrolysis reaction, which converts the amide groups into carboxylic acid (-COOH) groups [Tanaka, 1981].

In the basic solution the carboxylic acid pendant chains ionize to form the carboxylate ion (-COO⁻). These negatively charged groups repel each other which generate electrostatic repulsion forces.

These forces cause the polymer chains to be forced away from each other, allowing more water to enter the gel resulting in the hydration of the polymer chains. Once the carboxylate ions are formed an influx of counterions occurs inside the gel to diminish the net negative charges inside the hydrogel causing the concentration of ions to be higher inside the hydrogel than in the surrounding solution. This causes a difference in osmotic pressure and results in a flux of water into the hydrogel resulting in the swelling of the hydrogel.

2. Materials and Methods

2.1. Preparation of P(AAm-co-AAc) hydrogel and P(AAm-co-AAc) hydrogels-silver nanocomposites.

P(AAm-co-AAc) hydrogel composed of PAAm and PAAc were prepared by free radical solution polymerization in the presence of a Acrylamide and acrylic acid monomers (AM, AA) and N, N'-methylene-bis-acrylamide(MBA, cross linker) and N,N,N',N'-tetra methylethyl diamine (TEMED, accelerator), Potassium persulphates (KPS, initiator). Feed composition is given in Table 1. The total monomer concentration was kept at 4.0 M in each solution.

To prepare P(PAAm-co-AAc) hydrogels-silver nanocomposites, accurately weighed dry P(PAAm-co-AAc) hydrogels were equilibrated with water for 3 days and these P(PAAm-co-AAc) hydrogels were transferred to another beaker containing 10 ml of 5 mM Ag/TiO₂ aqueous solutions, allowed to equilibrate for 1 day. Here, most of the silver ions are exchanged from solution into hydrogel networks by anchoring through -COOH, -CONH₂, -OH groups of hydrogel chains and rest of metal ions were occupied in free-network spaces of hydrogels.

Table 1, feeds composition of P(PAAm-co-AAc) hydrogel

| Polymer | AM (mol/L) | AA (mol/L) | MBA (mol/L) | TEMED (V/V) |
|-------------------------|---------------|---------------|----------------|----------------|
| PAAm | 4 | - | 0.4 | 0.2 |
| Poly(AM-co-5 mol% AA) | 3.8 | 0.2 | 0.4 | 0.2 |
| Poly(AM-co-10 mol % AA) | 3.6 | 0.4 | 0.4 | 0.2 |

2.2. Swelling studies

P(PAAm-co-AAc) hydrogel and P(PAAm-co-AAc) hydrogels-silver nanocomposites disks were soaked in solutions of differing pH at room temperature for 24 h. The pH value of each solution was obtained by adding either hydrochloric acid or sodium hydroxide. After the hydrogel disks had equilibrated in each solution the degree of swelling was measured by equilibrated weighing each disk. The swelling ratio (Q) of the gels was calculated from equation: $Q = W_e/W_d$, where W_e is the weight of water in the swollen hydrogel and W_d is the dry weight of the pure hydrogel.

3. Results and Discussion

In this study, we have developed smaller size and finer distribution of silver nanoparticles in P (PAAm-co-AAc) hydrogel networks composed of poly(acrylamide) with acrylic acid polymeric chains. The advanced feature of this methodology is that the nanoparticles simply prepared at room temperature in presence of green stabilizers. In these experiments, the P(PAAm-co-

AAc) hydrogels were allowed to swell in the Ag/TiO₂ solutions and reduced, throughout the gel networks. the PAAm cross-linked networks act as reservoir for metal ions uptake and the ions are anchored through carboxylic, amide, and hydroxyl groups of carbohydrate polymers and thereby holds large amounts of metal ions in their network and facilitate the reducing process as well as helps in stabilization. The carbohydrate polymers in hydrogel networks arrest the agglomeration of silver nano particles. The concept of silver nanoparticles synthesis in P(PAAm-co-AAc) hydrogel networks is schematically presented in Fig 1. It is quite interesting to point out that silver nanoparticle are formed exclusively inside the hydrogel networks and no particles formation is observed in the surrounding medium, that strictly confirm that hydrogel networks are binding to the silver ions as well as storing the nanoparticles without releasing into the media. The basic feature of hydrogel is that it can absorb and hold huge amount of water/solvent in its network structures and release over a period of time (usually from weeks to months). This special property is very important to load the metal ions and formation of metal nanoparticles from reduction reaction. Fig. 2 Shoes the effect of pH on the equilibrium swelling ratio of the P(AAm-co-AAc) and P(AAm-co-AAc)-Ag nanocomposite.

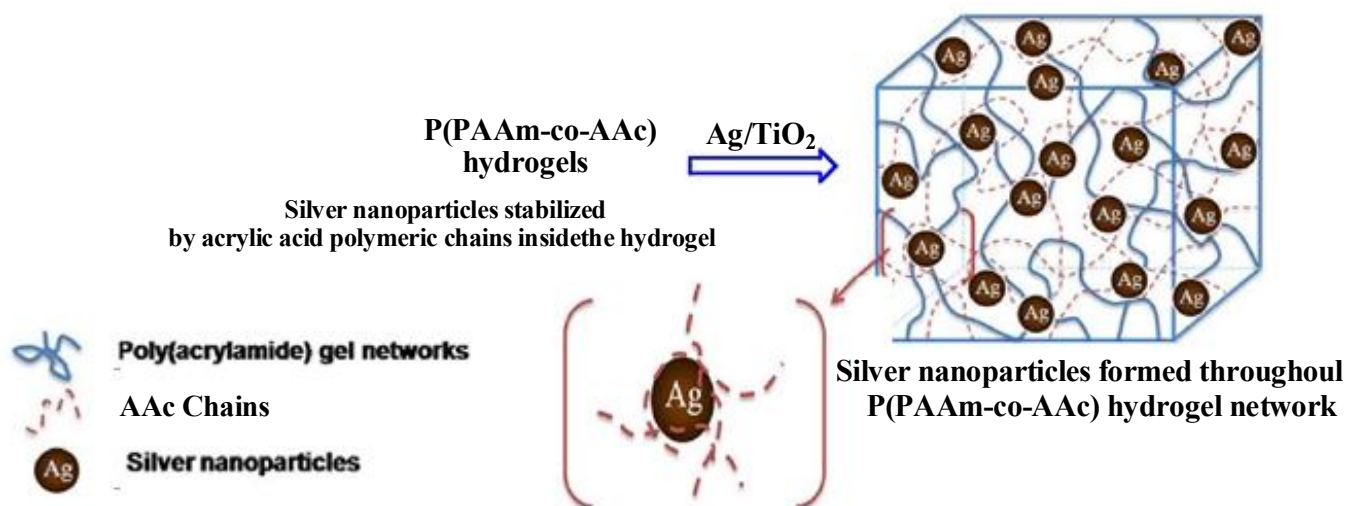


Fig 1. Synthesis of silver nanoparticles throughout P(AAm-co-AAc) hydrogel networks

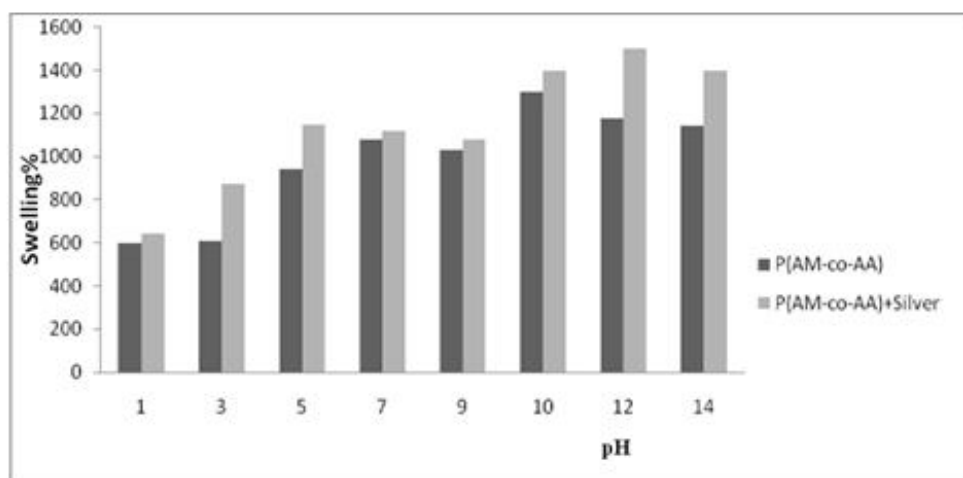


Fig. 2. Effect of pH on the equilibrium swelling ratio of the P(AAm-co-AAc) and P(AAm-co-AAc)-Ag nanocomposite

The finer details of the particles and their morphology were investigated by scanning electron microscopy (SEM). The micrograph (Fig. 3.) exhibited an average silver nanoparticle diameter between 50-70 nm.

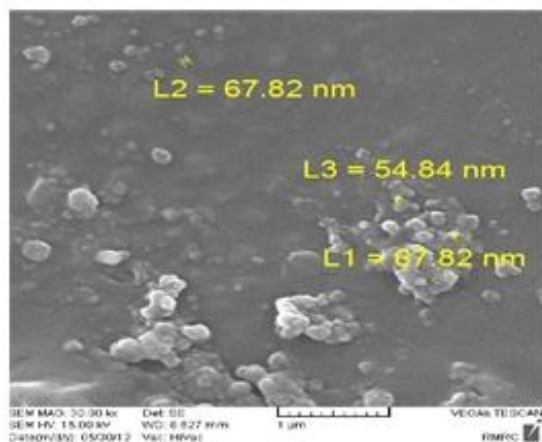


Fig. 3. SEM image of the P(AAm-co-AAc)-Ag/TiO₂

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