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Preparation of a novel pH-responsive silver nanoparticle/poly (HEMA–PEGMA–MAA) composite hydrogel

Yuanqing Xiang [a,b], Dajun Chen [a,*]

[a] College of Materials Science and Engineering, State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 200051, China
[b] Shanghai Gaoqiao BASF Dispersion Co. Ltd., Shanghai 200137, China

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Abstract

In this paper, series of novel pH-responsive silver (Ag) nanoparticle/poly(2-hydroxyethyl methacrylate (HEMA)–poly(ethylene glycol) methyl ether methacrylate (PEGMA)–methacrylic acid (MAA)) composite hydrogel were successfully prepared by in situ reducing Ag^+ ions anchored in the hydrogel by the deprotonized carboxyl acid groups. X-ray diffraction (XRD), UV–vis spectrophotometry, transmission electron microscopy (TEM) and electric conductivity tests were used to characterize the composite system. It was found that the size and morphology of the reduced Ag nanoparticles in the composite hydrogels could be changed by loading the Ag^+ ions at various swelling ratios of hydrogel. Moreover, compared to the pure poly(HEMA–PEGMA–MAA) hydrogel, not only did the Ag nanoparticle/poly(HEMA–PEGMA–MAA) composite hydrogels exhibit much higher swelling ratio and faster deswelling rate, but also higher pH switchable electrical properties upon controlling the interparticle distance under pH stimulus. The pH responsive nanocomposite hydrogel reported here might be a potentially smart material in the range of applications including electronics, biosensors and drug-delivery devices.

Keywords: Silver nanoparticles; Nanocomposite hydrogel; Electrical conductivity; Swelling; Deswelling

1. Introduction

In the past decades, metal nanoparticles have been extensively investigated for their unique properties and for providing important building blocks for the construction of functional structures [1]. Incorporating them into polymeric matrices has been proved to be an effective method to enhance the functions of the polymeric materials [2]. These metal nanoparticle/polymer nanocomposite materials exhibited novel combination properties of metal nanoparticles and polymers that were attractive for the potential applications in catalysis, optics, electronics, sensor and biomedicine [3]. It is well known that stimuli responsive hydrogels is a perspective functional materials and has attracted considerable attention in the recent research for their potential

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[*] Corresponding author. Tel.: +86 21 62373727; fax: +86 21 62193062.
E-mail addresses: xiangyq@sgbd.com.cn (Y. Xiang), cdj@dhu.edu.cn (D. Chen).

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applications in the biomedical and biotechnological field [4–6]. Silver (Ag) is an important commercially available metal and its nanoparticles are superior to other nanosized metal particles for their excellent electrical conductivity [7], antimicrobical effects [8] and optical properties [9]. Therefore, the combination of Ag nanoparticles and pH sensitive hydrogel is expected to constitute a new functional composite with properties of both hydrogel and Ag nanoparticles, such as pH responsive and electrical properties.

Currently, several successful methods have been carried out to obtain functional metal nanoparticle/hydrogel nanocomposites. For example, Willner's group [10,11] prepared gold nanoparticle/poly(*N*-isopropylacrylamide) (PNIPA) composite hydrogels with electrochemical properties by physically incorporating the pre-made gold nanoparticle into PNIPA matrix. A similar method was adopted by Mbhele [12] in the preparation of Ag/polyvinyl alcohol (PVA) composite with optical properties. Sershenl et al. [13–16] developed an alternative method based on that physical combination. They mixed the pre-made nanoparticles physically with various hydrogel precursors followed by gelation and obtained metal nanoparticle/hydrogel composites.

However, the homogeneous dispersion of metal nanoparticles in these hydrogels is a key challenge due to the easy agglomeration of nanoparticles and the high viscosity of hydrogels [17]. Recently, several approaches have been reported to obtain composites with well-fined size and morphology of the metal nanoparticles [18–20]. A more effective approach reported by Wang et al. [21–23] is the in situ reduction of metal ions in the hydrogel. In this method, the metal ions were anchored in the hydrogel network by the functional groups of the hydrogels before in situ reduction. It can effectively inhibit the aggregation of the metal particles. This method requires the particular modification of the hydrogel with functional groups capable of interacting with the metal precursor ions. In most cases, those functional groups, such as thiol, pyridyl and amine, are not environmentally friendly.

In this work, the deprotonized carboxylic acid groups (COO^-) of the pH responsive hydrogel were used directly as the anchoring reagent of the silver (Ag) ions. Novel pH-responsive Ag nanoparticle/poly(HEMA–PEGMA–MAA) composite hydrogels were successfully prepared by in situ reducing the anchored Ag^+ ions. The structure and properties of the nanocomposite hydrogel were characterized by X-ray diffraction (XRD), UV–vis spectrophotometer, transmission electron microscopy (TEM) and electric conductivity meter.

2. Experimental

2.1. Materials

2-Hydroxyethyl methacrylate (HEMA, TCI Chemical Co. Tokyo, Japan) and methacrylic acid (MAA, Shanghai Experiment reagent Co., Ltd., China) were purified by vacuum-distillation and stored at −5 °C before used. *N*,*N*′-Methylenebisacrylamide (MBA, SIGMA Chemical Co., St. Louis, MO) and poly(ethylene glycol) methyl ether methacrylate (PEGMA with mean polymerization degree of 21, Aldrich.) were used as received. Ammonium persulfate (APS), *N*,*N*,*N*′,*N*′-tetramethylenediamine (TEMED), $AgNO_3$ and $NaBH_4$ were of analytical grade and used as received.

2.2. Preparation of the poly(HEMA–PEGMA–MAA) (PHPM) hydrogel

The PHPM hydrogel was prepared by free radical polymerization in deionzed water/methanol solution. Before polymerization, the monomers of HEMA, PEGMA, MAA and the cross-linker MBA were added into the deionized water/methanol solution under stirring, sequentially. And then, nitrogen was used to remove the dissolved oxygen from the reaction solution. To initiate the polymerization, 50 μl APS solution (5 wt% in deionized water) and 30 μl TEMED were added into the reactive system as an initiator and accelerator, respectively. Then the reactive solution was poured into a glass mould quickly. The polymerization was carried out at 45 °C for 15 h. When the reaction completed, the hydrogel was cut into the pieces with the same size and immersed in repeatedly changed deionized water for 72 h to remove any residual monomer. For comparison, poly(HEMA–PEGMA) (PHP) hydrogel was also prepared using the same method.

2.3. Preparation of the Ag nanoparticle/PHPM nanocomposite hydrogels

In order to prepare the nanocomposite hydrogel, the same PHPM hydrogel samples were allowed to swell to the desired swelling ratio (SR = 1, 4, 10 and 20, respectively) in the $H_3BO_3/CaCl_2$ buffer solution (pH 8). And then, PHPM hydrogel samples with desired swelling ratio were immersed in aqueous 0.01 mol/l $AgNO_3$ for 10 h, so that a 1:1 mol/mol COOH/Ag^+ ratio was achieved. The gel samples then were immersed in 0.02 mol/l $NaBH_4$ aqueous solution after removing the surface excess $AgNO_3$ solution with filter paper. The reduction of Ag^+ salt into Ag nanoparticles was carried out at room temperature for 2 h. The prepared nanocomposite hydrogels were washed in deionized water for at least 2 days. The PHPM1, PHPM4, PHPM10 and PHPM20 corresponded to the PHPM nanocomposite hydrogel embedded Ag nanoparticles prepared by reducing the Ag^+ ions loaded at swelling ratio of 1, 4, 10 and 20, respectively.

2.4. Characterization of Ag nanoparticle/PHPM nanocomposite hydrogels

2.4.1. FTIR spectrometry

The characteristic functional groups of the PHPM hydrogel and Ag^+ ion-PHPM hydrogel complexes were analyzed by attenuated total reflection-Fourier transform infrared spectrometer (ATR-FTIR, Nicolet Impact NEXUS-670). The infrared spectra of the Ag nanoparticle/PHPM20 nanocomposite hydrogels were recorded by Nicolet Impact NEXUS-670 Fourier transform infrared spectrometer (FTIR). The dried sample was grounded with dried potassium bromide (KBr) powder and compressed into a disc, and then was subjected to analysis.

2.4.2. UV–vis spectrometry

Ag nanoparticle/PHPM nanocomposite hydrogels were allowed to swell in deionized water, and then were placed on the cell of 1 cm path length quartz cuvette, with the incident light beam being perpendicular to the radial direction of the samples. The cuvette was then filled with deionized water. UV–vis spectra were obtained using the PE Lambda35 spectrometer over the 200–700 nm range with 1 nm resolution and background correction using deionized water.

2.4.3. X-ray diffraction (XRD)

XRD patterns of the Ag nanoparticle/PHPM nanocomposite hydrogel was measured using Rigaku DMAX-2000 X-ray diffractometer with the Cu Kα radiation ($\lambda = 1.54056$ Å) at a scanning rate of $2^\circ\ s^{-1}$ in 2θ ranging from 30° to 90°. The sample for XRD was supported on glass substrates.

2.4.4. Transmission electron microscopy (TEM)

TEM observation was carried out using Hitachi H-800 transmission electron microscopy. Before measurement, the air-dry samples were further dried in the vacuum oven at 65 °C for 2 h. The samples for observation were cut into ultrathin pieces (Ultracut E, Reichert-Jung Co.).

2.4.5. Electrical conductivity measurements

The electrical conductivity measurements of the nanocomposite were done using hydrogel-modified electrodes, as prepared in the literature [19]. The electrical conductivity was recorded on the DDS-11A electric conductivity meter, Fangzhou Inc., Chengdu, China.

2.4.6. Swelling measurements

Swelling measurements were preformed at 25 °C by immersing dried Ag nanoparticle/PHPM nanocomposite hydrogels in the $H_3BO_3/CaCl_2$ buffer solution (pH 8). The weights of swollen hydrogels were measured at different time after removing the surface water with filter paper. Swelling ratio (SR) is calculated as follows: $SR = (W_s - W_d)/W_d$, where W_s is the weight of the swollen hydrogel at a given time during swelling and W_d is the weight of dry hydrogel.

2.4.7. Deswelling kinetics analysis

The deswelling kinetics of Ag nanoparticle/PHPM nanocomposite hydrogels were measured gravimetrically at 25 °C. The nanocomposite hydrogels (same initial size) were allowed to swell to the same equilibrium swelling ratio in the $H_3BO_3/CaCl_2$ buffer solution (pH 8) at 25 °C before the deswelling measurement. Then, the swollen nanocomposite hydrogels were transferred into the H_3PO_4/Na_2HPO_4 buffer solution (pH 2) and measured their weight at different time during collapse of the hydrogels. Water retention (WR) is calculated as follows: $WR = W_t/W_s$, where W_t is the weight of the nanocomposite hydrogel at a given time during deswelling. W_s is the weight of swollen nanocomposite hydrogel.

3. Results and discussion

To obtain smaller sizes and finer distribution of metal nanoparticles, the interaction of the hydrogel matrix with the metal precursor and the resulting metal colloid is important [23,24]. In this experiment, the same PHPM hydrogel samples were allowed to swell in the $H_3BO_3/CaCl_2$ buffer solution (pH 8), deprotonizing of carboxylic acid (COOH) groups, because carboxylate anion (COO^-) groups can bind Ag^+ ions more tightly than COOH groups by complexation [25,26]. Then, the Ag^+ ions were loaded into gel network at various swelling ratios of the PHPM hydrogel to modulate the formation of Ag nanoparticles after the addition of a reducing reagent $NaBH_4$. Fig. 1 shows the ATR-FTIR spectra of the PHPM hydrogel and Ag^+ ions-PHPM20 hydrogel. It can be seen that the asymmetric stretching band of COOH occurs at the 1660 cm^{-1} in the ATR-FTIR spectrum of PHPM hydrogel, while it shifts to low wavenumber 1600 cm^{-1} and a new weaken peak 1570 cm^{-1} occurs in the ATR-FTIR spectrum of Ag ions-PHPM20 hydrogel. It indicated that complexation took place between the COO^- groups and Ag^+ ions [27]. Fig. 2 shows the FTIR spectra of PHPM hydrogel and Ag nanoparticle/PHPM20 composite hydrogel. It is found that the characteristic absorptions of PHPM hydrogel and Ag nanoparticle/PHPM20 composite hydrogels are quite similar except for the absorption bands at 3600 cm^{-1}, corresponding the –OH stretching. The disappearance of the –OH stretching peak implies that the interaction also exists between the reduced Ag nanoparticles and COO^- groups.

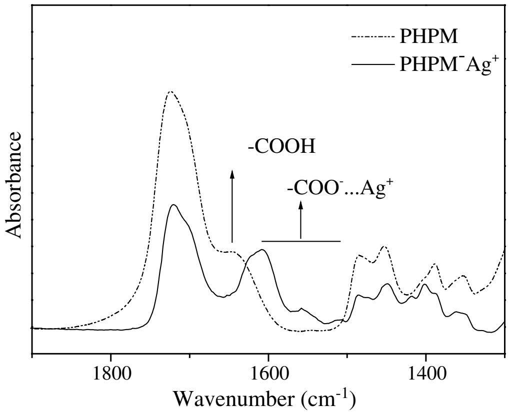

Fig. 1. ATR-FTIR spectra of the PHPM hydrogel and Ag^+ ions-PHPM20 hydrogel.

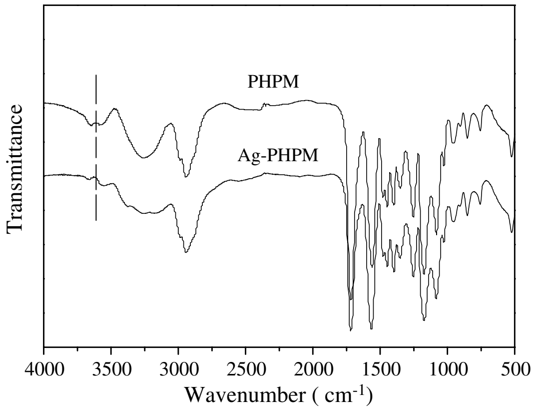

Fig. 2. FTIR spectra of the PHPM hydrogel and Ag nanoparticle/PHPM20 composite hydrogel.

Fig. 3 shows a typical X-ray diffraction (XRD) pattern of Ag nanoparticle/PHPM20 composite hydrogel. It can be observed that sharp diffraction peaks occur, which corresponds to the face-centered cubic structure of metallic Ag. It indicated that high crystalline silver nanoparticles formed in the nanocomposite hydrogel [28].

Fig. 4 shows the UV–vis absorbance spectra of Ag nanoparticle/PHPM composite hydrogels

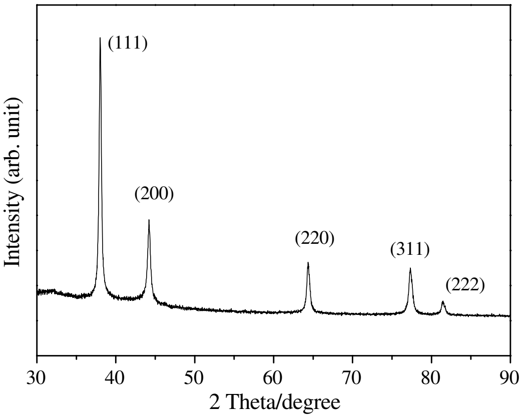

Fig. 3. XRD pattern of the Ag nanoparticle/PHPM20 composite hydrogel prepared by in situ reducing Ag^+ ions loaded at equilibrium swelling ratio of hydrogel (SR = 20).

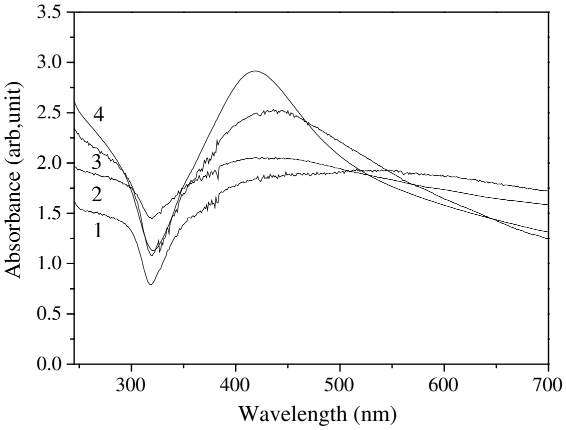

Fig. 4. UV spectra of the Ag nanoparticle/PHPM composite hydrogel prepared by in situ reducing Ag^+ ions loaded at various swelling ratios of hydrogel (1) SR = 1; (2) SR = 4; (3) SR = 10; (4) SR = 20.

prepared by in situ reducing Ag^+ ions, which were loaded at various swelling ratios of hydrogel. It can be seen that the UV–vis spectra of nanocomposite hydrogels exhibit some differences due to that Ag^+ ions were loaded at different swelling ratios of hydrogel before reduction. In the curve of sample 4 that was prepared by in situ reducing Ag^+ ions loaded at equilibrium swelling ratio of 20, a peak is observed at around 425 nm. It corresponds to the characteristic of the surface-plasmon of the silver nanoparticles [29,30]. The UV–vis spectrum of sample 3 that was prepared by reducing Ag^+ ions loaded at swelling ratio of 10 shows that the absorption of the peak decreases and the position of the peak red-shifts (430 nm). Moreover, a shoulder shifted to higher wavelengths is also seen in the curve. This spectral trend continues with the loaded swelling ratio of Ag^+ ions further deceasing (sample 2 and 1). Jiang et al. [28,31] reported that the observed red-shift of the peak is attributed to the aggregation of Ag nanoparticles. Therefore, the red shifting of peaks observed in this work can be also rationalized by being due to particle formation by aggregating and growing in the nanocomposite hydrogels with the loaded swelling ratio of Ag^+ ions decreasing before reduction. This result indicates that the different loading conditions of Ag^+ ions before reduction have important effect on the morphology of the reduced Ag nanoparticles.

Fig. 5 shows the TEM micrographs of the Ag nanoparticle/PHPM composite hydrogels prepared by in situ reducing Ag^+ ions loaded at various swelling ratios of hydrogel. It is clear that the Ag particles exhibit obvious difference in size and morphology, due to Ag^+ ions were loaded at different swelling ratios of hydrogel before reduction. The Ag particles were small, regular and well discrete in the nanocomposite hydrogel when Ag^+ ions were loaded at the equilibrium swelling ratio of hydrogel (SR = 20) (Fig. 5a), while the Ag particles were large, of irregular aggregated morphology in the nanocomposite hydrogel when Ag^+ ions were loaded at lower

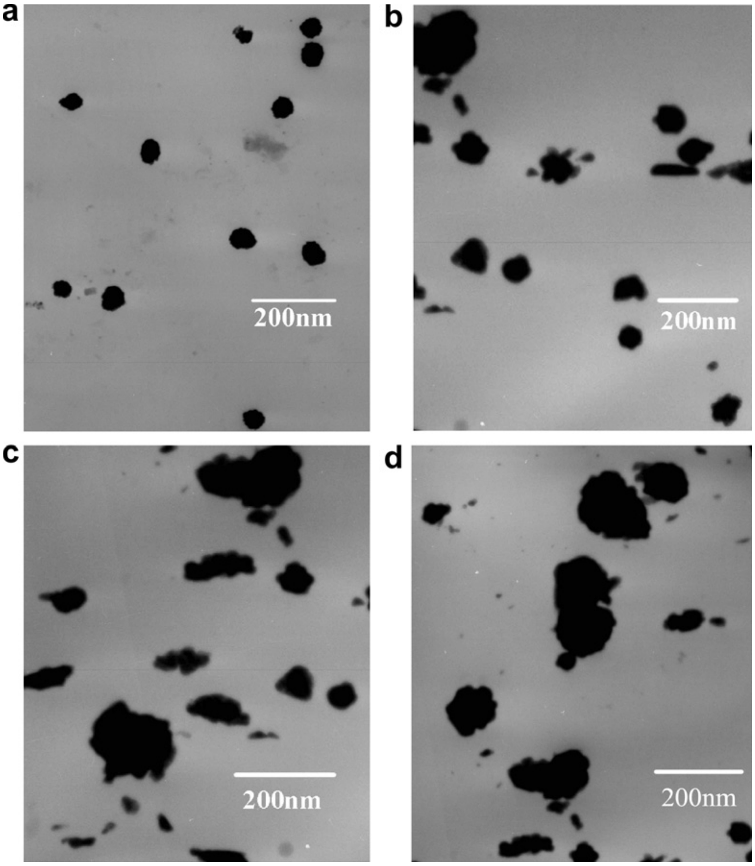

Fig. 5. TEM micrographs of the Ag nanoparticle/PHPM composite hydrogel prepared by in situ reducing Ag^+ ions loaded at various swelling ratios of hydrogel: (a) SR = 20; (b) SR = 10; (c) SR = 4; (d) SR = 1.

swelling ratios (Fig. 5d). When the loaded swelling ratio of Ag^+ ions is intermediate, the large aggregated Ag particles coexist with small, regular separated particles in PHPM nanocomposite hydrogels (Fig. 5b and c). The change trend of the size and the morphology of the reduced Ag nanoparticles with the loaded swelling ratio of Ag^+ ions changing are quite consistent with the result of the UV spectrometer analysis. It suggests that the size and morphology of the Ag nanoparticles in namocomposite hydrogels can be adjusted by loading Ag^+ ions at various swelling ratios of the PHPM hydrogel. In order to illustrate the importance of COOH groups in the PHPM hydrogel, the corresponding non-containing COOH groups PHP hydrogel was synthesized for Ag/PHP composite preparation purposes. Fig. 6 shows the TEM micrographs of the Ag/PHP and Ag/PHPM composite hydrogel prepared by in situ reducing Ag^+ ions loaded at the same swelling ratio of 10. It is clear that the Ag particles are large and irregular aggregated morphology in the Ag/PHP nanocomposite hydrogel, which is different from that in the Ag/PHPM nanocomposite hydrogel. This result confirms that the size and morphology of Ag nanoparticles in the Ag nanoparticle/PHPM nanocomposite hydrogel can be modulated upon the presence of COO^- groups, which is illustrated in Fig. 7.

In the PHP hydrogel, the Ag^+ ions diffuse randomly in the gel network due to absence of binding. After reduction, the Ag particles rapidly aggregate to form big and irregular aggregates due to that the polymer layer in the PHP hydrogel network cannot effectively prevent particle aggregation [31]. However, in the PHPM hydrogel, and due to strong electrostatic interaction, the Ag^+ ions are anchored by the COO^- groups. The FTIR results also support that some interaction exists between the Ag colloids and the COO^- groups. Therefore, the Ag colloids will be still anchored at the sites where COO^- groups are located, this effectively inhibiting the aggregation of Ag nanoparticles. Additionally, the borohydride and borate in water are adsorbed by the Ag nanoparticles on their surface during the reduction of anchored Ag^+ ions. It also partly provides electrostatic repulsive force to inhibit the aggregation of Ag colloids [32,33]. In this way, separated and regular Ag nanoparticles are achieved in the PHPM composite hydrogel. It becomes clear that the higher the amount of COO^- is, the better the Ag^+ ions are anchored, which results in the smaller and finer dispersed Ag nanoparticles in the PHPM composite hydrogel. It was found in our early study [34] that the COOH could deprotonize when the PHPM hydrogel swelled in the H_3BO_3/$CaCl_2$ buffer solution (pH 8), which directly reflected in the swelling ratio of pH-responsive hydrogel. Accordingly, in order to change the size and morphology of the reduced Ag nanoparticles in the PHPM composite hydrogel, we can load Ag^+ ions at the various swelling ratios of the PHPM hydrogel.

It is well known that the Ag has excellent electrical conductivity properties [6], so the combination of PHPM hydrogel with Ag nanoparticles is expected to result in a new functional material with electronic properties. Electrical conductivity is an effective parameter to characterize the electronic properties of composites. Therefore, the electrical conductivity of the Ag nanoparticle/PHPM

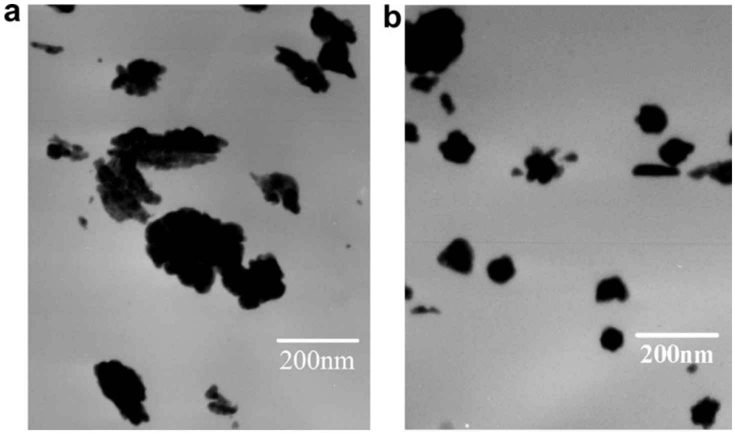

Fig. 6. TEM micrographs of the Ag/PHP (a) and Ag/PHPM (b) composite hydrogel prepared by in situ reducing Ag^+ ions loaded at the same swelling ratio of 10.

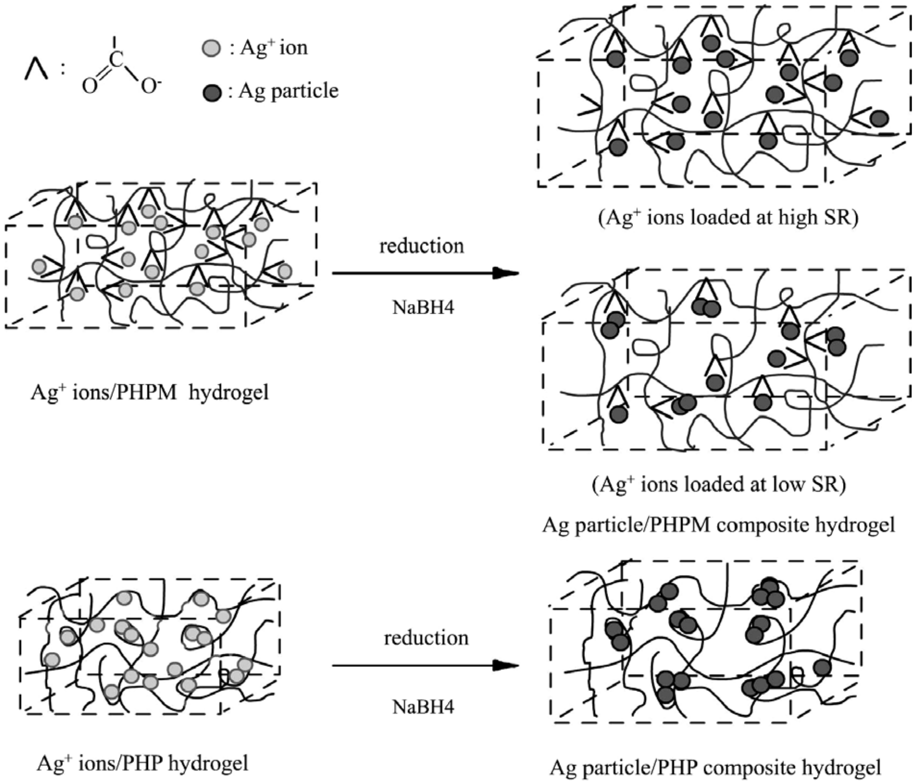

Fig. 7. Schematic representation of the formation of Ag nanoparticles in the PHP hydrogel and PHPM hydrogel.

nanocomposite hydrogel was measured when immersed the nanocomposite hydrogel in the various buffer solutions (pH 1–9), as shown in Fig. 8. It is found that the electrical conductivity of pure PHPM hydrogel changes little when the pH changes from 9 to 1. However, the Ag nanoparticle/PHPM composite hydrogels exhibit different electrical conductivity curves. When the pH is higher, the electrical conductivity of nanocomposite hydrogel is slightly dependent on pH. As decreasing the pH, closed to the pK_a of MAA (p$K_a = 4.13$), a sudden increase of the electrical conductivity is observed in nanocomposite hydrogel, which then remains steady even with further decreasing the pH. Moreover, the electronic properties of the nanocomposite hydrogel show excellent pH-switchable characteristics (insert curve in Fig. 8). The sudden change of electrical conductivity and the "on/off" switching behavior in nanocomposite hydrogel may be attributed to the well-dispersed Ag nanoparticles and the pH-responsive nature of PHPM hydrogels. At high pH values, the nanocomposite hydrogel is swollen due to the deprotonation of COOH groups. Due to the swelling, the distance between Ag nanoparticles is large enough, this acting as a barrier for Ag nanoparticles to come into contact with one another. The electrical conductivity of the Ag nanoparticle/PHPM nanocomposite hydrogel like as that of the pure PHPM hydrogel only depends on the ion transmission in gel network due to their nature of polyelectrolyte gel, which results in a lower level

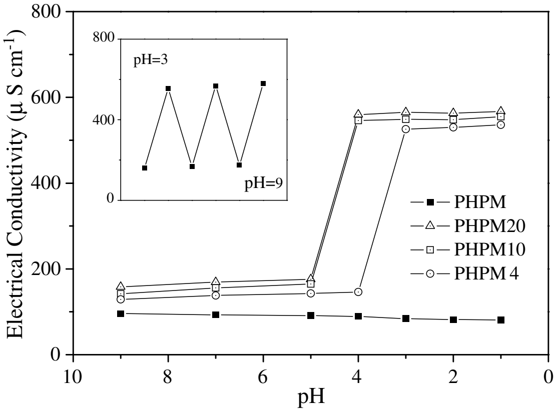

Fig. 8. Relationship between the electrical conductivity of the Ag nanoparticle/PHPM composite hydrogels prepared by in situ reducing Ag^+ ions loaded at various swelling ratios of hydrogel.

of conductivity. As the pH decreases close to the pK_a of MAA, the PHPM hydrogel undergoes a change in conformation due to protonation of COO^- groups. In this way, the intrachain collapse occurs, resulting in dramatic decrease of the gel volume. It causes the distance between the Ag nanoparticles to dramatically reduce and makes the Ag nanoparticles become close-packed or compacted in the nanocomposite hydrogels, which lead to a significantly increased conductivity value [18,35].

Furthermore, the effect of the Ag nanoparticles on the swelling and deswelling behavior of PHPM nanocomposite hydrogel was investigated, as shown in Fig. 9 and Fig. 10. From the swelling kinetics curves, it can be found that the Ag nanoparticle/PHPM composite hydrogels exhibit much higher swelling ratios and fast swelling rates compared to the corresponding pure PHPM hydrogel. The improvement of swelling ratio in the Ag nanoparticle/PHPM nanocomposite hydrogel may be attributed to the presence of Ag colloids with surface charges in the gel network, which results in an afflux of water to balance the build-up of ion osmotic pressure [21]. On the other hand, it is possible that some of the crosslinking gets broken during the reducing reaction, which leads to the decrease of the crosslink density. As a result, the Ag nanoparticle/PHPM nanocomposite hydrogels swell quickly and achieve higher swelling ratio.

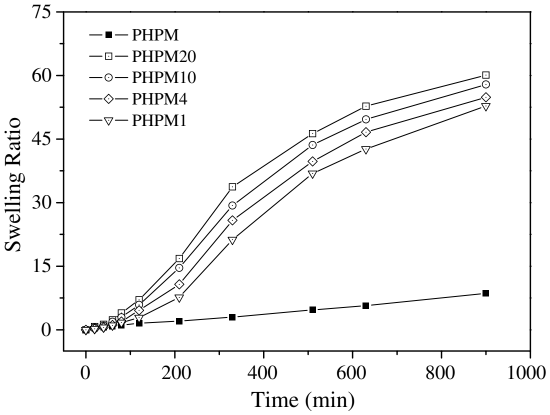

Fig. 9. Swelling kinetics of the pure PHPM hydrogel and the Ag nanoparticle/PHPM composite hydrogels prepared by in situ reducing Ag^+ ions loaded at various swelling ratios of hydrogel.

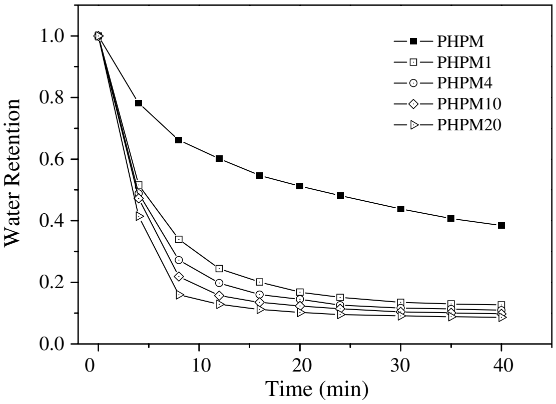

Fig. 10. Deswelling kinetics of the pure PHPM hydrogel and Ag nanoparticle/PHPM composite hydrogels prepared by in situ reducing Ag^+ ions loaded at various swelling ratios of hydrogel.

At the same time, from the swelling kinetics curves, it is obvious that the Ag nanoparticle/PHPM nanocomposite hydrogels exhibit much faster deswelling rate than the corresponding pure PHPM hydrogel. For example, the Ag nanoparticle/PHPM20 nanocomposite hydrogel, prepared by in situ reducing the Ag^+ ions loaded at equilibrium swelling ratio of PHPM hydrogel ($SR = 20$), rapidly loses about 90% of water in the acidic mediums and reaches the equilibrium water content within 15 min, while the pure PHPM hydrogel only losing about a 30% of water over the same time period. The rapid deswelling rate of the Ag nanoparticle/PHPM nanocomposite hydrogels may be attributed to the following two reasons. On one hand, the introduced Ag nanoparticles can act as the dispersed reservoirs and provide water releasing channels for the interior water in the gel. Similar results have been reported in the inorganic nanoparticle/ hydrogel nanocomposite prepared by Durme et al. [36]. In their studies, they speculated that uniformly distributed inorganic domains can act as nano-sized water reservoirs inside the polymer matrix. The huge interphase region between the inorganic nanoparticles and the polymer matrix in the nanocomposite leads to a dramatic decrease of the characteristic diffusion length of water molecules through the nanocomposite hydrogels. In this way, these hydrophilic reservoirs will quickly dehydrate acting as water releasing channels for the interior water when the nanocomposite hydrogel deswells, similar to the hydrophilic PEO graft chains in the reported comb-type hydrogels [37]. As expected, this effect will be more obvious in the nanocomposite hydrogel embedded much smaller and finer distributed Ag nanoparticles. On the other hand, because there exist strong interaction between the COO^- groups and Ag^+ ions, as mentioned above, the random polymer chains may be affected by the regulating of the COO^- groups and thus turn into a relatively regular arrangement, which is similar to the arrangement of the polymer chains caused by hydrogen bond in the cold-treated hydrogel [38]. When the deswelling occurs, the Ag particle/PHPM nanocomposite hydrogels can dehydrate in step and exhibit a fast deswelling rate.

4. Conclusion

Series of novel pH responsive Ag nanoparticle/PHPM nanocomposite hydrogel were prepared by in situ reducing the Ag^+ ions anchored to deprotonized carboxylic acid groups with sodium borohydride. The size and morphology of the Ag nanoparticles in PHPM nanocomposite hydrogel could be changed by loading the Ag^+ ions at various swelling ratios of PHPM hydrogel before reduction. Compared with the pure PHPM hydrogel, the Ag nanoparticle/PHPM nanocomposite hydrogel exhibited not only much higher swelling ratio and faster deswelling rate, but also pH switchable electrical properties upon controlling the interparticle distance under pH stimulus.

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