A kind of smart gold nanoparticle–hydrogel composite with tunable thermo-switchable electrical properties

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A well-dispersed gold nanoparticle–poly-*N*-isopropylacrylamide (PNIPAm) hydrogel composite with thermo-switchable electrical properties was prepared by the co-polymerization of Au nanoparticles with attached vinyl groups with NIPAm. The Au nanoparticles and the composite are characterized by TEM, UV-Vis, FTIR, and NMR. At the same time, the electrical conductivity, cyclic voltammetry and constant-pontential technique were used to demonstrate the electrical properties of the composite. It was found that the electrical properties of the composite show a tunable property with changing temperature and the electrical conductivity changes by two orders of magnitude at the transition temperature (T_{tran}). The T_{tran} of the composite can be adjusted from 0 °C to 40 °C by changing the concentration of Au nanoparticles, the degree of cross-linking or the composition of composite. The change in electrical properties is reversible in a heating and cooling cycle.

Introduction

Embedding colloidal metal nanoparticles into polymer matrices is an effective method of enhancing the functions of these materials.[1] The use of metal nanoparticles as structural and functional units for the construction of sensing, photoelectrochemical, and nanoelectronic devices has gained a substantial momentum in the past few years.[2] In particular, the electronic properties of nanoparticles offer great promise for development of nano- and quantum-electronics.[3] Recently, strategies have been developed for the syntheses of functional metal or metal iron-polymer hybrid systems exhibiting tailored electronic properties.[4] Of particular interest is the conjugation of gold nanoparticles with smart polymers such as poly-*N*-isopropylacrylamide (PNIPAm),[5] which has been studied extensively because of the conjugate's ability to swell or collapse reversibly in response to temperature stimuli.[6] It has been shown that the cell size of a crystallized colloid array embedded in a hydrogel can be changed by the shrinking and swelling of the polymer matrix.[7] Thermo-responsive PNIPAm shows potential application in the creation of "smart" material systems.[8] On the other hand, the use of Au nanoparticles as functional units in the field of sensing, photoelectrochemical, nanoelectronic devices has attracted great interest, because of their extraordinary electrical and optical properties,[9] since a reliable and facile method of preparing alkanethiol-protected Au nanoparticles has been reported by Brust *et al.*[10] The electronic properties of Au nanoparticles show great promise for the micro-devices field.[4c] The combination of PNIPAm with the dielectric properties of gold nanoparticles has resulted in a new material.[4d] At present, mainly two different techniques are commonly used to prepare the Au nanoparticle–PNIPAm composite, *i.e.* the "breathing mechanism"[11] and "*in situ* forming Au nanoparticles inside an existing PNIPAm template".[12] Using the "breathing mechanism", by which Au nanoparticles are incorporated into the gel using its property of being highly swollen in aqueous solution ("breathing in") and shrinking dramatically in an aprotic solution ("breathing out"), the gold nanoparticles are fixed in the hydrogel only by physical entanglement or hydrogen bonding interactions between the polymer chains and the citrate surface of the nanoparticles. Alternatively, the latter method needs a hydrogel containing functional groups (such as thiols) to be prepared first, which is similar with the "grafting-to" technique. It has not been reported that these kinds of nanocomposites can be prepared directly in the presence of Au nanoparticles.

In this paper, Au nanoparticles with vinyl groups that can participate in the reaction as the monomer are first prepared. Using this basis, one promising strategy was to prepare a functional gold nanoparticle–PNIPAm composite in one-step by co-polymerization of monomer and functional Au nanoparticles under heating (as illustrated in Scheme 1). The smart material shows excellent tunable electrical properties by temperature stimuli.

Experimental

Materials

All materials were of commercial source (Acros). *N*-Isopropylacrylamide (NIPAm) was re-crystallized in toluene and dried in vacuum at room temperature. 2,2′-Azobis(isobutyronitrile) (AIBN) was re-crystallized from methanol. Tetrahydrofuran

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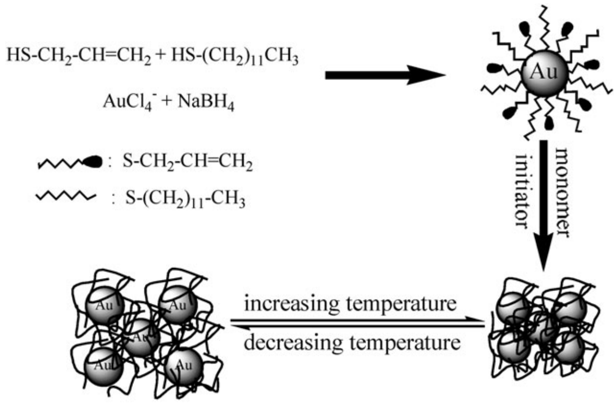

Scheme 1 Schematic illustration of the preparation of the Au nanoparticle–PNIPAm composites.

(THF) was freshly distilled prior to use. Ethane glycol dimethacrylate (EGDMA), allyl mercaptan, *n*-dodecanethiol, methacrylic acid (MAA), butyl methacrylate (MBA), sodium borohydrate (NaBH$_4$) and hydrogen tetrachloroaurate tetrahydrate (HAuCl$_4 \cdot 4H_2O$) were used as received.

Syntheses

Preparation of the Au nanoparticles with vinyl groups. Using a modified literature method,[10] vinyl groups were introduced to the surface of Au nanoparticles by incorporating allyl mercaptan into the reaction system.

Preparation of the polymer-modified electrodes and Au nanoparticle–PNIPAm composites. Using methods reported in ref. 13 the polymer-modified electrodes were prepared. Through the same process, a gold electrode with the Au nanoparticle–PNIPAm composite (geometrical area *ca.* 0.019 mm^2) attached was prepared for the measurement of cyclic voltammetry. In order to increase the adherence of the composite, the gold electrode was coated with allyl mercaptan by dipping the electrodes in 35 mM allyl mercaptan THF solution for 2 h after being polished with a polishing cloth, and then washed with trichloromethane, ethanol, and water under ultrasonication.

Instrumentation and characterization

UV-Vis spectroscopy, ^{1}H NMR and FTIR spectra. The absorbances of the reaction mixture solution and composite were recorded from 400–800 nm with a UV-Visible spectrophotometer (Shimadzu UV-2401 PC). The ^{1}H NMR spectra were obtained with a Bruker AMX 300 Hz spectrometer using chloroform (CDCl$_3$) as a solvent. Infrared analysis (FTIR) spectra of the Au nanoparticles and the nanoparticle–hydrogel composite were recorded in the range 4000–650 cm^{-1} with a Perkin-Elmer Spectrum one.

Swelling ratio. The swelling ratio of the hydrogel in distilled water, SR, is calculated by measuring the weight of the Au nanoparticle–PNIPAm composite as follows:

$$SR = (W - W_0)/W_0$$

where W is the weight of the Au nanoparticle–PNIPAm composite in the swollen state and W_0 is the weight of the composite in the dry state.

Electrochemical measurements. The measurement of the electrical conductivity of the composite was carried out using polymer-modified electrodes. The thickness of the hydrogel between foam nickels was 1 mm, which was controlled by the thickness of the mould. The electrical conductivity was recorded on a DDS-11A electric conductivity meter (Fangzhou Inc, Chengdu, China). The constant-potential measurement was recorded on an HDV-7C constant-potential meter, Fangzhou Inc, Chengdu, China, using the same specimens. Experiments were performed in pure water, maintaining a constant potential of 2 V.

Cyclic voltammetry was performed using a locally built pontentiostat interfaced with a Lenovo compatible PC, along with in-house software, produced by Fangzheng Inc, Shanghai China. A conventional three-electrode cell, consisting of the Au nanoparticle–PNIPAm composite-modified Au electrode, a glassy-carbon auxiliary electrode and a saturated calomel electrode (SCE) connected to the working volume with a Luggin capillary, was used. 0.1 M KClO$_4$ was used as the background electrolyte. The cyclic voltammetry was performed in the presence of 0.01 M K$_3$Fe(CN)$_6$–K$_4$Fe(CN)$_6$ (1 : 1) mixture as a redox probe.

Results and discussion

Preparation of the Au nanoparticles coated with vinyl groups and the Au nanoparticle–PNIPAm composite

Functionalised gold nanoparticles with vinyl groups were prepared using a literature method.[10] In contrast to the previous methods in which multi-step reactions are required to prepare the reactive group-coated Au nanoparticles,[14] this route involves a one-pot reduction of HAuCl$_4$ by NaBH$_4$ in the presence of allyl mercaptan. The introduction of vinyl groups onto the Au nanoparticles is confirmed by FTIR (Fig. 1a) and NMR (Fig. 1b). In comparison with the FTIR of the monomer mixture, the S–H stretch (2650 cm^{-1}) has disappeared and the CH=CH$_2$ stretch (1630 cm^{-1}) is kept. The FTIR results clearly show that allyl mercaptan is bound to the gold nanoparticles. This is also supported by the ^{1}H NMR spectrum of Au nanoparticles, in which the resonances labeled (δ = 5.0 ppm and δ = 5.8 ppm) represents the three protons of vinyl groups. The TEM photographs of the nanoparticles[13] reveal that they are spherical with the size ranging from 5 nm to 10 nm.

In the presence of the functionalised Au nanoparticles, red (same as the solution) and transparent Au nanoparticle–PNIPAm composites are obtained by radical polymerization under heating to 60 °C for 24 h. The morphology of the Au nanoparticles being well-dispersed in PNIPAm has been confirmed by transmission electron microscopy (TEM).[13] These results are confirmed by the UV-Vis spectra of gel and solution (Fig. 2). The UV-Vis spectrum of the gold nanoparticle sample is a very sensitive reporter of particles' aggregation state. Absorbance bands at longer wavelengths represent inter-particle plasmon excitation. The UV-Vis traces of the reaction mixture solution and the Au nanoparticle–PNIPAm composite have the same absorption maximum near 528 nm, characteristic of the surface-plasmon resonance of well-spaced Au

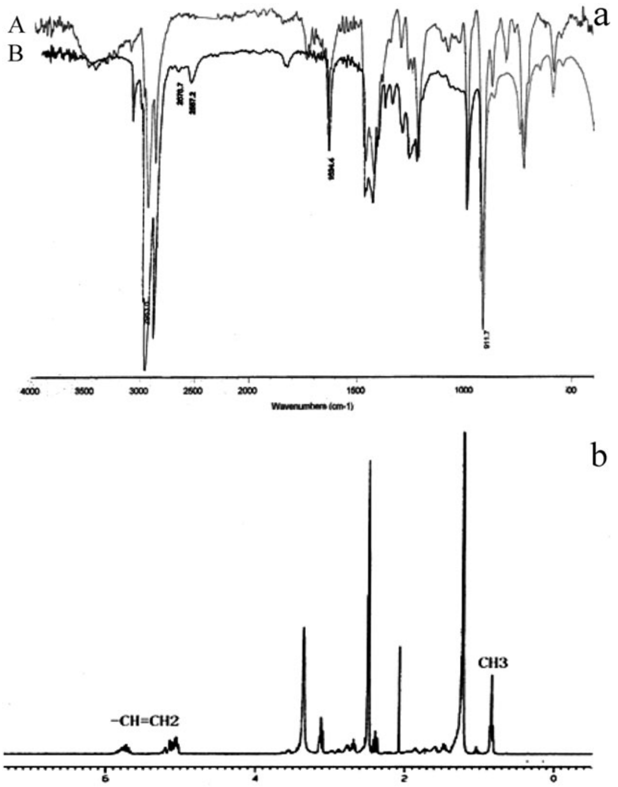

Fig. 1 (a) The FTIR spectrum of Au nanoparticles (A) and the mixed ligand (B); (b) ^{1}H NMR spectrum of Au nanoparticles.

nanoparticles. As a result, the well-dispersed Au nanoparticles in PNIPAm establish the basis of achieving the thermo-switchable electrical property of the composite.

The tunable electrical properties of the Au nanoparticle–PNIPAm composite

To investigate the effect of temperature on the electronic properties of the Au nanoparticle–PNIPAm composite, a cyclic voltammogram was used. Fig. 3 shows the cyclic voltammograms of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ in the presence of the shrunken Au nanoparticle–PNIPAm composite in comparison to that of the electrode modified with the shrunken PNIPAm without Au nanoparticles. No electrical response of $Fe(CN)_6^{3-/4-}$ is observed with the shrunken nanoparticle-free PNIPAm at 40 °C, indicating that the electrode is insulated by the polymer film. In the presence of the Au nanoparticle–PNIPAm composite, the reversible redox wave observed proves that the conductivity of the composites is enhanced because of the existence of Au nanoparticles. The electrical response of $Fe(CN)_6^{3-/4-}$ was even further enhanced at 40 °C because of a shorter inter-particle spacing in the shrunken PNIPAm. This demonstrates that the electron hopping between the Au nanoparticles incorporated in the PNIPAm became easier in the state of shrunken gel than in the state of swollen gel. These results are in accordance with previous reports.[4] The composite shows an excellent tunable electrical properties.

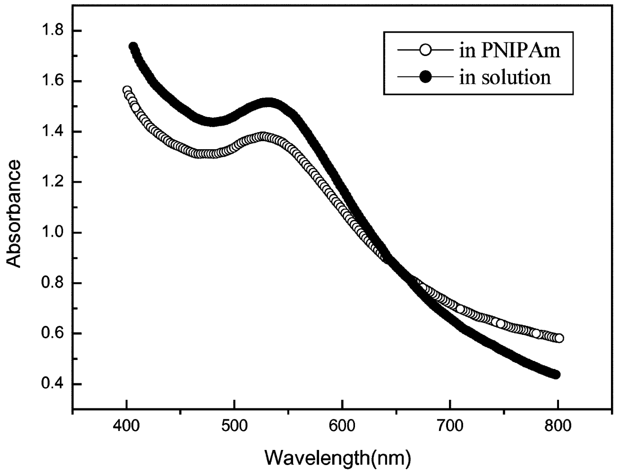

Fig. 2 The UV-Vis spectrum of Au nanoparticle–PNIPAm composite and Au nanoparticle–NIPAm solution.

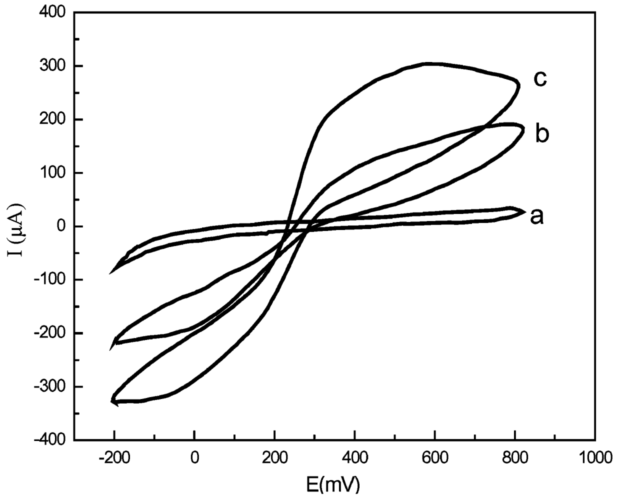

Fig. 3 Cyclic voltammograms of $Fe(CN)_6^{3-/4-}$, 0.01 M, at the PNIPAm functionalized Au electrode (a) at 40 °C, without incorporated Au nanoparticles; (b) at 20 °C, with incorporated Au nanoparticles; (c) at 40 °C, with incorporated Au nanoparticles. Data recorded in 0.1 M $KClO_4$ aqueous solution; scan rate 100 mV s^{-1}. The dosage of Au nanoparticles was 0.2 ml per 1 ml of reaction mixture. The concentration of Au nanoparticles solution was 0.25 mg ml^{-1}.

The thermo-sensitive properties of the Au nanoparticle–PNIPAm the composite

It is necessary to understand the characteristic response of the composite to temperature stimuli in order to investigate the tunable electrical properties of the composite with adjusting temperature. The influence of Au nanoparticles on the thermo-sensitive properties of the Au nanoparticle–PNIPAm composite is examined by the change of swelling ratio with temperature (Fig. 4). The results show that the swelling ratio of the composites exhibits a remarkable decrease with rising temperature from 18 °C to 32.5 °C. But with an increase in the amount of Au nanoparticles, the swelling degree of the composites decreases clearly because the Au nanoparticles participate in the reaction not only as functional units and monomers but also as a cross-linker. The increase in the degree of cross-linking in the composite leads to a decrease in the swelling ratio.

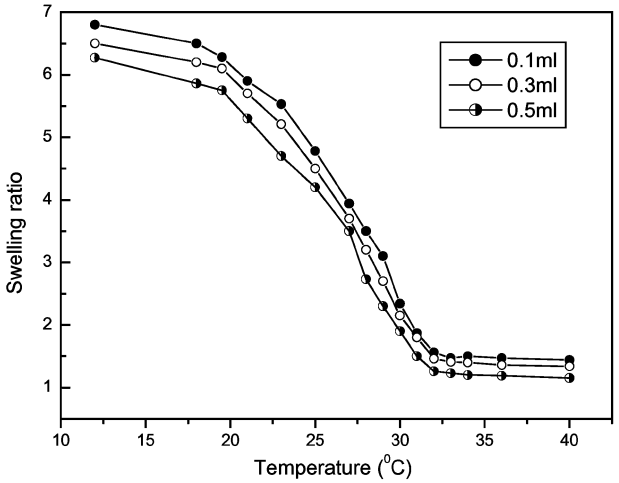

Fig. 4 Effect of temperature on the swelling ratio of composites with different Au nanoparticle content. The concentration of Au nanoparticles was 0.25 mg ml^{-1}. The volume of the reaction mixture was 1 ml.

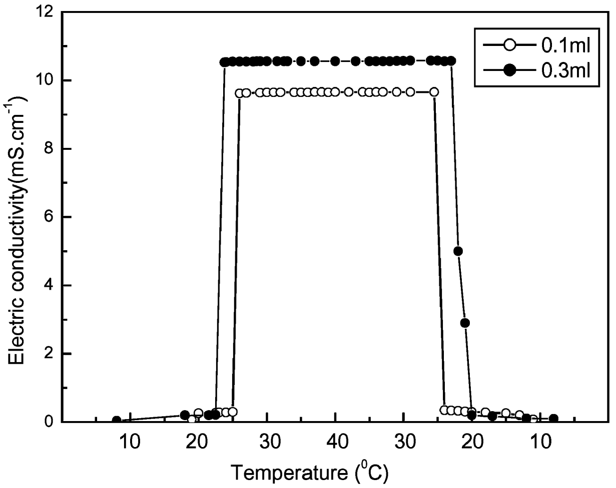

Fig. 5 The relationship between the electric conductivity (mS cm^{-1}) of Au nanoparticle–PNIPAm composite and the environmental temperature. The ratio of increasing temperature is 0.3 °C min^{-1} and the concentration of the Au nanoparticles solution was 0.25 mg ml^{-1}.

The thermo-switchable electrical conductivity of the composite

In order to investigate the tunable electronic properties of the composite in detail, the effect of temperature on the electrical conductivity of the composite was investigated, as shown in Fig. 5. Electrical conductivity is an effective parameter to characterize the electronic properties of the composite. It was found that the electrical conductivity of the composite with 0.3 ml of Au nanoparticles remains constant below 22 °C and has a maximum at 22.5 °C with a steep increase and a plateau at higher temperatures. The electrical conductivity then reduces again at 20.5 °C when the temperature is decreased, with a similarly sudden change. The second T_{tran} (20.5 °C) exhibits slightly lower than the first T_{tran} (22.5 °C) because of the hysteresis effect of polymer chains. As shown in Fig. 4, the composite shows an excellent swelling state at relatively low temperatures. The gel network is more homogeneous and Au nanoparticles are uniformly dispersed within it. The large inter-particle distance acts as a barrier to electron hopping through the PNIPAm, resulting in a lower level of electrical conductivity.[15] With increasing temperature, hydrogen bonds between the monomer side groups and water molecules are broken; the intrachain collapse occurred, PNIPAm undergoes changes in conformation and the gel becomes heterogeneous.[16,17] A decreased swelling ratio of the composite leads to the distance between Au nanoparticles being diminished gradually. At T_{tran}, the distance between Au nanoparticles reduces and the Au nanoparticles become close-packed or in contact in the gel. Both tunnelling and contact effects would help to develop the conductive path and increase the conductivity value.[18] The electrical conductivity changes by two orders of magnitude for a temperature change about 0.1–0.3 °C. The electronic properties of the composite show an excellent thermo-switchable characteristic. The "on–off" switching mechanism is attributed to the response of the temperature stimuli sensitive PNIPAm chain.

In order to study the thermo-switchable electronic properties of the composite in detail, the constant-potential technique was used. In the experiment, the current required to maintain a constant voltage between working and counter electrodes is recorded against time. At the same time, the temperature of the system is changed between 40 °C and 10 °C. Fig. 6 shows the current transients of the gold nanoparticle–PNIPAm composite with changing temperature. It is clear that the shrunken composite exhibits a much higher current than the swollen one. As the temperature is changed, an abrupt jump of current is observed between 40 °C and 10 °C. The results are the same as the change of electrical conductivity. The thermo-switchable electrical properties of the composite are demonstrated further.

From Fig. 6, it can also be observed that the electrical conductivity change of the composite through a heating–cooling cycle is repeatable and reproducible. This is because the distance between Au nanoparticles is increased or decreased with the swelling or shrinking of PNIPAm at different temperatures. This leads to the reversible change of the barrier

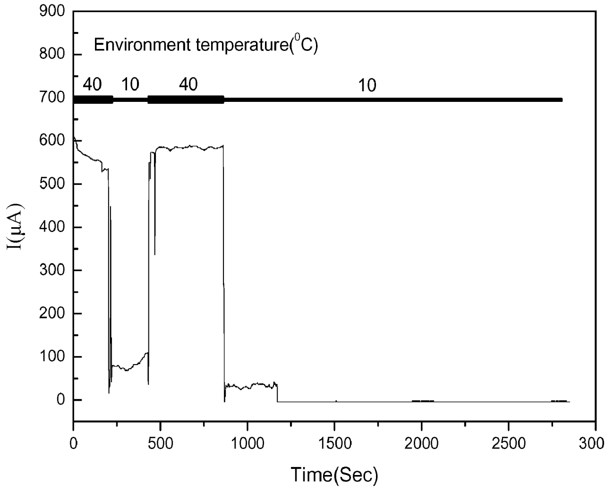

Fig. 6 The constant-potential current transients of the Au nanoparticle–PNIPAm composite with 0.3 ml Au solution in 1 ml reaction mixture. The concentration of Au solution was 0.25 mg ml^{-1}.

between Au nanoparticles with the temperature fluctuation. The electronic properties of the composite present excellent thermo-switchable properties.

In addition, it can be seen from the Fig. 5 that the T_{tran} can be reduced by increasing the content of Au nanoparticles. So the adjustable electrical properties of the composite can be studied in succession.

The effect of the concentration of Au nanoparticles and the degree of cross-linking in the composite on T_{tran}

The reduction in the T_{tran} of the composite with an increase in the amount of Au nanoparticles and degree of cross-linking of PNIPAm can be observed from Fig. 7. This reduction is because the increase in the number of Au nanoparticles in the composite makes the mean average distance and potential barrier between particles become smaller and results in the creation of a more perfect conductive network, which leads to the charge carriers being able to tunnel from one Au nanoparticle to another at lower temperatures. On the other hand, a higher degree of cross-linking lowers the swelling ratio.[19] A small volume expansion of the composite leads to continuities of the conducting network at lower temperature. In other words, increasing the concentration of Au nanoparticles and the degree of cross-linking are beneficial to obtaining the conducting network at a lower temperature.

The effect of the composition of the composite on T_{tran}

Fig. 8 shows the transition temperature (T_{tran}) of the Au nanoparticle–PNIPAm composite as a function of the content of hydrophilic monomer and hydrophobic monomer. The T_{tran} of the composite falls from 27.5 °C to 5 °C with increasing MBA concentration, but rises from 23 °C to 38 °C with an increase in MAA concentration. It is clear that the T_{tran} of the composite can be adjusted by changing the composite's composition. This is explained by the effect of the hydrophilic monomer and hydrophobic monomer on the phase transition of the PNIPAm.[20] The hydrated state of PNIPAm is changed by the introduction of hydrophilic monomer (MAA) and hydrophobic monomer (MBA). The hydrogel is able to maintain its hydrated state at higher temperatures with the addition of the hydrophilic group, but the addition of hydrophobic group leads to a destruction of the hydrated state at lower temperatures.

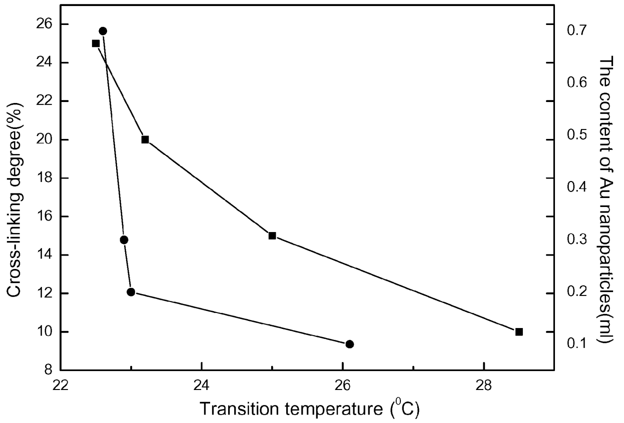

Fig. 7 The effect of the concentration of Au nanoparticles (●) and degree of cross-linking (■) on the transition temperature of the composite. The concentration of the Au solution was 0.25 mg ml^{-1}.

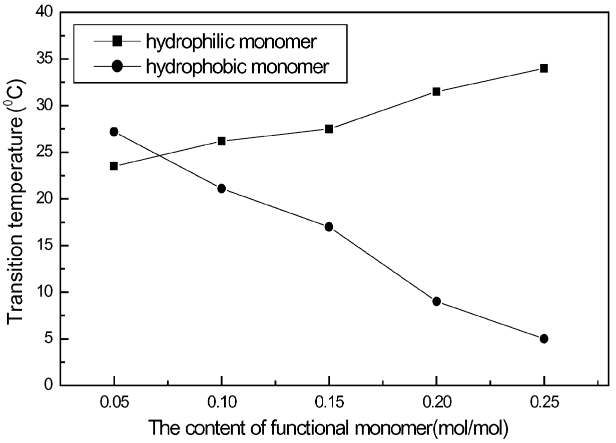

Fig. 8 The relationship between the content of hydrophilic monomer (MAA) and hydrophobic monomer (MBA) and the T_{tran} temperature of the Au nanoparticle–PNIPAm composite.

Conclusions

In conclusion, we have prepared a new kind of smart material, in which gold nanoparticles are well-dispersed in a PNIPAm hydrogel. The electrical properties of the gold nanoparticle–PNIPAm composite are tunably thermo-switchable and reversible upon changing the environmental temperature. By changing the constitution of the composite, the T_{tran} can be adjusted from 0 °C to 40 °C. The thermo-switchable electrical properties of the composite may mean that the smart material will have many potential applications in sensors field.

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