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A Photothermally Smart Hydrogel Material with Fast Response Properties

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Abstract. Hydrogel is a kind of functional polymer material. Because of its excellent characteristics such as high-water absorption, biocompatibility and stimulus response, hydrogel is widely used in biological tissue engineering, drug-controlled release, wastewater treatment, chemical mechanical devices, household products and other fields. The traditional hydrogels often have some disadvantages, such as slow response rate and fragile, which limit the application range of hydrogels. In this paper, we prepared a photo curable hydrogel photothermal response driving material. Because PNIPAAm hydrogel has excellent thermal driving response effect, it will shrink when the temperature is higher than 32 ℃, and gold nanoparticles are good photothermal response materials. Therefore, the hydrogel actuator can realize fast response driving, and has excellent photothermal response efficiency and good environmental adaptability. The research scheme is to first prepare gold nanoparticle sol with appropriate concentration, and then synthesize PNIPAAm /AuNPs nano hydrogel. Its performance was characterized by SEM, TEM and UV spectroscopy, and its driving performance was studied.

Keywords. Hydrogel, smart materials, gold nanoparticles

1. Introduction

A smart actuation material is a kind of actuation material that can manufacture various actuators according to the changes of the external environment and internal state [1]. Researchers typically make sensors or actuators from this material. In the past few years, the researchers have produced actuators using smart material such as muscle tissue [2], and plant fibers [3]; shape memory materials such as graphite and graphene oxide (GO) [4] and carbon nanotubes (CN) [5]; piezoelectric composites smart such as hydrogel materials such as poly(N-Isopropylacrylamide) (PNIPAM) [6].

Smart hydrogels can change their own shapes according to different environments, and can be divided into photo responsive hydrogels, temperature responsive hydrogels, and pH responsive hydrogels according to different physical or chemical responses [7]. Smart hydrogels can sense and respond to external stimuli differently than conventional

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hydrogels. Temperature responsive hydrogels use the effect of different temperatures on intermolecular hydrogen bonds to achieve their shrinkage and expansion. Due to these temperature-sensitive properties, PNIPAAm is a suitable candidate for various biomedical applications, such as drug delivery, tissue engineering, and biosensing [6].

Gold-based nanostructures, such as gold nanoshells, gold nanocages, and gold nanorods (AuNRs), have been used as photothermal conversion reagents [8]. AuNRs are considered promising photothermal reagents because they have high absorption coefficients, especially within the NIR region where it is higher than other nanoparticles with narrow spectral bandwidths [9,10]. The tunable optical resonance in the NIR region makes AuNRs particularly attractive for in vivo applications as photothermal therapeutic agents [11].

In this work, polymerization was initiated under UV light irradiation to form a photothermally smart hydrogel material with fast response properties. Gold nanoparticles are good photothermal response materials, so this hydrogel material can achieve fast response driving and has excellent photothermal. This material has high response efficiency and good environmental adaptability, and can be used in soft robotics, special environmental detection, medical and other fields in the future.

2. Experimental Section

2.1. Materials and Chemicals

PDMS prepolymer (Sylgard 184 Silicone Elastomer kits) was purchased from Dow Corning. Chloraurate Tetrahydrate, sodium citrate dihydrate, N, N'-Methylenebis (acrylamide) (MBAA), dimethyl sulfoxide (DMSO), and allyl disulfide were purchased from Fisher. 2,4,6-Trimethylbenzoyl ethyl phosphate(TPO-L)was purchased from TCI. N-isopropylacrylamide (NIPAAm), N, N-Bis(acryloyl) cystamine (BACA) was purchased from Sigma. All chemicals were used as received.

2.2. Fabrication of Gold Nanoparticles (AuNPs)

1.0000 g of chloroauric acid was added to an appropriate amount of secondary distilled water to make a 0.0243 mol /L of chloroauric acid tetrahydrate solution. 1.000 g of sodium citrate was added to an appropriate amount of secondary distilled water to make a 0.034 mol / L of sodium citrate dihydrate solution. 250 μL of auric acid to 250 ml of water to make a seed solution. The seed solution was then heated to its boing point with a stirring speed of 600 rpm. 20 ml of 1 wt.% sodium citrate dihydrate solution was then added into the seed solution followed by an immediate increase in the stirring speed to 1000 rpm.

2.3. Fabrication of the Hydrogel

In this paper, the hydrogel precursor solution was obtained by mixing 40 wt.% NIPAAm monomer, 1.5 w.t%, 2.0 w.t%, 3.0 wt% BIS in DMSO. Then 0.5 wt% AuNPs, 0.2 wt% photoinitiator TPO-L and a specific amount of BACA were added to the precursor solution. Afterwards, the prepolymer solution was injected into PDMS

molds and covered with TMSPMA-treated coverslips. The UV photopolymerization was carried out for 120 seconds.

3. Results and Discussion

Figure 1 shows the preparation process of the photothermally driven photocurable hydrogel material, which is obtained by the polymerization of NIPAm, BACA, BIS and AuNPs. NC hydrogels chemically bound with gold nanoparticles were dispersed in aqueous solution through radical polymerization, and the surface of gold nanoparticles was introduced into vinyl groups by the interaction of RS-Au bonds. The hydrogel column was cured by UV light for 120 s in PDMS molds. Rapid bending under near-infrared laser irradiation at 808 nm via excellent photothermal properties of AuNPs and driving performance of NIPAm. At high temperature, the effect of hydrogen bonds is weakened, and the hydrophobic groups aggregate in water to agglomerate, causing the molecular chain to shrink and the polymer to shrink.

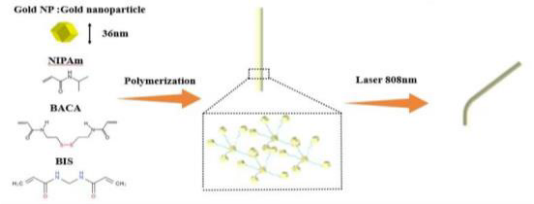

Figure 1. Preparation mechanism of hydrogel materials.

250 μL of auric acid to 250 ml of water to make a seed solution. The seed solution was then heated to its boing point with a stirring speed of 600 rpm. 20 ml of 1 wt.% sodium citrate dihydrate solution was then added into the seed solution followed by an immediate increase in the stirring speed to 1000 rpm. The solution was boiled for an additional 6 minutes to a burgundy color, and the hot plate was turned off. In the preparation process, the amount of reducing agent was changed by the control variable method. Four groups of AuNPs were prepared with 5ml, 10ml, 15ml and 20ml of sodium citrate dihydrate solution respectively. As show in figure 2(a), the more the amount of reducing agent, the darker the color of the configured solution.

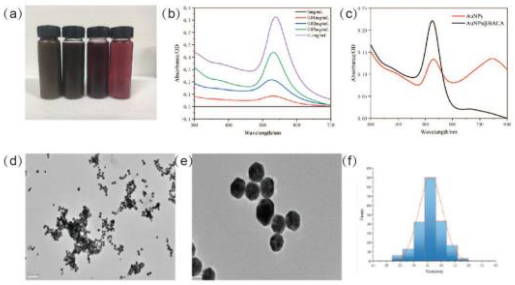

Figure 2. (a) AuNPs with different concentrations. (b) UV-visible absorption spectrum of AuNPs. (c) UV-visible absorption spectrum of AuNPs/BACA. (d-e) TEM analysis of AuNPs. (f) Results from a particle size analysis of AuNPs.

The absorbance of AuNPs was by using a UV-Vis-NIR spectrometer (Shimadzu uv-3101). As shown in figure 2(b), the concentration of gold nanoparticles was qualitatively compared by molecular ultraviolet-visible absorption spectroscopy. The absorption peak of gold nanoparticles was 532nm. The obtained results show that the synthesized gold nanoparticles have better peak shape and narrower peak range, and with the increase of concentration, the characteristic absorption peak shifts to the direction of long wave number.

Figure 2(c) shows the addition of BACA-modified AuNPs. From the ultraviolet-visible (UV-vis) absorption spectrum, with the addition of BACA, the characteristic peak positions of gold nanoparticles for light absorption of specific wavelengths changed, and the obtained functionalized gold nanoparticles. Therefore, the photothermally responsive hydrogel-driven material prepared in this paper can respond to near-infrared light.

As shown in figure 2(d), TEM analysis verified the surface morphology and distribution uniformity of AuNPs. The gold nanoparticles prepared in the experiment have good dispersibility. The size of the small particle size is relatively uniform and basically round or oval, while the size and morphology of the large particle size are uneven. Particle size analysis showed that the particle size distribution of the experimentally prepared particles was in the 36±nm.

EDS analysis revealed specific adsorption RS-Au bonds on the surface of gold nanoparticles after adding a specific amount of BACA to the gold nanoparticles (figure 3). The corresponding elemental distribution map shows that BACA is uniformly distributed on the surface of AuNPs.

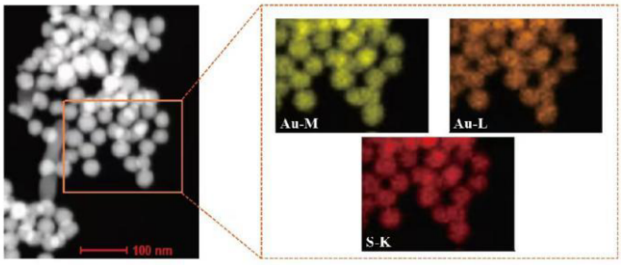

Figure 3. TEM analysis of AuNPs/BACA.

As shown in figure 4, the surface morphology of the hydrogel material was observed with a Supra 40VP scanning electron microscope. The dried hydrogel samples were obtained by freeze-drying for 48 h. Due to the poor electrical conductivity of the sample, the sample was subjected to gold spraying operation and then placed in a scanning electron microscope for observation. The SEM images used secondary electron mode with a working distance (WD) of 8.9 mm and an accelerating voltage of 10.0 kV. As shown in figure 4, figures 4 (a)-(c) uses 1.5wt% BIS, Figures 4(d-f) use 3.0wt% BIS, and the average pore size of the hydrogel is 4.61 microns and 2.07 microns. Hydrogels with higher crosslinking density had smaller pores, which in turn showed smaller pore size and denser structure in the SEM image. At the same time, the elemental analysis of the hydrogel material is carried out as shown in figure 4(g). The yellow spots representing gold atoms are uniformly dispersed on the whole picture, indicating that the gold nanoparticles are uniformly distributed in the hydrogel as shown in figure 4(g).

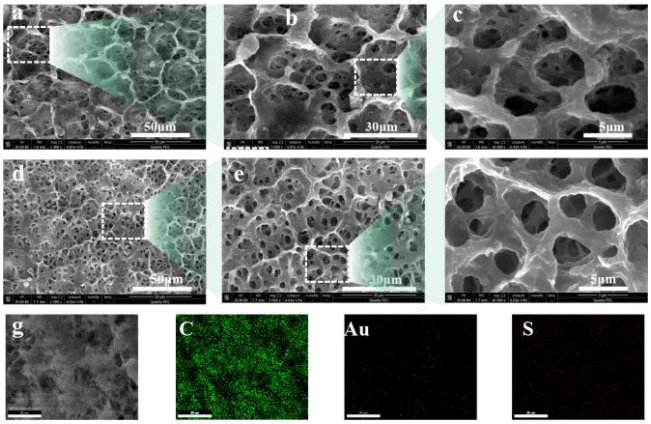

Figure 4. Surface analysis of the hydrogel nanocomposite. Scanning electron microscope images of hydrogels with (a-c) 1.5 wt.% BIS, (d-f) 3.0 wt.% BIS. (g) EDS analysis of the hydrogel.

The hydrogel precursor solution was poured into the cube mold and cured under UV lamp irradiation for 15 minutes to obtain the hydrogel block. The initial measured width is 12.33mm. After immersing it in hot water at 45°C for 30s, the width of the hydrogel block becomes 11.74mm as shown in figure 5(a), which shows that the hydrogel has good shrinkage performance. In this paper, a biomimetic petal hydrogel structure was also prepared. The obtained hydrogel petals will deform and shrink after being placed in water at 45°C for 10 seconds, as shown in figure 5. Thermal reaction performance is good.

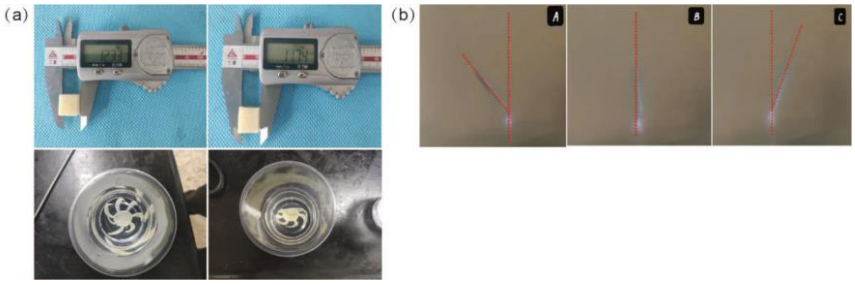

Figure 5. (a) The heat shrinks and the thermal response of hydrogel. (b) Light-driven hydrogel actuator.

The driving performance of the hydrogel was tested with an infrared laser with a light intensity of 400 mW. At the beginning, the state of the hydrogel column is bent to the left, as shown in figure 5(b-A), the state of the hydrogel column becomes upright when the laser is irradiated for 4 s, as shown in figure 5(b-B), and the hydrogel column bends to the right when the laser is irradiated for 6 seconds, as shown in figure 5(b-C).

4. Conclusions

In this study, a hydrogel material containing AuNPs as a light-to-heat conversion source was formulated, and an actuator whose shape changed rapidly upon light illumination was fabricated and demonstrated. First, the preparation of gold

nanoparticles adopts the chemical reduction method. Reduction of gold in the form of chloroauric acid ions to zero-valent gold, aggregation into gold nanoparticles. After preparation, dispersion and purification, gold nanoparticles with a particle size distribution of about 36 nm were finally obtained. Second, the AuNP/PNIPAAm columnar gel was synthesized by UV light curing method by chemically binding AuNPs with PNIPAm as the matrix, adding a specific amount of BACA, and adsorbing on the surface of AuNPs in the form of RS–Au bonds. Therefore, a photocurable hydrogel photothermal responsive material was fabricated.

Since the NIPAAm hydrogel shrinks when the temperature reaches above 37 degrees Celsius, its thermally driven structure is designed. Through the characterization of its properties, it is proved that the material will shrink in volume after being heated, and it can deform when placed in water at 45 degrees Celsius for 10 seconds, that is, it has thermal shrinkage and thermal driving properties. The prepared hydrogel can be deformed when irradiated by laser and has a good photothermal response drive. Therefore, this hydrogel material can realize fast response drive, and has excellent photothermal response efficiency and good environmental adaptability, and can be used in soft robotics, special environmental detection, medical and other fields in the future.

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