

Preparation of Photo-thermal Cellulose Nanocrystal-based Hydrogel

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Abstract: Cellulose nanocrystal (CNC) prepared by hydrolysis of cotton linters with sulfuric acid was used to react with chloroauric acid to manufacture a gold nanoparticle/CNC composite. The composite was then graft-copolymerized with N-isopropylacrylamide to obtain a photo-thermal ultrafine gold nanoparticles/CNC-based hydrogel. The hydrogel was studied by performing scanning electron microscopy, and it was found that the prepared hydrogel had a network structure. The temperature of the hydrogel increased from 25°C to 39°C and its volume decreased by 30% when it was exposed to visible light (400~750 nm) for 1 h. The experiment results indicated that the prepared photo-thermal CNC-based hydrogel has thermal responsiveness and photo-thermal properties.

Keywords: CNC; gold nanoparticle/CNC composite; CNC-based hydrogel; photo-thermal hydrogel



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1 Introduction

Cellulose nanocrystal (CNC) generally refers to rod-shaped nanocrystals separated from cellulose with a width of 5 to 70 nm and an average length of several hundred nanometers. Since it is derived from biomass, nanocellulose has intrinsically the advantages of non-toxicity and biocompatibility. It has a high tensile strength because the crystalline cellulose has a high Young's modulus. In addition, nanocellulose has greater chemical activity, and can be modified as a catalyst support for catalysis reactions^[1-4]. Therefore, it can be applied in a wide range of applications, such as in chemical, food, pharmaceutical, composite materials, and new energy fields.

Gold nanoparticles (AuNPs) are nanosized gold particles having small size effect. In addition, they have a large specific surface area, high surface energy and catalytic activity, and unique physical and chemical properties, including surface effect, surface plasmon resonance (SPR) effects, and quantum size effects^[5-8]. However, due to the

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strong surface activity of the AuNPs and the strong van der Waals force between the particles, they easily aggregate in a solution. Nevertheless, monofunctional nanofillers only confer or improve a specific property of host matrices, whereas multifunctional nanofillers can provide multiple properties for the resultant nanocomposites. CNC has the function of being stabilizers, dispersants, and templates, which make them good carriers for AuNPs^[9-10].

Photo-thermal AuNP/nanocellulose-based hydrogels are smart hydrogels containing AuNPs with thermosensitive effect at specific wavelengths of illumination^[11]. AuNPs that have the SPR effect are self-assembled on nanocellulose, which causes the AuNPs/nanocellulose composite-based hydrogel to heat itself when exposed to a specific wavelength of light. At a critical temperature, volume shrinkage of hydrogel occurs, i.e., it discharges excess water to regulate drug release^[11]. The photo-thermal AuNP/nanocellulose-based hydrogel modified with poly(N-isopropylacrylamide) to impart heat sensitivity, may cause a volume change when the ambient temperature changes^[12-13]. In the preparation of photo-thermal AuNP/nanocellulose-based hydrogels, water molecules and hydrogen bonds are generated by amide bonds, so photo-thermal AuNP/nanocellulose-based hydrogels are prone to swelling to a large volume in the presence of water. In the polymer hydrogel system, there are intermolecular hydrogen bonds and intramolecular hydrogen bonds. When the ambient temperature is lowered, the hydrogen bonding force between the hydrogel macromolecule and the water molecule plays a leading role. The solvation between them increases, and the water molecules around the macromolecule form a regular solvated shell layer that is hydrogen bonded. At this point, the hydrophobic group is surrounded by solvated water molecules. At this time, the hydrogel absorbs water resulting in volume expansion. The intermolecular hydrogen bond is destroyed as the temperature increases, and the hydrophobic group is thus exposed. The hydrogen bonding inside the macromolecule is dominant, and the hydrogel network

undergoes volume shrinkage^[14]. Photo-thermal UAuNP/CNC-based hydrogels with an unique three-dimensional network structure was prepared in this study. The hydrogels have a number of specific advantages; e.g., they are insoluble in water and exhibit a very good biocompatibility and swelling ratio so that they can be used as pharmaceutical loads for drug release^[15-18].

2 Experimental

2.1 Materials

Cotton linters with a moisture content of 8% were supplied by Fumin Chemical Fiber Co., Ltd. (Shandong, China). Sulfuric acid (98 wt%), sodium hydroxide, and potassium persulfate (KPS) were of analytical grade and purchased from the Guangzhou Chemical Reagent Factory (Guangzhou, China). Gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), N-isopropyl acrylamide (NIPAm), and N,N'-methylenebisacrylamide (MBA) were purchased from Shanghai Aladdin Co., Ltd., China. All these chemicals were used without further purification.

2.2 Preparation of CNC

CNC was prepared from cotton linters by acid hydrolysis according to a previously reported method^[19]. First, 64 wt% H_2SO_4 and dry cotton linters were added with a ratio of 13.5:1 (w/w) in a beaker. The mixture was stirred at 45°C for 90 min, and then diluted 10 times to terminate the reaction with water. The reactant was centrifuged and washed 3 times. The reaction residue was collected and dialyzed for 3 days until the pH value was neutral. Finally, uniform CNC was obtained by ultra-sonication at 40°C for 3 min and stored at 4°C for further experiments^[19-20].

2.3 Preparation of UAuNP/CNC composites

UAuNPs were prepared in the presence of CNC according to an established method with some modifications. HAuCl_4 (9.71 mmol/L, 542 μL) was put into a 50 mL CNC (0.5 wt%) suspension at 65°C under constant magnetic stirring for 45 min and pH value of 12 which was adjusted by using 0.5 mol/L NaOH.

2.4 Preparation of photo-thermal CNC-based hydrogel

1 g of NIPAm and 0.035 g of MBA were added into 20 mL of UAuNPs/CNC composite suspensions and shaken uniformly, and then transferred to a 50 mL centrifuge tube. The grafted polymerization was initiated by adding 0.0565 g of KPS at 25~35°C and kept for 24 h. The obtained hydrogel was immersed in deionized water and stored in an environment of 3°C for analysis.

2.5 Characterization

X-ray diffraction (XRD) patterns of freeze-dried UAuNP/CNC composites were collected on a D8 Advance X-ray diffractometer (Bruker Corporation, Germany) using Ni-filtered Cu K α radiation ($\lambda=0.15418$ nm) at 40 kV and 20 mA. Data were collected over the 2θ range of 5°~90° with a scan step size of 0.04° at a scanning rate of 1°/min. UV-vis absorption spectra from 400 nm to 1000 nm were obtained on an Agilent Technologies HP-8453 spectrophotometer (Karlsruhe, Germany) with deionized water as the blank. The morphologies and sizes of the AuNPs were observed by transmission electron microscopy (TEM) (H-7650, Hitachi, Japan) at 80 kV accelerating voltage. Fourier transform infrared spectroscopy (FT-IR) spectra of neat CNC and UAuNP/CNC composites in KBr discs were recorded using a Vector 33 spectrometer (Bruker, Germany) from 500 to 4000 cm⁻¹.

3 Results and discussion

3.1 Preparation of UAuNPs/CNC composites

When HAuCl₄ was added to the CNC suspension, the UAuNP was formed on the CNC, which acted as both a supporting substrate and a reducing agent. When a suitable ratio of CNC and HAuCl₄ was employed, the gold particles would be UAuNP and formed UAuNPs/CNC composites, which were identified by XRD analysis. Fig.1 shows the XRD patterns of CNC and UAuNPs/CNC composites.

Compared to the XRD pattern of CNC, that of UAuNPs/CNC composites had many changes after

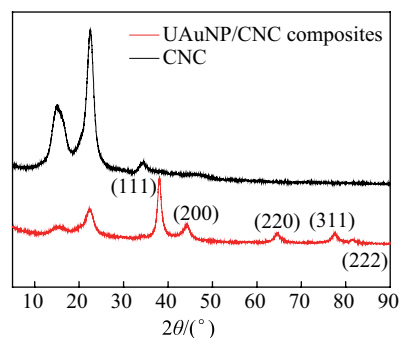


Fig.1 XRD patterns of CNC and UAuNP/CNC composites

reaction, with characteristic peaks appearing at $2\theta=38.1^\circ$, 44.1° , 64.6° , 77.4° , and 81.7° , corresponding to Au (111), (200), (220), (311), and (222) crystal planes, respectively, which indicated the formation of crystalline gold particles^[21-22].

3.1.1 Effect of CNC concentration on UAuNP/CNC composite

The effect of CNC concentration on the UAuNPs/CNC composite is illustrated in Fig.2 and Fig.3. According to Fig.2, as the CNC concentration increased, the amount of UAuNP/CNC composite produced increased, indicating that the increase in the concentration of CNC as a reducing agent was beneficial to the completion of the reaction of UAuNP/CNC composite. Moreover, as the concentration of CNC increased, the SPR bands narrowed substantially, indicating that both the general monodispersity and homogeneity (size distribution) of the UAuNPs improved^[23-24]. Fig.3 shows more clearly that as the concentration of CNC increased, the resulting UAuNP/CNC composite dispersibility

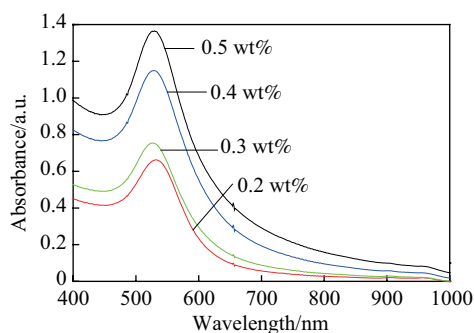


Fig.2 UV-vis absorption spectra of UAuNP/CNC composites prepared using different concentrations of CNC (0.2 wt%, 0.3 wt%, 0.4 wt%, and 0.5 wt%)

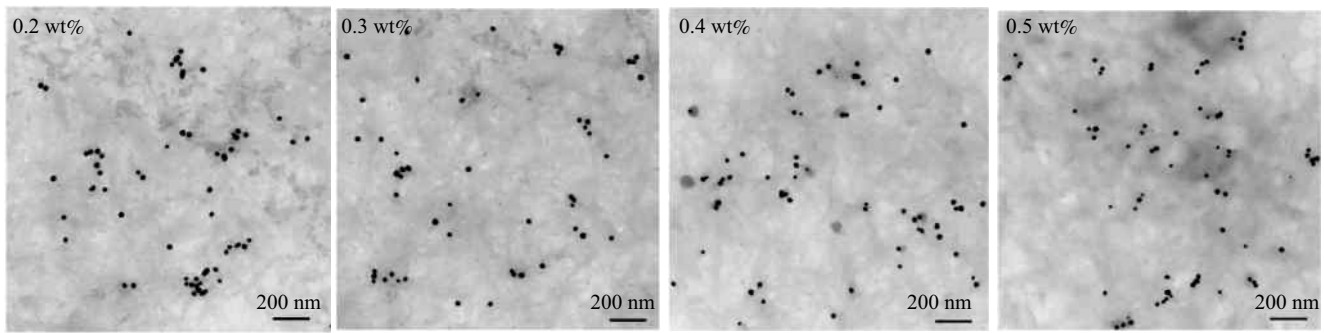


Fig.3 TEM images of the UAuNP/CNC composites prepared using different concentrations of CNCs (0.2 wt%, 0.3 wt%, 0.4 wt%, and 0.5 wt%)

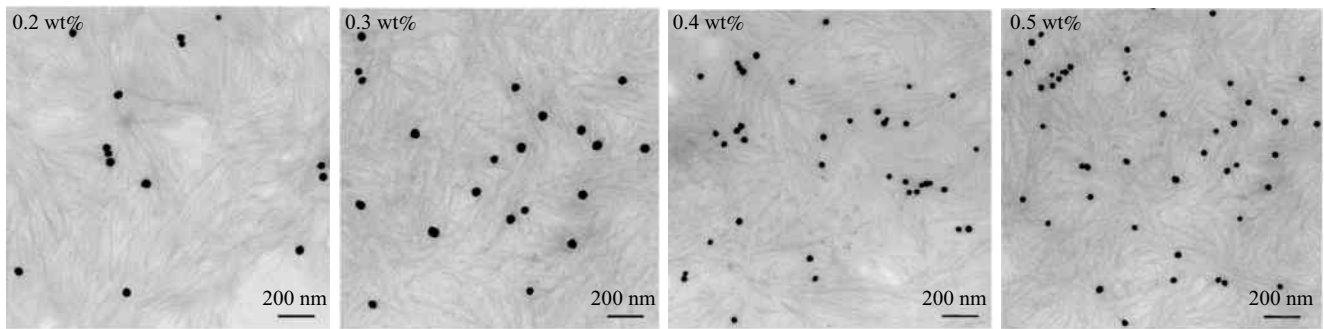


Fig.4 TEM images of the UAuNP/CNC composites prepared using different concentrations of HAuCl_4 (0.2 wt%, 0.3 wt%, 0.4 wt%, and 0.5 wt%)

improved. However, the CNC concentration had no significant effect on the particle size of the UAuNP/CNC composite.

3.1.2 Effect of HAuCl_4 concentration on UAuNP/CNC composite

The concentration of HAuCl_4 also has a certain effect on the UAuNP/CNC composite. Fig.4 and Fig.5 show that as the concentration of HAuCl_4 increased, the amount of UAuNP/CNC composite produced increased. This is because the reactant content had increased. However, it

could be observed from Fig.4 that the concentration of HAuCl_4 had an effect on the particle size and dispersion of UAuNP/CNC composite.

3.1.3 Effect of pH value on UAuNP/CNC composite

pH value is also an important influence condition for UAuNP/CNC composite. As can be seen from Fig.6, with the increase of the pH value from 4.47 to 12.50, a blue shift of the UV spectrum occurred, indicating that the size of the UAuNP decreased. It can be seen in Fig.7 that as the pH value increased, the particle size of

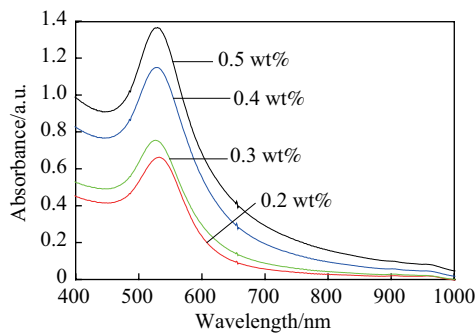


Fig.5 UV-vis absorption spectra of UAuNP/CNC composites prepared using different concentrations of HAuCl_4 (0.2 wt%, 0.3 wt%, 0.4 wt%, and 0.5 wt%)

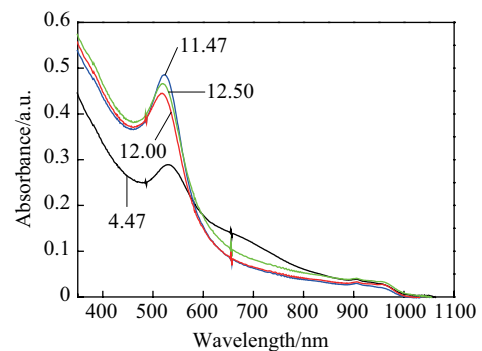


Fig.6 UV-vis absorption spectra of UAuNP/CNC composites prepared under different pH values (4.47, 11.47, 12.00, and 12.50)

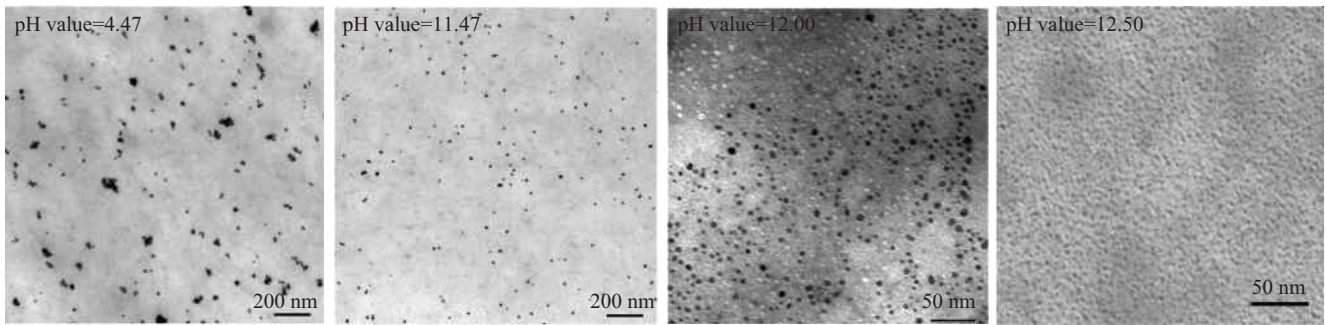


Fig.7 TEM images of the UAuNPs/CNC composites prepared under different pH values (4.47, 11.47, 12.00, and 12.50)

the UAuNPs gradually decreased. This indicates that the pH value has a great influence on the particle size of the UAuNPs, and the alkaline condition was more favorable for forming smaller UAuNPs.

3.2 Preparation of photo-thermal UAuNP/CNC-based hydrogel

3.2.1 Characterization of UAuNP/CNC-based hydrogel

The FT-IR spectra of the CNCs and photo-thermal UAuNP/CNC-based hydrogel are illustrated in Fig.8. It could be seen from Fig.8 that there are peaks appearing around 2904, 1433, 1656, 3342, 1059 and 1164 cm^{-1} on the FT-IR spectrum of CNC. The peaks are characteristic vibration peaks of CNC. On the FT-IR spectrum of the UAuNPs/CNC-based hydrogel, it can be seen that peaks appear around 1660, 1546 and 1158 cm^{-1} , which corresponds to the amide I band (N—C=O) vibration peak, amide II band (N—H) vibration peak and vibration peak of C—C on isopropyl of the monomeric NIPAm, indicating that NIPAm was successfully grafted on the UAuNPs/CNCs composites.

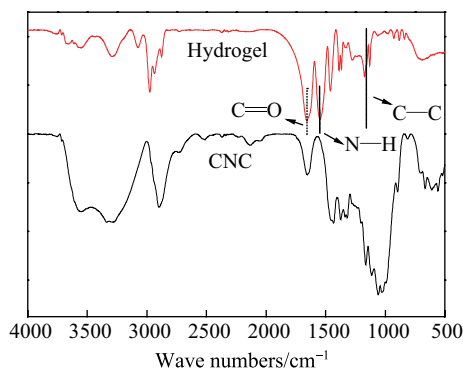


Fig.8 FT-IR spectra of the CNC and photo-thermal UAuNP/CNC-based hydrogel

In vacuum freeze-drying, the moisture in the composite hydrogel evaporated without destroying the internal structure of the hydrogel in the swollen state, which allowed the original internal morphology of the hydrogel to remain intact.

Fig.9 is an SEM image of the photo-thermal UAuNP/CNC-based hydrogel showing its porous structure which is an important factor affecting its swelling behavior.

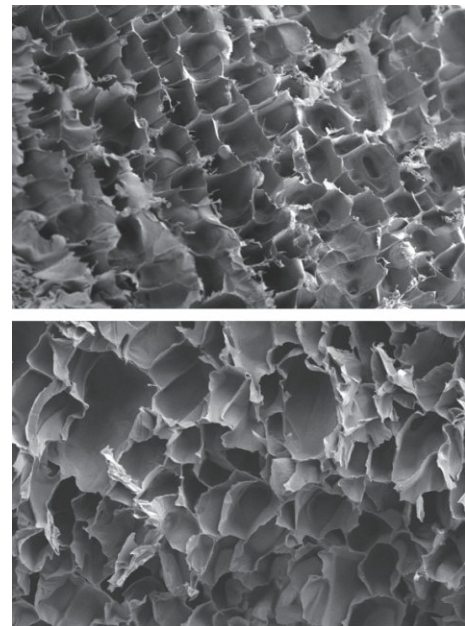


Fig.9 SEM images of the photo-thermal UAuNP/CNC-based hydrogel

Fig.10 (a) is the photo-thermal UAuNP/CNC-based hydrogel obtained after lyophilization, and Fig.10 (b) is the photo-thermal UAuNP/CNC-based hydrogel after swelling equilibrium. It can be clearly observed that the hydrogel after swelling equilibrium is expanded in volume compared with the dried hydrogel.

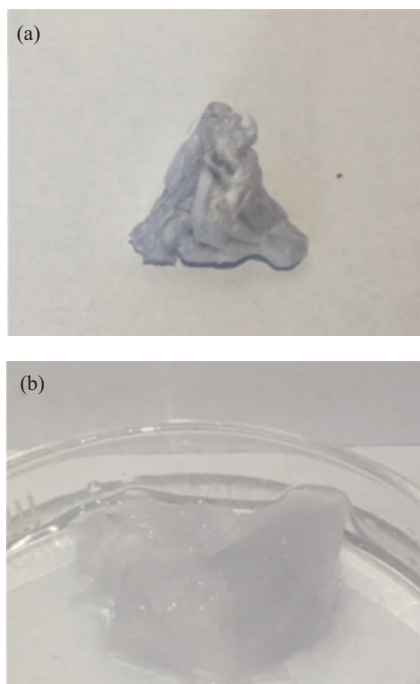


Fig.10 Photo-thermal UAuNP/CNC-based hydrogel in lyophilized state (a) and saturated swollen state (b)

3.2.2 Photo-thermal experiment

Fig.11(a) is the photo-thermal UAuNPs/CNC-based hydrogel, which shows a purplish red color because of adding UAuNPs. Fig.11(b) is a heat-sensitive nanocellulose-based hydrogel as a control group which is colorless and transparent. SPR possessed by the UAuNPs shows a photo-thermal effect. When illuminated with a specific wavelength, the heating of the UAuNPs causes the dehydration of the hydrogel. Heat-sensitive nanocellulose-based hydrogel without UAuNPs was used in blank comparison experiments because the heat generated by the instrument itself causes errors in the results.

Fig.12 shows the changes in the photo-thermal UAuNP/CNC-based and heat-sensitive nanocellulose-based hydrogels before and after illumination.

As can be seen from Fig.12(b), the amount of water released by

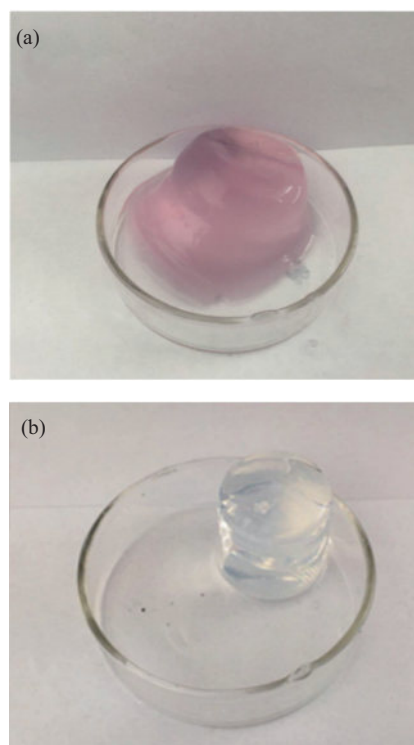


Fig.11 Photo-thermal UAuNP/CNC-based hydrogel (a) and heat-sensitive nanocellulose-based hydrogel (b)

the photo-thermal UAuNP/CNC-based hydrogel (Fig.12(bi)) was more than that by the heat-sensitive nanocellulose-based hydrogel (Fig.12(bii)). It was calculated that the percentage of dehydration of the photo-thermal UAuNP/CNC-based hydrogel was

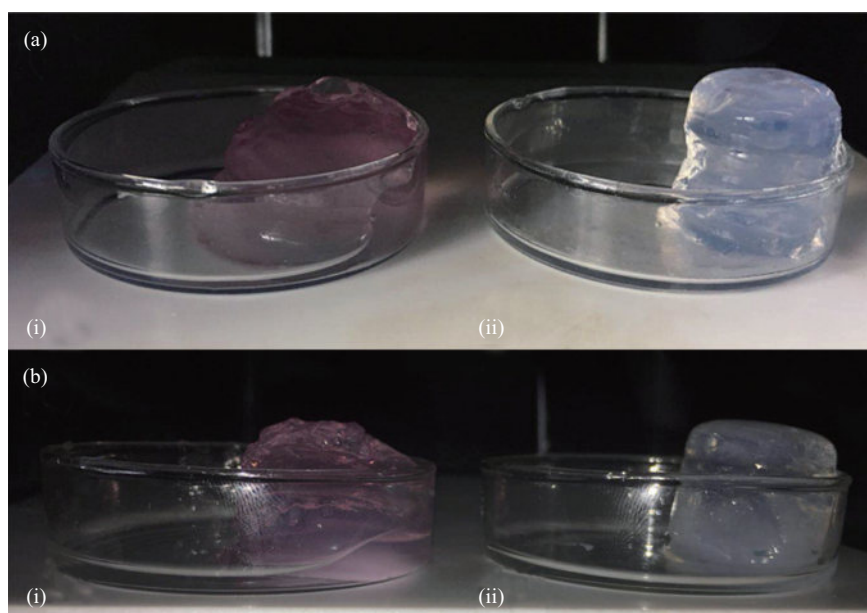


Fig.12 Photo-thermal experiment of UAuNPs/CNC-based hydrogels (i) and nanocellulose-based hydrogel (ii) before the illumination of light (a) and after the illumination of light (b)

29.9%, while the percentage of dehydration of heat-sensitive nanocellulose-based hydrogel was 17.7%. And when exposing to light with a specific wavelength (400~750 nm) for 1 h, the temperature of the photo-thermal UAuNP/CNC-based hydrogel increased from 25°C to 39°C and its volume decreased by 30%. The UAuNPs exhibits a photo-thermal effect, and this property can be applied to the photo-thermal UAuNP/CNC-based hydrogel, which can cause it to heat under light conditions, thereby causing dehydration of the hydrogel.

4 Conclusions

Ultrafin gold nanoparticlives/cellulose nanocrystal (UAuNP/CNC) composite can be prepared by controlling the pH value and the concentration of CNC and Gold (III) chloride trihydrate (HAuCl₄). Increasing the concentration of CNC can improve UAuNP/CNC composite dispersion, while increasing the concentration of HAuCl₄ led to a higher number of UAuNPs loaded onto CNC during the formation process. Further, a higher pH value was favorable for forming smaller-sized UAuNP/CNC composite particles.

The photo-thermal UAuNP/CNC-based hydrogel has a porous structure. The photo-thermal properties of UAuNP/CNC-based hydrogel were studied. It was found that the photo-thermal UAuNP/CNC-based hydrogel possesses higher dehydration rate than the heat-sensitive nanocellulose-based hydrogel under specific wavelengths of light (400~750 nm). It proved that the UAuNPs will heat up itself under the illumination due to the unique plasmon resonance effect, which causes the hydrogel to dehydrate.

Acknowledgments

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