

ORIGINAL ARTICLE

Preparation of photo-responsive hybrid materials based on hydrogels involving imidazolium-presenting gold nanoparticles

Kazuo Tanaka¹, Kensuke Naka², Eisuke Miyoshi¹, Asako Narita¹ and Yoshiki Chujo¹

In this study we developed hydrogel-based hybrid materials with gold nanoparticles that have tunable optical properties under light irradiation. Attaining the stimuli-responsive dynamic changes in the solid material from the optical properties of the gold nanoparticles depended on the interparticle distance, and we designed hydrogel-based organic–inorganic hybrids with gold nanoparticles. Homogeneously dispersed states of the modified gold nanoparticles were achieved in the hydrogel with the interaction of the imidazolium units tethered to both the nanoparticle surfaces and the side chains of the networks. Initially, we found that the absorption properties could be changed by swelling and shrinking the hydrogels. Next, by using the photo-responsive mono-carboxylate linker, we induced the photo-triggered modulation of the absorption properties of the hydrogels. These results can be explained by a change in the interparticle distance within the hydrogel matrix.

Polymer Journal (2016) 48, 177–181; doi:10.1038/pj.2015.89; published online 7 October 2015

INTRODUCTION

The development of organic–inorganic hybrid materials is a topic of great importance because of the high potential of these materials to present unique properties different from the intrinsic characteristics of each component. In particular, because of their high transparency and durability, hybrid materials are regarded as a suitable scaffold for the construction of functional optical materials.^{1–3} Recently, using hybridization to fix unstable nanostructures or short-lived states inside materials has allowed the achievement of a number of interesting properties, such as oxygen-resistant phosphorescence⁴ and multi-colored emissions.^{5,6} Moreover, by employing heteroatom-containing functional units called as the element blocks,⁷ the introduction of new functionalities was accomplished, including the ability to generate heat under microwave irradiation.^{8,9} Furthermore, the disadvantages of conventional hybrids, such as low conductivity, were overcome.¹⁰ In general, owing to the intrinsic stability of inorganic materials, hybrid materials are highly robust.^{11–15} Therefore, hybridization is a valid strategy to enhance the thermal and mechanical properties of polymeric materials.¹⁶ However, this also means that the hybrids show poor tunability after shape formation. Therefore, there are still significant difficulties in preparing hybrids that demonstrate dynamic changes in their properties when exposed to external stimuli.¹⁷

Gold nanoparticles (gold atoms; Au_n, $n < 100$) exhibit a characteristic light absorption that originates from the coherent oscillation of the conduction band electrons (surface plasmon oscillations) induced by interaction with an electromagnetic field.^{18,19} Because it is possible

to tune their optical properties through the assembly states of the nanoparticles, biosensors or stimuli-responsive materials have been fabricated based on modified gold nanoparticles.^{20,21} We have recently reported the synthesis and unique aggregation behavior of imidazolium-presenting gold nanoparticles.^{22,23} The aggregation states can be observed by performing an anion exchange under mild conditions.²² In addition, the interparticle distances between the gold nanoparticles in the aggregates varied depending on the counteranion used. Moreover, water-dispersive aggregates were achieved by including a photo-responsive linker, and the interparticle distances in the aggregates were tuned by the light irradiation.²³ Although we have established the simple tools needed to precisely control the aggregation morphology of the particles, these dynamic changes can be observed only in the fluid state. It is important to understand the dynamic changes in the dispersion/aggregation states of the nanoparticles under mobility-restricted conditions and to obtain the optical properties as observed in the fluids to fabricate functional materials based on the tunable properties of gold nanoparticles.

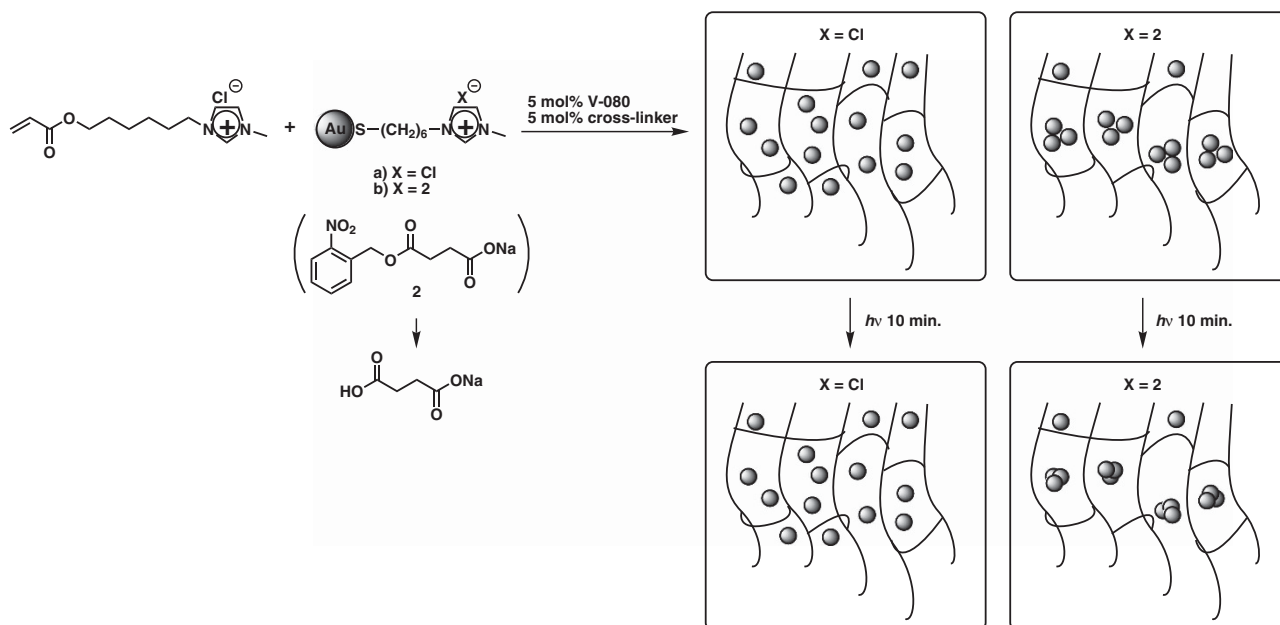
We have presented a series of organic–inorganic hybrid gels composed of organic linkers and inorganic crosslinking points.^{24–27} Moreover, various types of nanoparticle-based functional materials have been reported via surface modification with nanoparticles.²⁸ To maintain the mobility of the particles and the material properties of a solid, we focused on hydrogels^{29–31} as scaffolds to achieve the stimuli-responsive dynamic changes in the solid materials, exploiting the optical properties of the gold nanoparticles. Herein, we present the preparation of hydrogel-based hybrid materials with gold

¹Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, Japan and ²Faculty of Molecular Chemistry and Engineering, Graduate School of Science and Technology, Kyoto Institute of Technology, Kyoto, Japan

Correspondence: Professor Y Chujo, Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyō-ku, Kyoto 615-8510, Japan.

E-mail: chujo@chujo.synchem.kyoto-u.ac.jp

Received 8 July 2015; revised 5 August 2015; accepted 14 August 2015; published online 7 October 2015



Scheme 2 Schematic model of the photoreaction with the synthesized hydrogels.

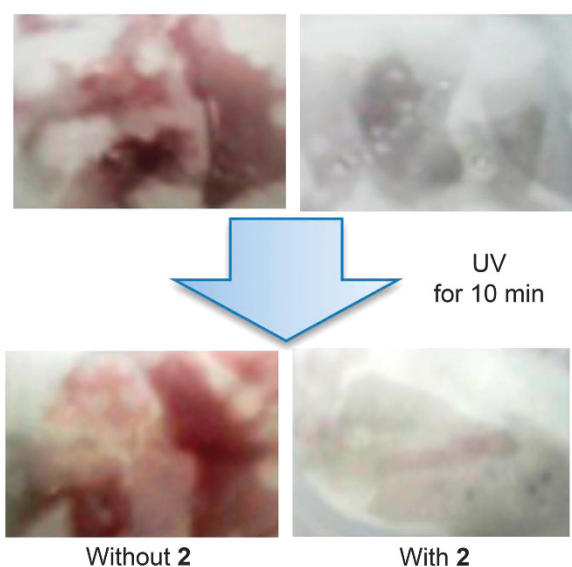


Figure 3 Changes in the appearance of the nanoparticle-containing hydrogels with and without 2.

was removed from the water and excess moisture was removed with a Kimwipe before the weight was measured (185 mg).

Photoreactions

The typical procedure is described here: the sample was placed in a quartz glass test tube that was located on the center of spiral-shaped mercury lamp. Then, the sample was irradiated with UV light at room temperature.

RESULTS AND DISCUSSION

To achieve the stimuli-responsive behavior and tunable properties of the hydrogel by performing an anion exchange, we designed a hydrogel possessing imidazolium units along the side chains of the hydrogel network and the nanoparticle surface. Gold nanoparticles modified with methylimidazolium cations NPIm and vinyl monomer

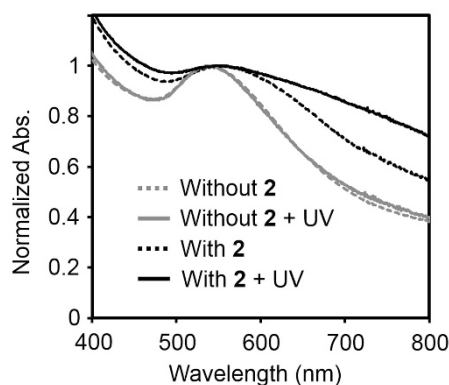


Figure 4 Absorption changes of the hydrogels with and without 2 by ultraviolet (UV) irradiation.

1 tethering the imidazolium unit were synthesized as described in previous reports.^{22,32,33} After the preparation of each material, NPIm was dispersed in an aqueous solution of 1, and hydrogelation was induced in the presence of a water-soluble azo-initiator VA-080 and the crosslinker tetraethylene glycol diacrylate (Scheme 1). After incubation for 20 h at 80 °C, a blue-colored transparent film was obtained (Figure 1). To evaluate the maximum capacity of the hydrogel with NPIm, the polymerization was performed at various feed ratios of 1 and NPIm. After hydrogelation, the synthesized hydrogels were soaked in water (Supplementary Figure S1). Desorption was observed to occur from the hydrogel prepared using a mixture containing 100 mg of 1 and 10 mg of NPIm. Therefore, we prepared hydrogels using 1 mg of NPIm and <100 mg of 1. The products exhibited a high moisture absorbency. In addition, in the swollen state, the gels showed poor mechanical robustness. Therefore, the samples readily adopted irregular shapes, as shown in Figure 1.

The polymerization was monitored by Fourier transform infrared spectroscopy (Supplementary Figure S2). Absorptions at 1415 (out-of-plane vibration), 983 and 839 cm⁻¹ (out-of-plane bending vibration of vinyl C-H) disappeared after a 20-h incubation period. From these

results, we concluded that the polymerization was complete. From thermogravimetric analysis, the residue was 0.75 wt% (Supplementary Figure S3). This value is consistent with the theoretical weight percentage of Au as calculated from the feed ratio (0.80 wt%). These results suggest that the gold nanoparticles are incorporated quantitatively into the hydrogel networks. Elemental analysis also supports the quantitative introduction of gold nanoparticles into the hydrogel networks (calcd. $(C_{13}H_{24}ClN_2O_2)_{0.95}(C_{14}H_{22}O_7)_{0.05}(C_{10}H_{21}ClN_2S)_{0.02}(Au)_{0.11}$, found $(C_{13}H_{24}ClN_2O_2)_{0.87}(C_{14}H_{22}O_7)_{0.04}(C_{10}H_{21}ClN_2S)_{0.02}(Au)_{0.10}(H_2O)_{0.08}$).

The swelling behavior of the synthesized hydrogels was also examined (Figure 1). The synthesized hydrogels were observed to efficiently absorb water. The weight of the hydrogel was significantly elevated after swelling in distilled water to 185 from 27 mg. The swelling ratio of the hydrogel was calculated to be 691%. The hydrogel exhibited color changes before and after swelling. By washing the hydrogel with water, the color changed from blue to red. From the UV–vis absorption spectra, the absorption band at 561 nm derived from the surface plasmon resonance of the gold nanoparticles shifted to 515 nm after the washing treatment (Figure 2). These data are representative of the interparticle separation between adjacent nanoparticles within the hydrogel and indicate that the interparticle distance should be enlarged in the swollen state. It is likely that each particle is isolated by swelling the hydrogel because the nanoparticles interact strongly with the hydrogel network via the imidazolium moieties.

Finally, we investigated stimuli-responsive changes in the optical properties based on the gold nanoparticle-containing hydrogels. A schematic illustration of the system is shown in Scheme 2. To achieve the light-responsive behavior, we used a photo-cleavable linker.²³ In the presence of the mono-carboxylate linker **2** with a photo-cleavable ester, NPIIm can form water-dispersive aggregates. Triggered by UV irradiation, the linker should be transformed into the dicarboxylate, leading to tight binding with the gold nanoparticles. As a result, the observed red-shift of the absorption band can be expected, particularly when these changes proceed in the aggregates. Therefore, it may be presumed that the restricted mobility of the nanoparticles is negligible. To probe the validity of this scenario, the hydrogel was prepared using the same method described previously in the presence of **2**. The gelation proceeded with the aggregation of gold nanoparticles. After washing with distilled water, red-colored hydrogels were obtained (Figure 3).

To investigate the photo-responsive behavior of these hydrogels, a low-pressure mercury lamp was used to directly irradiate the prepared hydrogels for 10 min. Before and after photo-irradiation, the UV–vis spectra were recorded (Figure 4). In the absence of **2**, no significant changes were observed by UV–vis spectroscopy. In contrast, a small increase in the absorption within the longer wavelength region was observed for the hydrogel involving **2** after UV irradiation. A corresponding slight color change was observed for the sample containing **2** (Figure 3). These data indicate that the interparticle distance is reduced by UV irradiation. It should be noted that the nanoparticle aggregation can be induced by light irradiation even in the spatially restricted matrix, leading to a change in optical properties.

CONCLUSION

We accomplished a light-driven absorption change derived from the modulation of the interparticle distance in the aggregates of gold nanoparticles within a hydrogel matrix. Our results resolve a significant issue, that is, whether the functions originating from nanostructures can be preserved in solid materials. The detected

optical properties of the hydrogel matrix originated from the dispersion and aggregation states of the gold nanoparticles. Furthermore, these changes can be induced by light irradiation. In particular, even under mobility-restricted conditions, properties derived from the aggregation state of the gold nanoparticles can be achieved. This strategy is feasible for dynamically regulating the nanostructures within the matrix. Thus, it can be said that our concept is valid for developing nanostructured materials with tunable properties.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ACKNOWLEDGEMENTS

This work was partially supported by a Grant-in-Aid for Scientific Research on Innovative Areas ‘New Polymeric Materials Based on Element-Blocks (No. 2401)’ (25102521) of The Ministry of Education, Culture, Sports, Science and Technology, Japan.

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Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)