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Liquid Metal Nanoparticles as High Efficient Photoinitiator to Develop Multifunctional Hydrogel Composites

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Keywords: liquid metal, photoinitiator, radical polymerization, hydrogel, composites

Abstract

Liquid metal (LM) composites are a class of emerging soft multifunctional materials promising for a variety of applications, yet the chemistry properties of LM have not been fully understood. Here we report that LM nanoparticles can directly perform as a photoinitiator for radical polymerization and the in-situ development of highly tough and multifunctional LM hydrogel composites. It is revealed that the photocatalytic activity of LM nanoparticles originates from the oxide layer on LM. Significantly, positively charged metal-organic framework (MOF) nanoparticles are used to stabilize LM nanoparticles in aqueous solutions, where the MOF can anchor on the surface of LM nanoparticles by electrostatic interaction while help to preserve the unshielded oxide layer, therefore realizing the high efficient photo-initiation and polymerization. The LM nanoparticle initiated photopolymerization is shown to develop hydrogel composites featuring excellent stretchability, stimuli-responsiveness and sustained photocatalytic activity. The photocatalytic polymerization initiated by LM nanoparticles not only deepens the understanding on the semiconductor properties of the oxide skin on LM, but also broadens the application scenarios of multifunctional LM/polymer composites in smart materials, wearable electronics, and soft robotics.
1. Introduction

Gallium-based liquid metal (LM) with a unique combination of fluidity, metallic conductivity, low toxicity, and specific surface chemistry has emerged as a promising class of materials for diverse applications from stretchable electronics\textsuperscript{1, 2} and soft robotics\textsuperscript{3, 4} to biomedicine\textsuperscript{5, 6} and catalysis.\textsuperscript{7, 8} Due to the ultrahigh surface tension of LM,\textsuperscript{9} polymers or organic ligands are widely used to help disperse bulk LM into micro/nanoparticles which can be further used in the development of functional composites and devices.\textsuperscript{10-12} In those systems, the organic molecules play a key role in lowering the surface energy and stabilizing the LM particles through various chemical/physical interactions with the LM surface.\textsuperscript{13-15} However, the ultimate contact and wrapping of organic molecules onto the LM particles will greatly shield the chemical properties of the LM particles.\textsuperscript{16} It is revealed that polymerization can be triggered during the ultrasonication of LM-monomer dispersion, in which the freshly generated LM particles can facilitate electron transferring to the surrounded monomers.\textsuperscript{17, 18} While the reaction rate is rapidly decayed when the ultrasonication cannot enable sufficient production of fresh LM particles or when the LM surface is wrapped by polymer products.\textsuperscript{19} Specific initiators can be immobilized on the surface of LM particles to prepare stable dispersion which can be used for surface-initiated atom transfer radical polymerization and thus the development of LM-polymer nanocomposites,\textsuperscript{20} yet the sophisticated synthesis procedure would suppress further downstream applications.

The gallium-based LM can instantaneously form a passivating oxide layer upon exposure to oxygen, in the form of Ga$_2$O$_3$ nanocomposites (~0.5-3 nm thickness) which is dictated by the thermodynamically more favorable elements from the dynamic continuum surface.\textsuperscript{21-23} The presence of an oxide skin can protect the LM from further oxidation and influence other physicochemical properties of the LM surface. Many metal oxides such as TiO$_2$, ZnO, and Fe$_2$O$_3$ demonstrate semiconductivity when they are in the form of nanomaterials and have been widely employed for photocatalytic reactions,\textsuperscript{24, 25} such as initiating radical polymerization,\textsuperscript{26}. 
removal of organic pollutants and recovery of precious metals. Photochemically initiated polymerization is prominent of its spatiotemporal manipulability and wide applicability. However, the semiconductor-based photocatalytic properties of the nanoscale oxide skin on LM particles is still elusive.

Herein, we report the photocatalytic capability of LM nanoparticles for high efficient initiation of radical polymerization and following in-situ development of multifunctional LM hydrogels. With the great stabilization effect of metal-organic framework (MOF) nanoparticles to LM by electrostatic interaction, the LM nanoparticles can be processed to a dispersion with high stability and excellent solution reprocessability. Under ultraviolet light irradiation, the LM nanoparticles can produce a large amount of hydroxyl radicals for the photoinitiated polymerization of vinyl monomers (Figure 1a), which was exclusively attributed to the nanoscale Ga$_2$O$_3$ layer. In stark contrast to traditional metal oxide nanocatalysts and organic photoinitiators, the LM nanoparticles demonstrate an exceptional toughening effect for the prepared hydrogel composites. Moreover, the LM nanoparticles can retain its photocatalytic capacity after the formation of hydrogels, which can be used for the further fabrication of double-network stimuli-responsive hydrogels as well as the adsorption and photocatalytic degradation of organic pollutants. This work would offer a great opportunity not only for broadening the research of photocatalysis of LM but also for developing multifunctional LM hydrogel composites toward broad applications.

2. Results and Discussion

We here combine eutectic gallium indium (EGaIn) alloy with MOF nanoparticles by ultrasonic mixing, producing a stable and solution-reprocessable nanopowdery composite, termed LM nanocomposite (Figure 1b). MOF is an emerging porous crystalline material promising in various applications, such as adsorption, separation, and catalysis. The positively charged MOF nanoparticles can anchor on the surface of EGaIn nanoparticles by electrostatic
interaction, where porous structures will form according to the nanoparticle aggregation theory. Therefore, the anchoring of MOF nanoparticles could facilitate the exposure of the solid Ga$_2$O$_3$ layer on LM particle for the photoinitiation of radical polymerization. Using zeolitic imidazolate framework-8 (ZIF-8) as a typical example, we fabricated a series of LM nanocomposites containing different volume of EGaIn (40 vol%–70 vol%, Figure S1), where the LM nanoparticles are anchored and stabilized by ZIF-8 nanoparticles, and the amount of anchored ZIF-8 nanoparticles will decrease with a higher EGaIn content in the LM nanocomposite. The size of the ZIF-8 nanoparticles is around 380 nm while the size distribution of the LM particles is 520~1670 nm, as determined by dynamic light scattering (Figure S2). The LM nanocomposites can maintain the crystallinity of ZIF-8 and demonstrate an amorphous peak of Ga$_2$O$_3$ with increasing content of LM, as shown in the powder X-ray diffraction (PXRD) curves (Figure S3). Moreover, the transmission electron microscopy (TEM) image displays that the ZIF-8 nanoparticles firmly encircle and adhere to the LM nanoparticle (Figure 1c), verifying the exceptional stabilization effect of MOF nanoparticles to LM particles. The scanning electron microscope (SEM) image and corresponding energy dispersive X-ray spectrometry (EDS) mapping further prove the homogeneous dispersion of LM nanoparticles and ZIF-8 nanoparticles in the LM nanocomposite (Figure 1d). The decoration of MOF nanoparticles to LM particles would not only effectively prevent the coalescence of LM particles, but also expose the bare oxide layer of LM particles. Such stabilization effect can be realized by various positively charged MOFs such as ZIF-67, UiO-66, and MIL-101(Cr) (Figure S2), and the developed LM nanocomposites can preserve the structural and crystal properties of original MOFs (Figure S4).

The LM nanocomposites can be re-dispersed in various solvents (e.g., water, acetone, ethyl acetate, and tetrahydrofuran) with good colloidal stability even after 7 days (Figure S5). The measured surface charge and hydrodynamic diameter of the LM nanocomposites vary accordingly with the changes of LM volume fractions (Figure S6), which confirms the
electrostatic interaction between LM and MOF nanoparticles. When dispersed into ionic solutions with various concentrations (Figure S7), the colloidal stability of the dispersion would decline as the ionic concentration increases. This should be due to the extraneous ions would disrupt the electrostatic stability of the ZIF-8 stabilized LM particles. On the other hand, the LM oxide layer will be removed when strong acid or base are added, resulting in coalescence and sedimentation. Considering the effect of LM content on colloidal stability, we selected the LM nanocomposite with 60 vol% LM for subsequent studies.

The photocatalytic activity of LM nanocomposite for radical polymerization was thereafter demonstrated with a typical vinyl monomer, acrylamide (AAm). As shown in Figure 2a, an aqueous solution containing 10 wt% AAm and 1 wt% LM nanocomposite could polymerize to a gel under UV irradiation at room temperature for 2 h, as confirmed by rheological test (Figure S8). It should be noted that the penetration depth of UV light to the precursor solution is about several millimeters according to the UV-vis absorbance curve of the LM nanocomposite dispersion (Figure S9). Therefore, the thickness of the precursor solution should be well controlled. In contrast, the control experiments using ZIF-8 or pristine LM nanoparticles as catalysts cannot form a gel. Although the LM particles can initiate polymerization, it shows poor stability in the monomer solution that results in a supernatant in the dispersion. Moreover, the combination of gallium oxide and MOF also shows the same photocatalytic effect for initiating polymerization (Figure S10). Other stabilizers such as 2-methylimidazole and silica nanoparticles have been used to stabilize LM nanoparticles and their performance is comparable to MOF nanoparticles (Figure S11). Without irradiation or catalyst, the monomer solution almost remained unchanged after 2 h (Figure S12a). It should be noted that the photopolymerization shows limited performance in organic solvents (Figure S12b). The polymerization product was identified by $^1$H NMR and FT-IR spectroscopy. The emerging signals at chemical shift ($\delta$) of ~1.5 ppm and ~2.06 ppm can be assigned to the methylene protons and methine protons in polyacrylamide (PAAm), respectively (Figure 2b).$^{17}$ The FT-
IR spectra further confirmed the production of PAAm as the C=C stretching vibration at 1619 cm$^{-1}$ nearly disappeared (Figure 2c). To study the polymerization kinetics, the evolution of monomer conversion has been plotted with time (Figure 2d). The conversion shows a progressive increase and would achieve a high value of 98% after irradiation for 2 h, agreeing well with the rise of the suspension viscosity (Figure 2e). In addition, the catalyst amount has a significant influence on the conversion, where it would go above 80% with a catalyst content of 0.7 wt% or higher (Figure 2f). The size of LM particles will also affect the conversion, as the LM particles with a size distribution of 120~500 nm demonstrate a faster growing of conversion within 1 h (Figure S13). The better photocatalytic performance is possibly due to a larger specific surface area of smaller LM particles. Moreover, the photopolymerization initiated by LM requires less time than sonication assisted radical polymerization compared to previous studies as summarized in Table S1. This LM nanocomposite initiated photopolymerization is applicable to various vinyl monomers, such as N-isopropylacrylamide, 2-hydroxyethyl acrylate, and methacrylic acid (Figure S14).

Active hydroxyl radicals (•OH) generally play a critical role in the photopolymerization initiated by semiconductor-type photoinitiators. $^{37,38}$ We therefore hypothesize that the bare and exposed oxide layer on LM nanoparticles will generate electron/hole pairs upon light excitation, which lead to the oxidization of water and the production of •OH for initiating the radical polymerization of vinyl monomers (Figure 1a). To verify the hypothesis, photocatalytic •OH production over the LM nanocomposite has been examined using terephthalic acid (TA) as fluorescent probe (Figure 3a). $^{39}$ The detection for LM nanocomposite shows the most intense fluorescent signal with 2 h irradiation (Figure 3b and Figure S15), implying a high •OH production rate. In contrast, the intensity plot of ZIF-8 displays an identical trend as the control experiments, which indicates the incapacity for ZIF-8 producing •OH. $^{40}$ To be noted, the pristine LM nanoparticles produces •OH with a much lower rate compared to LM nanocomposite, possibly due to the poor stability of LM nanoparticles in solution, which is
accordant with the photopolymerization ability by LM nanoparticle previously shown in Figure 2a. The role of •OH in the photopolymerization has further been corroborated by introducing a •OH scavenger into the monomer solution before irradiation, and as expected, it could deplete the produced •OH and inhibit the polymerization (Figure S16). Moreover, we also demonstrated the pivotal effect of the LM oxide layer on the polymerization by using the LM nanocomposite/monomer suspension which was pretreated by hydrochloric acid to remove the oxide layer. Accordingly, the degree of polymerization considerably decreased with incremental HCl concentration for pretreatment (Figure S17).

Given the superior capability of •OH generation by LM nanocomposite which is a representative property of many metal oxides-based semiconductors, its electronic band structure was established to illustrate the photocatalytic mechanism. UV-Vis diffuse reflectance spectroscopy was used to study the optical bandgap of LM nanocomposite. In order to find out the bandgap a direct transition with Tauc plot model $(\alpha h\nu)^2 \propto (h\nu-E_g)$ was applied, where $\alpha$ is the absorption coefficient, $h\nu$ is the photon energy, and $E_g$ is the optical energy bandgap, respectively. As shown in Figure 3c, the Tauc plot calculated from the UV-Vis spectrum (Figure S18) exhibits the $E_g$ value of LM nanocomposite estimated to be 5.10 eV, in agreement with previously reported result of Ga2O3.40 In addition, the work function ($\Phi$) of LM nanocomposite has been measured by Kelvin probe force microscopy (KPFM) and $\Phi_{LM \text{ nanocomposite}}$ was calculated to be 4.48 eV, where the detailed calculation can be found in Figure S19. Furthermore, valence band X-ray photoelectron spectra (VB-XPS) was performed to assess the location of the valence band edge of LM nanocomposite. Figure 3d demonstrates the difference between Fermi energy level and valence band edge for LM nanocomposite is about 2.90 eV. As a result, the band position of LM nanocomposite together with reactive oxygen species (ROS) reaction potential can be profiled, as illustrated in Figure 3e. From the band diagram we can see that the potential of photogenerated holes in valence band of LM nanocomposite (2.88 V vs.
NHE) are positive enough to oxidize water to •OH (2.68 V vs. NHE), which supports the •OH generation by irradiated LM nanocomposite shown in Figure 1a.

Since the oxide layer on Ga-based LM is a dynamic continuum and tends to change in aqueous solution, the possible oxidation and conversion of LM nanocomposite is studied after photocatalysis. LM nanocomposite is collected from the nanocomposite gel by water dilution and centrifugation. After photocatalysis, the LM nanocomposite presents a similar morphology to origin in SEM images (Figure S20). However, the EDS analysis suggests a relatively higher oxygen element content for the LM nanocomposite after photocatalysis, hinting the oxidation of LM during the photocatalytic process. Moreover, PXRD results show that the LM nanocomposite displays a much enhanced Ga$_2$O$_3$ amorphous peak around 20 of 35° after photocatalysis and nearly unchanged crystalline peaks of ZIF-8 (Figure 3f), further revealing the oxidation of LM nanocomposite. Notably, there are emerging crystalline peaks for the LM nanocomposite after photocatalysis (Figure 3g), which could be assigned to GaOOH, the oxidation product of LM in water. As shown in Figure 3h, the XPS O 1s deconvoluted spectra also verify the formation of hydroxide (GaOOH) for the peak appearing at 532.5 eV. Meanwhile, Ga 2p3 spectra show an increased ratio of Ga$^{3+}$/Ga$^{0}$ after photocatalysis substantiating the oxidation of LM nanocomposite (Figure S21). Due to the further oxidation and formation of GaOOH, the band structure of LM nanocomposite after photocatalysis has also been characterized (Figure 3d-e), where the material demonstrates a similar band diagram though with a more positive valence band (2.9 V vs. NHE). To test the photocatalytic performance of LM nanocomposite after photocatalysis, we pretreated the pristine LM nanocomposite in water with UV irradiation for various durations (2-8 h). The •OH generation ability of the pretreated LM nanocomposite was measured by the fluorescent method described previously (Figure S22). Compared to the pristine, pretreated LM nanocomposite demonstrated a much higher capacity for producing •OH as manifested by the stronger fluorescent signals, which can be attributed to the more positive valence band of the LM
nanocomposite. Accordingly, the photocatalytic polymerization using these pretreated LM nanocomposite displayed a sharper increase of suspension viscosity (Figure S23), validating the better photocatalytic performance of the pretreated LM nanocomposite.

LM/polymer nanocomposites usually display a highly improved toughness in comparison to pristine polymer due to the unique energy dissipation mechanism of LM inclusion. After introducing a little amount of crosslinker, 0.05 wt% N, N'-methylene-bis-acrylamide (MBAA), into the monomer solution, a chemically crosslinked PAAm hydrogel can be fabricated by LM nanocomposite. As shown in Figure 4a and Table S2, the PAAm hydrogel initiated by LM nanocomposite shows the highest toughness of 533.7 kJ m$^{-3}$ with a fracture strain of 1573%, outstanding the PAAm hydrogels initiated by photocatalytic TiO$_2$ nanoparticles or traditional organic photoinitiator. The toughening effect has also been proven definitely due to the LM particles as shown in Figure S24. The toughness of the hydrogel made by Irgacure2959 and ZIF-8 is much lower than the hydrogel made by LM nanocomposite. Moreover, the fluorescent microscopy image of the LM nanocomposite initiated PAAm hydrogel demonstrates a homogeneous dispersion of LM particles in the gel matrix as dyed by fluorescein isothiocyanate (FITC, Figure 4b). The SEM image of freeze-dried hydrogel confirms the inclusion of LM nanocomposite in the PAAm hydrogel. Importantly, the mechanical properties of the PAAm hydrogel can be manipulated by the content of LM nanocomposite or water. Figure 4c and Table S3 illustrate that the hydrogel toughness will be further increased to 1341.6 kJ m$^{-3}$ with a relatively higher LM nanocomposite content at 5 wt%, but it could decrease with a much higher loading of LM nanocomposite, which is common in most nanofiller toughened polymer composites. In addition, the stretchability of the hydrogel can be improved by a higher water content due to lower crosslinking, while the toughness is not affected.

As the LM nanocomposite remains intact in the hydrogel after photopolymerization even with enhanced photocatalytic capability, the fabrication of double-network (DN) hydrogels can be achieved via the in-situ photoinitiation of soaked second monomer (Figure 4d). By
introducing a temperature responsive polymer-poly(N-isopropylacrylamide) (PNIPAM) as the second network, the DN hydrogel shows both highly improved toughness (Figure 4e and Table S4) and additional temperature-responsive appearance change (Figure 4f). Moreover, we also demonstrate that the photocatalytic LM-hydrogel can be used for organic pollutant degradation (Figure 4g). Rhodamine-6G (Rh-6G) was selected as a model organic compound. The hydrogel was put into Rh-6G contained water solution for adsorption, followed by the evaluation of the photocatalytic degradation performance. As shown in Figure 4h, the characteristic absorption peak of Rh-6G centered at 530 nm degrades significantly and almost diminishes within 120 min, implying the great photocatalytic degradation performance of the hydrogel containing LM nanocomposite. The dye degradation property of the hydrogel depends on the photocatalytic activity of the contained LM nanocomposite. It is well-known that the photocatalytically active nanomaterials can generate ROS which can react with the dye to form other species and is thus responsible for the discoloration of the dye. A quantitative study shows that the relative absorbance ($A_t/A_0$) of Rh-6G promptly decreases after irradiation for 1 h with a dye degradation rate up to 80%, which can further increase to 98% after 2 h illumination (Figure 4i). In the control experiments, negligible decreases of the dye absorbance are observed for samples without illumination or in the hydrogel without photocatalyst (Figure S25), signifying the effective degradation of organic molecules by the LM nanocomposite. Moreover, the dye degradation rate of the LM composite hydrogel can maintain at a level higher than 94% even after five dye degradation cycles (Figure S26), displaying the durability of the photocatalytic ability of the LM hydrogel.

3. Conclusion
In summary, LM nanoparticles has been demonstrated with excellent photocatalytic capability for radical polymerization and multifunctional hydrogel preparation. Positively charged MOF nanoparticles can stabilize LM particles via electrostatic interaction and afford the LM
nanoparticles with great processability as well as colloidal stability in various solvents. Upon UV illumination, the photogenerated holes in the Ga₂O₃ layer on LM nanoparticles can generate a large amount of hydroxyl radicals responsible for the photopolymerization. Moreover, LM nanoparticles after photocatalysis revealed its further oxidation but improved photocatalytic performance. Exploiting nanomaterials as photoinitiators has received growing attention in recent years.²⁶,²⁷ The introduction of nanomaterials can simultaneously manipulate the function of polymers, especially the mechanical properties. Compared to organic photoinitiators,⁴⁷ the LM nanocomposite used for initiating photopolymerization possesses great potential for the fabrication of highly tough, stimuli-responsive, and photocatalytically active LM hydrogels. The LM hydrogels showed remarkable photocatalytic performance for organic pollutant degradation. We envision that LM nanoparticles integrated with MOF stabilizer are promising for producing LM/polymer composites applicable in stretchable electronics, water remediation, and smart materials.

4. Experimental

**Materials:** EGaIn alloy (Ga 75.5%/In 24.5%, melting point of 15.7°C) was purchased from Sigma-Aldrich. Analytical reagents including zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O), 2-methylimidazole, terephthalic acid, zirconium(IV) chloride (ZrCl₄), chromium(III) chloride hexahydrate (CrCl₃·6H₂O), cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O), acrylamide (AAm), N, N’-methylene-bis-acrylamide (MBAA), methacrylic acid (MAA), N-isopropylacrylamide (NIPAM), N, N-dimethylacrylamide (DMAAM), 2-hydroxyethyl acrylate (HEA), water-soluble photoinitiator Irgacure 2959, and rhodamine 6G (Rh-6G) were purchased from J&K Scientific Ltd. and used as received. Titanium oxide (TiO₂) with average size of 100 nm was purchased from Aladdin Biochemical Technology Co., Ltd. Deionized water from the Milli-Q system was used in all experiments.
**Synthesis of ZIF-8 particles:** A 5 ml volume of an aqueous solution of Zn(CH₃COO)₂·2H₂O (300 mg) was added to 5 ml of an aqueous solution of 2-methylimidazole (1200 mg) with gentle stirring. After 15 s the transparent mixture turned white and was then left undisturbed at room temperature for 2 h. The resulting ZIF-8 particles were collected by centrifugation at 9000 rpm and washed three times with methanol. The product was dried at 100°C for 12 h in a vacuum oven.

**Synthesis of UiO-66 particles:** In a typical synthesis, ZrCl₄ (34.9 mg) and terephthalic acid (24.9 mg) were dissolved in 10 ml of 2.1 M acetic acid in dimethylformamide and transferred to a scintillation vial, which was placed in a preheated oven at 120°C for 12 h. The particles were then collected by centrifugation at 9000 rpm and washed three times with methanol. The product was dried at 100°C for 12 h in a vacuum oven.

**Synthesis of ZIF-67 particles:** Typically, Co(NO₃)₂·6H₂O (116 mg) and 2-methylimidazole (328 mg) were each dissolved in 10 ml of methanol. The former salt solution was poured into the latter ligand solution under stirring. The mixture was magnetically stirred at 400 rpm for 2 h at room temperature. The purple product was collected by centrifugation at 9000 rpm and washed three times with methanol, followed by vacuum drying at 100°C for 12 h.

**Synthesis of MIL-101(Cr) particles:** Typically, CrCl₃·6H₂O (133 mg) was dissolved in 5 ml deionized water, followed by the addition of 1.88 ml formic acid. Terephthalic acid (83 mg) was then added and the mixture was heated at 210°C for 8 h. After cooling to room temperature, the resulting mixture was collected by centrifugation at 9000 rpm and washed twice with deionized water and twice with methanol sequentially. The green product was dried at 100°C for 12 h in a vacuum oven.

**Preparation of the LM/MOF nanocomposite:** EGaIn (fixed at 200 mg) and MOF particles with different volume fraction of EGaIn (40-70 vol%) were added into 15 ml of ethanol in a 50 ml centrifuge tube. The mixture was then ultrasonicated in an ice-water bath for 20 min (Branson 450, power of 300 W with 25% amplitude). The nanocomposite sample in the
powdery form was obtained after the evaporation of ethanol in a polytetrafluoroethylene mold and following mild grinding in a mortar. Without further description, the LM nanocomposite with an EGaIn volume fraction of 60 vol% was used for photocatalytic applications.

**Photocatalytic radical polymerization:** Typically, water-soluble vinyl monomers were dissolved in water with the concentration of 10 wt%, followed by adding LM nanocomposite (1 wt% to water) as the photocatalyst. After a short sonication process (1 min) in an ultrasonic bath to disperse the catalyst, the suspension was bubbled with N₂ for 5 min and then put into a glass mold with the size of 60 mm in diameter and 2 mm in height, and the mold was covered by a customized quartz sheet. The precursor was then placed under UV irradiation (365 nm light, 36 W, 1.5 mW/cm²) for polymerization. An aliquot of sample was taken at different time intervals (0-120 min) for viscosity test.

To calculate the conversion, the samples with different reaction time (0-120 min) were washed with ethanol three times to remove monomer and obtain polymer nanocomposite by drying at 60°C in a vacuum oven. The conversion was then calculated by the equation (1):

\[
\text{Conversion} = \frac{m_{\text{composite}} - m_{\text{catalyst}}}{m_{\text{monomer}}} \times 100\% \quad (1)
\]

Where \( m_{\text{composite}} \) is the mass of dried polymer nanocomposite, \( m_{\text{catalyst}} \) is the mass of LM nanocomposite, and \( m_{\text{monomer}} \) is the mass of initial added monomer.

For the photocatalytic radical polymerization with TiO₂ nanoparticle (1 wt%) or Irgacure 2959 (0.1 wt%) as photoinitiator, the process is similar to above.

**Preparation of PAAm hydrogel:** Monomer AAm (20 wt%) and crosslinker MBAA (0.05 wt% to monomer) were first dissolved in water, followed by adding LM nanocomposite (1 wt% to water) as the photocatalyst. After the dispersion of LM nanocomposite under ultrasonication for 1 min and N₂ bubbling for 5 min, the suspension was poured into a glass mold (25 mm×25 mm×1.5 mm) and covered by a glass slide for the photocatalyzed polymerization. The chemically crosslinked PAAm hydrogel can be obtained after UV irradiation for 2 h.
**Preparation of PAAm-PNIPAM DN hydrogel:** The DN hydrogel was prepared by a second monomer soaking method. Typically, as-prepared PAAm hydrogel was soaked in an aqueous solution containing 20 wt% NIPAM and 0.05 wt% MBAA for 12 h. The gel was then surface washed by water and put into a glass mold for the construction of the second network under UV irradiation for 2 h.

**Hydroxyl radical measurement:** •OH was determined by the fluorescence method using terephthalic acid as a probe molecule. Terephthalic acid (0.5 mM), sodium hydroxide (2 mM), and catalysts (0.5 mg ml⁻¹) were dispersed in 10 ml aqueous solution. Samples were collected at different irradiation time intervals and filtrated by 0.22 μm membrane to exclude the influence of catalysts. Fluorescence spectra of generated 2-hydroxy terephthalic acid was measured by a Hitachi F-7000 fluorescence spectrophotometer, where 2-hydroxyterephthalic acid could emit fluorescence at 425 nm when excited at 315 nm. Control experiments were conducted without UV irradiation or without catalyst.

**Scavenger quenching experiment:** Isopropanol was used as the •OH scavenger to quench the polymerization process. The scavenger with different concentrations (10⁻⁴ -10⁰ M) was added into the precursor suspension before UV irradiation. The shear viscosity of the reaction system was measured after 2 h photopolymerization.

**Dye degradation experiment:** Rh-6G was selected as the dye for hydrogel adsorption and in-situ photocatalytic degradation. The PAAm hydrogels were immersed in Rh-6G aqueous solution (10⁻⁵ M) for 2 h and then sandwiched by two glass slides, followed by UV irradiation for different durations (0-2 h, 365 nm light, 36 W, 1.5 mW/cm²). The dye degradation was measured by the absorbance of the leach liquor of irradiated hydrogels. The control experiments were performed under same conditions.

**Characterization:** SEM images and EDS mapping data were obtained by FEI Quanta 450 FEG equipped with Oxford EDS accessories. For the observation of hydrogel structures, the samples were first freeze-dried by a benchtop freeze dryer (Labconco FreeZone 71020). TEM
image was observed on Philips/FEI Tecnai 12 transmission electron microscope. The
topography and contact potential measurements were performed on Bruker Dimension Icon in
KPFM mode in ambient conditions. The size and zeta potential of MOFs and LM
nanocomposites were measured by Malvern Zetasizer Nano-ZS ZEN3600 using ethanol as the
dispersion medium. XPS analysis was conducted on a PHI 5802 X-ray Photoelectron
Spectrometer. The $^1$H NMR spectrum was recorded on a Bruker Avance III 400MHz NMR
system in D$_2$O. FT-IR was measured by PerkinElmer Spectrum 100. PXRD was recorded on a
Bruker D2 Phaser diffractometer. Optical images were taken by a Nikon D5500 camera. The
shear viscosity measurements were performed on a rotational rheometer (Malvern Kinexus
Lab+). The fluorescence microscopic image was observed by an upright fluorescence
microscope (Nikon Eclipse Ni-E), where the hydrogel was dyed by 10$^{-5}$ M FITC in water.
Tensile tests were conducted on AMETEK TCM 100 with a 50 N force sensor. UV-Vis
spectroscopy was performed to obtain the optical absorption spectra and bandgaps on an
Agilent Cary 4000 spectrophotometer with internal diffuse reflectance accessories. The
reflectance curve of the PAAm-PNIPAM hydrogel was measured by a UV-Vis Spectrometer
(Ocean optics, USB4000) in the Reflectance mode.
**Figure 1.** Photocatalytic radical polymerization initiated by gallium-based LM. (a) Schematic illustration of photocatalytic radical polymerization by using EGaIn nanoparticles as photocatalyst to produce hydroxyl radicals under irradiation. R represents substituents of vinyl monomers, while hv is the photon energy. (b) Schematic illustration of the fabrication process of LM nanocomposite. Optical images show the LM nanocomposite and its redispersibility. (c) TEM image showing a MOF-stabilized LM nanoparticle. (d) The merge image of SEM image and EDS mapping of the LM nanocomposite containing ZIF-8. The Zn signal is from ZIF-8 while the Ga signal is from LM.
Figure 2. Photopolymerization of vinyl monomers initiated by the LM nanocomposite. (a) Photo images of the photocatalytic polymerization using different catalysts. NP: nanoparticle. (b) $^1$H NMR spectra of AAm monomer before and after polymerization. (c) FT-IR spectra of the monomer before and after polymerization, and the LM nanocomposite. (d) Evolution of the monomer conversion with irradiation time. Catalyst content is 1 wt%. (e) Evolution of the shear viscosity of monomer solution with irradiation time. (f) Dependence of monomer conversion on catalyst content for the photopolymerization. Irradiation time is 2 h.
Figure 3. Photocatalytic polymerization mechanism and band-structure characterization of the LM nanocomposite. (a) Schematic illustration of hydroxyl radical detection by TA. (b) Dependence of fluorescent intensity of 2-hydroxyterephthalic acid on time for various •OH detection conditions. The dots were the fluorescent intensities at 425 nm extracted from Figure S11. (c) Tauc plots of LM nanocomposite before and after photocatalysis obtained from UV-Vis diffuse reflectance spectra. (d) XPS valence band graphs for the LM nanocomposite before and after photocatalysis. (e) The band positions of LM nanocomposite with respect to the ROS formation potential. CB: conduction band, VB: valence band. (f) PXRD curves of LM nanocomposite before and after photocatalysis. (g) The enlarged image from Figure f showing the crystalline peaks of GaOOH after photocatalysis. (h) XPS O 1s spectra of LM nanocomposite before and after photocatalysis. The deconvoluted curve (blue) indicates the emergence of GaOOH, and O_ads represents the surface adsorbed oxygen.
Figure 4. Application of LM nanocomposite as photocatalyst for the fabrication of tough hydrogel and its performance in dye degradation. (a) Stress-strain curves of the chemically crosslinked PAAm hydrogels initiated by different photoinitiators. (b) Fluorescent microscopy image of the PAAm hydrogel initiated by LM nanocomposite. Inset is the SEM image of freeze-dried hydrogel. (c) Stress-strain curves of PAAm hydrogels fabricated with different contents of LM nanocomposite and water.

(d) Schematic illustration of fabricating DN hydrogel by the in-situ polymerization initiated by LM nanocomposite. (e) Stress-strain curves of PAAm hydrogel and DN hydrogel. (f) Reflectance spectra of the PAAm-PNIPAM DN hydrogel above and below lower critical solution temperature (LCST). Inset shows photo images of the DN hydrogel with temperature responsiveness. (g) Schematic illustration of dye degradation using the LM nanocomposite initiated hydrogel. (h) UV-Vis absorption spectra of Rh-6G adsorbed in the hydrogel after indicated duration of UV irradiation. Inset shows the photographs of initial hydrogel absorbed with Rh-6G turning to the hydrogel after dye degradation. (i) Photodegradation of Rh-6G in LM nanocomposite initiated hydrogel under UV irradiation. $A_0$ is the initial absorbance of the dye without any irradiation and $A_t$ is the absorbance of the dye at time (t).
ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/

- SEM images, size distribution, PXRD curves, redispersion ability, and ionic stability of the LM nanocomposites;
- Rheological frequency sweep of hydrogel;
- UV-vis absorbance curve of LM nanocomposite dispersion;
- Photographs of the photopolymerized hydrogels, photocatalytic polymerization without LM nanocomposite, photocatalytic polymerization in organic solvents, and polymerization of various vinyl monomers;
- Fluorescent spectra for hydroxyl radical detection;
- Scavenger quenching experiment results;
- HCl treatment experiment results;
- UV-Vis diffuse reflectance spectra, KPFM results, and XPS spectra of LM nanocomposites;
- Stress-strain curves of the PAAm hydrogels;
- Control experiments for the Rh-6G degradation;
- Retention efficiency of the LM composite hydrogel;
- Comparison of LM initiated photopolymerization with sonication assisted radical polymerization;
- Mechanical properties of the PAAm hydrogels (PDF)

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Notes

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