Mechanically Strong Metal–Organic Framework Nanoparticle-Based **Double Network Hydrogels for Fluorescence Imaging**

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ABSTRACT: Tough and multicolor-changing hydrogels have shown great potential in sensing devices, wearable electronics, and human-machine interfaces. However, most of these hydrogels are either mechanically weak or lack the multi-responsive color- change property. Here, we designed and fabricated gelatin/pHEAA hydrogels crosslinked by metal-organic framework (MOF) nanoparticles (NPs) and with a nanocomposite and double-	High Mechanical Property

network structure using a facile, one-pot method. The presence of vinyl-functional zeolitic imidazole framework-8 MOF NPs in hydrogels provided not only multiple chemical and physical interactions with polymer networks to strengthen their mechanical properties (a tensile strength of \sim 2.4 MPa, a fracture strain of \sim 14, and a fracture energy of ~14.10 MJ/m³) but also UV-triggered



multi-fluorescence changes ranging from primary red-green-blue to secondary yellow, magenta, cyan, and white colors. More importantly, MOF/gelatin/pHEAA hydrogels can be further fabricated to possess different fluorescence-responsive patterns for QR codes or potential information storage. This work provides a design concept and hydrogel systems for developing tough, multi-colorchanging hydrogels for imaging and other optical applications.

KEYWORDS: hydrogel, MOF, nanoparticle, fluorescence, sensor

1. INTRODUCTION

Photoluminescent hydrogels have attracted considerable attention for fundamental material designs and practical applications including artificial tissues,^{1,2} anti-counterfeiting,^{3,4} sensors,^{5,6} actuators,^{7,8} and *in situ* imaging.^{9,10} A common strategy for photoluminescent hydrogels is to introduce fluorescent nanoparticle (NP) fillers [e.g., AuNPs, upconverting NPs, and carbon dots (CDs)] into hydrogels to achieve multicolor photoluminescence and mechanical strength.¹¹⁻¹⁴ The extremely high internal surface area, nano-scale size, and organic-rich functional groups of these NP fillers allow them to establish multiple and complex interactions with the polymer matrix (e.g., hydrogen bonds, electrostatic interactions, and van der Waals contacts), which would strengthen the mechanical properties of the NP filler-incorporated hydrogels while still retaining their photoluminescent property. Several examples include carbon nanodot-crosslinked polyvinyl alcohol (PVA) hydrogels with green fluorescence and a tensile stress of ~0.5 MPa¹⁵ and CD/poly(methylacrylic acid) (CD/PMAAc) hydrogels with blue fluorescence and a maximal tensile stress of 5.8 MPa.¹⁶ On the other hand, the presence of NP fillers in hydrogels also increases spatial heterogeneity in network structures, pore size distributions, and crosslinking densities, all of which will adversely affect the macroscopic mechanical

properties.^{17,18} Additionally, these NP filler-incorporated hydrogels lacked multiple-color fluorescence. Thus, it still remains a great challenge for developing multiple-color fluorescence hydrogels with strong mechanical properties.

Different from conventional NP fillers, nano metal-organic frameworks (NMOFs), inheriting both merits of metalorganic frameworks (MOFs) and NPs, possess their unique properties in controllable pore structures, high surface area, and tunable surface ligands.¹⁹⁻²² Particularly, surface ligands on NMOFs (e.g., carboxylic or imidazole groups) allow us to provide steady bindings to host materials.^{23,24} However, NMOFs and hydrogels are two different types of materials, that is, while both NMOFs and hydrogels possess threedimensional nanoporous structures, they have unique and distinct molecular structures. NMOFs are solid crystalline materials with well-defined structures, while hydrogels are softwet materials containing a high water content (60-95 wt %)

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Figure 1. Step-by-step synthesis procedure of OFM + NMOF/gelatin/pHEAA hydrogel.



Figure 2. (a) Atomic structure of V-ZIF-8 NPs, (b) fluorescence of V-ZIF-8 and OFM + V-ZIF-8 NPs under 365 nm UV light, (c) FTIR spectra of ligand IM, V-ZIF-8, and OFM + V-ZIF-8 NPs, (d) PXRD patterns, and (e) TEM images of as-prepared V-ZIF-8 and OFM + V-ZIF-8 NPs.

and random polymer structures. Such contrasting properties between NMOFs and hydrogels prevent conventional design wisdoms to integrate both materials into the same system for achieving the desirable functions. Until recently, several NMOFs-hydrogels, including HKUST-1/PPCN hydrogels,²⁵ UiO-66/alginate hydrogels,²⁶ and MIL-100(Fe)/alginate hydrogels,²⁷ have been developed and used for wound healing, drug release, sensors, and water treatment. Among them, none



Figure 3. SEM images of the (a) V-ZIF-8/gelatin hydrogel, (b) V-ZIF-8/pHEAA hydrogel, and (c) V-ZIF-8/gelatin/pHEAA hydrogel. EDX element scanning and mapping: (d) overlay maps of C/N/O/Zn, (e) C, (f) N, (g) O, and (h) Zn element distributions in V-ZIF-8/gelatin/ pHEAA hydrogels.

of the NMOF-based hydrogels possessed multicolor photoluminescence and strong mechanical properties simultaneously.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of MOF NPs and MOF-Crosslinked Hydrogels. Motivated by these challenges, here, we designed and fabricated a novel type of NMOF/gelatin/pHEAA hydrogel with integrated nanocomposite and double-network structures, in which vinyl-functional zeolitic imidazole framework-8 (V-ZIF-8) NPs serve as organic fluorescent molecular [OFM, e.g., fluorescein (FL), rhodamine B (RhB), and 7-hydroxycoumarin (HC)] adsorbents and crosslinkers to empower multi-color fluorescence and strengthen the polymer matrix, while the double-network structure provides an efficient energy-dissipated backbone for mechanical enhancement. As depicted in Figure 1 via a stepby-step process, four different OFM + V-ZIF-8 NPs were first synthesized to emit respective colorless, red-orange, yellow, and blue colors by adsorbing OFM onto V-ZIF-8 NPs. It has been well documented for the adsorption of OFM on external surfaces and internal pores of ZIF-8 and their derivatives.^{28,29} Based on the size of the OFM (Figure S1), it is likely that RhB and FL are adsorbed on the external surface of V-ZIF-8, while HC is adsorbed on both the external surface and internal pores of V-ZIF-8. The synthesized organic ligand of imidazole (IM) was characterized by ¹H NMR (Figure S2) and synthesis details of V-ZIF-8/gelatin/pHEAA and OFM + V-ZIF-8/ gelatin/pHEAA hydrogels are presented in the Supporting Information. The resultant V-ZIF-8 NPs contained pores with a diameter of ~10 Å and rich vinyl imidazole (V-IM) ligands on the surface, and their molecular structures are shown in Figure 2a. Our V-ZIF-8 has a structure and size similar to those of 2-imidazolecarboxaldehyde (ZIF-90, Figure S3),³⁰ and we expect that V-ZIF-8 should have Langmuir and BET surface areas of 1320 and 1270 m² g⁻¹ similar to those of ZIF-90. Under 365 nm UV light, V-ZIF-8, RhB + V-ZIF-8, FL + V-ZIF-8, and HC + V-ZIF-8 NPs displayed colorless, red-orange, yellow, and blue in the solid state (Figure 2b), respectively. In Figure 2c, a side-by-side comparison of FTIR signals between different samples of V-IM, V-ZIF-8, and OFM + V-ZIF-8 revealed a common characteristic peak of C=C at 1640 cm⁻¹

in V-IM, V-ZIF-8, and OFM + V-ZIF-8 particles, representing carbon–carbon double bonds in the vinyl group. Compared with V-IM, OFM + V-ZIF-8 NPs produced a new peak at ~539 cm⁻¹, assigned to the stretching vibration of the newly formed Zn–N coordination bond. V-ZIF-8 NPs displayed characteristic peaks similar to those of OFM + V-ZIF-8 NPs and some new peaks corresponding to different OFM being introduced, including 1212 cm⁻¹ in RhB + V-ZIF-8, 722 cm⁻¹ in FL + V-ZIF-8, and 1355 cm⁻¹ in HC + V-ZIF-8.

PXRD patterns (Figure 2d) showed that the as-synthesized V-ZIF-8 NPs had the same structure as that of the simulated V-ZIF-8 NPs had The V-ZIF-8 NPs had a high crystalline structure, consistent with pure V-ZIF-8 NPs, indicating that the presence of OFM in V-ZIF-8 NPs does not disturb the crystal structure of V-ZIF-8 NPs. Similar results were also confirmed by TEM (Figure 2e). As compared to V-ZIF-8 NPs with a relative uniform size of ~40 nm, it is not surprising to observe that OFM + V-ZIF-8 NPs have heterogeneous morphologies and sizes. The addition of OFM facilitated the formation of crystal nuclei of V-ZIF-8, which in turn affected the self-assembly of Zn^{2+} and IM, leading to heterogeneous morphologies and sizes.

Next, V-ZIF-8 NPs or OFM + V-ZIF-8 NPs, gelatin, HEAA, and photo initiators were mixed together in the same pot, heated up to 60 °C, and cooled down to 25 °C for forming a rigid and brittle gelatin network and photo-polymerized for forming a soft and ductile pHEAA network as crosslinked by OFM + V-ZIF-8 NPs, ultimately resulting in a V-ZIF-8/ gelatin/pHEAA hydrogel or OFM + V-ZIF-8/gelatin/pHEAA hydrogels. We performed SEM and SEM-EDX to characterize the network structure/morphology of V-ZIF-8/gelatin/ pHEAA hydrogels and the distribution of V-ZIF-8 NPs inside the hydrogels, respectively. As shown in the SEM images Figure 3a,b, V-ZIF-8/gelatin and V-ZIF-8/pHEAA (some single network) hydrogels displayed similar heterogeneous pore structures with a wide pore size distribution from 10 to 40 μ m. Differently, the co-presence of gelatin and pHEAA networks in V-ZIF-8/gelatin/pHEAA hydrogels rendered the networks much denser than that of V-ZIF-8/gelatin and V-ZIF-8/pHEAA single-network gels, with a pore size distribution from 2 to 14 μ m (Figure 3c). In parallel, SEM-EDX images confirmed the presence and distribution of V-ZIF-8



Figure 4. (a) Concentration effect of V-ZIF-8 NPs on the mechanical property of V-ZIF-8/gelatin/pHEAA gels, (b) comparison of the mechanical property of gelatin/pHEAA gel, V-ZIF-8/gelatin/pHEAA gel ($C_{V-ZIF-8} = 0.1$ wt %), and OFM + V-ZIF-8/gelatin/pHEAA gels ($C_{OFM+V-ZIF-8} = 0.1$ wt %). Comparison of the mechanical property of (c) RhB + V-ZIF-8/gelatin/pHEAA and RhB + gelatin/pHEAA gels, (d) FL + V-ZIF-8/gelatin/ pHEAA and FL + gelatin/pHEAA gels, and (e) HC + V-ZIF-8/gelatin/pHEAA and HC + gelatin/pHEAA gels.

NPs in V-ZIF-8/gelatin/pHEAA hydrogels, as evidenced by the uniform distribution of Zn (purple) in the gel network (Figure 3d-h).

2.2. Mechanical Properties of MOF-Crosslinked Hydrogels. Since we have examined and discussed the effect of both network components on the mechanical properties of gelatin/pHEAA DN hydrogels in our previous work,³¹ here, we only investigated the concentration effect of V-ZIF-8 NPs (0-1 wt %) on the mechanical property of V-ZIF-8/gelatin/ pHEAA hydrogels at constant concentrations of 50 wt % of pHEAA and 8 wt % gelatin. Tensile tests in Figure 4a show that as the V-ZIF-8 NP concentration increased from 0 to 1 wt %, the tensile strain of V-ZIF-8/gelatin/pHEAA hydrogels monotonically decreased from ~ 15 to ~ 9 , while the tensile stress displayed the max. value of ~2.4 MPa at an optimal strain of ~14 at 0.1 wt % of V-ZIF-8. This clearly indicates the over-crosslinking effect of V-ZIF-8 NPs on V-ZIF-8/gelatin/ pHEAA hydrogels. Only optimal V-ZIF-8 NPs allow to form the compatible chemically linked pHEAA network with a heatinduced physical gelatin network, thus achieving the high strength of V-ZIF-8/gelatin/pHEAA gels. Thus, under optimal conditions, V-ZIF-8/gelatin/pHEAA hydrogels exhibited the highest toughness of ~14.10 MJ/m³ at 0.1 wt % of V-ZIF-8, the highest strength of ~2.4 MPa at 0.1 wt % of V-ZIF-8, and the largest stretchability of ~14 at 0.1 wt % of V-ZIF-8, respectively (Figure S4). As shown in Figure S5, as the concentration of V-ZIF-8 NPs increased from 0 to 1 wt %, the tearing energy of V-ZIF-8/gelatin/pHEAA hydrogels increased from 2735 to 3700 J/m². A significant enhancement of tearing energy was observed in the range of 0.5-1 wt %, consistent with the high crosslinking density of the gels in the same range. Furthermore, Figure S6 shows the side-by-side comparison of the mechanical property of gelatin/pHEAA DN hydrogels crosslinked by methylenebisacrylamide (MBA) (MBA/gelatin/ pHEAA), V-ZIF-8/gelatin/pHEAA, and gelatin/pHEAA, which exhibited tensile stresses/strains of 0.65 MPa/3.9, 2.4 MPa/14, and 1.9 MPa/15, respectively. Due to intrinsic differences in structures and chemistries between MBA and V-ZIF-8 NPs, MBA is efficient to form more and stronger

chemical crosslinks with HEAA monomers in the MBA/ gelatin/pHEAA gels, which differ from the less chemical crosslinks as induced by V-ZIF-8 NPs in V-ZIF-8/gelatin/ pHEAA gels because MBA crosslinkers have more crosslink sites than nano V-ZIF-8 crosslinkers under the same concentrations. This clearly indicates that the nano-MOF crosslinkers demonstrate the enhanced toughening effect as compared to MBA crosslinkers. Additionally, the swelling experiment also confirmed this conclusion. In Figure S7, the swelling ratios of gelatin/pHEAA, V-ZIF-8/gelatin/pHEAA, and MBA/gelatin/pHEAA were 11.6, 10.7, and 5.2, respectively. MBA/gelatin/pHEAA hydrogels were more resistant to swelling than the other two hydrogels, presumably because the more and strong chemical couplings between MBA and HEAA monomers enabled to create high crosslinking densities in the hydrogels.

At an optimal NP concentration (0.1 wt %) of V-ZIF-8 and OFM + V-ZIF-8, while all of V-ZIF-8/gelatin/pHEAA, RhB + V-ZIF-8/gelatin/pHEAA, FL + V-ZIF-8/gelatin/pHEAA, and HC + V-ZIF-8/gelatin/pHEAA hydrogels exhibited a very high mechanical toughness ($\sigma > 1.8$ MPa), the incorporation of V-ZIF-8 NPs and OFM + V-ZIF-8 NPs clearly enhanced the mechanical toughness by up to 26% (Figure 4b). For comparison, Figure 4c shows that RhB + gelatin/pHEAA hydrogels without V-ZIF-8 NPs reduced the tensile strain/ stress from 13/1.5 to 7.5/0.5 MPa as the RhB concentration increased from 0.01 to 0.1 wt %. Similarly, RhB + V-ZIF-8/ gelatin/pHEAA hydrogels at 0.1 wt % of RhB + V-ZIF-8 NPs (14.5/2.38 MPa) exhibited a much higher tensile strain/stress than RhB + gelatin/pHEAA hydrogels without V-ZIF-8 (7.4/ 0.57 MPa) at an RhB concentration of 0.1 wt %. Similar trends of changes with gelatin/pHEAA hydrogels' adsorbing of FL and HC were observed (Figure 4d,e). In Figure 4d, while all FL + gelatin/pHEAA hydrogels exhibited similar tensile strains, their tensile stress decreased from 1.49 to 0.60 MPa as the FL concentration increased from 0.01 to 0.1 wt %. Meanwhile, the FL + V-ZIF-8/gelatin/pHEAA hydrogel at 0.1 wt % of FL + V-ZIF-8 NPs (1.83 MPa) showed a much higher tensile stress than the FL + gelatin/pHEAA hydrogel at 0.1 wt

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Table 1. Summary of Typical Photoluminescent Hydrogels for Their Structural, Mechanical, and Fluorescent Properties

hydrogel	structure	property	ref
OFM + NMOF/gelatin/pHEAA	nanocomposite double network	multi-color fluorescence, good fatigue resistance, σ/ϵ : 2.38 MPa/1450%	this work
EuW ₁₀ /VIPS/C ₁₀ IPS	zwitterionic single network	monochrome fluorescence, organic solvent responsiveness, $\sigma/\varepsilon:~0.25~{\rm kPa}/650\%$	32
PCAD/CMC	single network	blue and green color, σ/ϵ : 12 kPa/150%	33
TPPE/PAAc	single network	monochrome fluorescence, self-healing, σ/ϵ : 5 kPa/5700%	34
Ln ³⁺ /CDs/P(AAm-co-AAc)	nanocomposite single network	multi-color fluorescence, multi-stimuli responsive	13
CDs/PVA	nanocomposite single network	monochrome fluorescence, self-healing, σ/ϵ : 0.45 MPa/150%	15
CDs/PMAAc	nanocomposite single network	monochrome fluorescence, σ/ϵ : 5.5 MPa/175%	16
SiO ₂ /TiO ₂ /Laponite/PAAm	nanocomposite single network	monochrome fluorescence, σ/ϵ : 207 kPa/1700%	35
Ln ³⁺ /alginate/PVA	double network	bicolor fluorescence, antibacterial activity, σ/ϵ : 0.6 MPa/400%	36
Ln ³⁺ /alginate/PAAm	double network	multi-color fluorescence, good cytocompatibility, σ/ϵ : 1.1 MPa/1700%	37
Ln ³⁺ /PVA/PAAcNa	double network	bicolor fluorescence, strain sensor, σ/ϵ : 0.5 MPa/350%	38
YAG/Ce/alginate/PAAm	nanocomposite double network	white color, σ/ε : 0.2 MPa/650%	39



Figure 5. (a) Optical images at 365 nm UV light, (b) fluorescence spectra (Ex = 365 nm), and (c) chromaticity coordinates (CIE) of blue-, red-, green-, yellow-, magenta-, white-, and cyan-emitting OFM + V-ZIF-8/gelatin/pHEAA hydrogels. (d) Exquisite bicolor patterns of the Universe and the four-color pattern of a pinwheel. (e) A RhB + V-ZIF-8/gelatin/pHEAA-based QR code that can be recognized by a smart phone under 365 nm UV light.

% of FL (0.60 MPa). Consistently, Figure 4e shows that the HC + gelatin/pHEAA hydrogel slightly decreased its tensile stress from 1.48 to 1.24 MPa as the concentration of HC increased from 0.01 to 0.1 wt %, while the HC + V-ZIF-8/gelatin/pHEAA hydrogel at 0.1 wt % of HC + V-ZIF-8 NPs (2.06 MPa) presented the higher tensile stress than the HC + gelatin/pHEAA hydrogel at 0.1 wt % of FL (1.24 MPa). We compared our nano-MOF DN hydrogels with a number of typical photoluminescent hydrogels for their structural, mechanical, and fluorescent properties in Table 1. Evidently, OFM + NMOF/gelatin/pHEAA readily outperformed other hydrogels with single-network, double-network, or nano-composite structures in terms of mechanical properties and multicolor fluorescence.

To better understand the role of NMOFs in energy dissipation of NMOF/gelatin/pHEAA hydrogels, we performed successive loading–unloading tests on V-ZIF-8/ gelatin/pHEAA hydrogels of different concentrations of V-ZIF-8 NPs (0–1 wt %). As shown in Figure S8a–f, during the consecutive loading–unloading cycles, all the hydrogels showed obvious hysteresis behaviors, where hysteresis loops

increased with the tensile strain. Meanwhile, the hysteresis loop area and the maximum tensile stress of V-ZIF-8/gelatin/ pHEAA hydrogels increased with the V-ZIF-8 NP concentration at the same strain. For example, the dissipated energy/ the maximal tensile stresses (calculated from the hysteresis loops area) of V-ZIF-8/gelatin/pHEAA hydrogels were 0.19 MJ/0.31, 0.34 MJ/0.40, 0.43 MJ/0.50, 0.72 MJ/0.74, and 0.81 MJ/0.78 MPa at the strain of 5 with the V-ZIF-8 NP concentrations of 0, 0.05, 0.1, 0.5, and 1 wt %, respectively. At the V-ZIF-8 NP concentration of 0.1 wt %, V-ZIF-8/gelatin/ pHEAA hydrogels exhibited the best fatigue resistance, as evidenced by the facts that the hydrogels increased their tensile stress from 0.14 to 1.74 MPa and dissipated energy from 0.06 to 2.75 MJ/m³, even after tensile strain increased from 1 to 11 via 11 loading-unloading cycles. Additionally, every reloading-unloading curve was partially overlapped with its previous loading-unloading curve. This means that the nanocomposite hydrogels are partially recovered after the reloading process even without any resting time, indicating that the nanocomposite hydrogel possesses a fast self-recovery property. High toughness and efficient energy dissipation of V-ZIF-8/

gelatin/pHEAA hydrogels are likely attributed to several factors. First, when a pulling force was applied to the V-ZIF-8/gelatin/pHEAA hydrogel, the triple helix of gelatin started to separate from each other and resulted in the first gelatin network breaking. However, disassociating of the triple helix was followed by breaking of the reversible hydrogen bond to dissipate energy.³¹ Second, the random coil polymer chains of pHEAA started to move under the external applied force to relieve the stress. Third, the nano-reinforcement effects of the V-ZIF-8 NPs endowed the hydrogel with high toughness.^{40,41}

2.3. Fluorescent Properties and Applications of MOF-Crosslinked Hydrogels. We investigated the multi-color fluorescent property of OFM + V-ZIF-8/gelatin/pHEAA hydrogels. At a first glance, RhB + V-ZIF-8/gelatin/pHEAA, FL + V-ZIF-8/gelatin/pHEAA, and HC + V-ZIF-8/gelatin/ pHEAA hydrogels emitted the characteristic red, green, and blue colors under excitation at 365 nm, respectively (Figure 5a). Apart from the original red-green-blue (RGB) fluorescence of RhB + V-ZIF-8, FL + V-ZIF-8, and HC + V-ZIF-8, we further fabricated hydrogels to emit multiple secondary colors by controlling the NP amounts and ratios of mixed RhB + V-ZIF-8, FL + V-ZIF-8, and HC + V-ZIF-8. As shown in Figure 5a, upon separately mixing RhB + V-ZIF-8 and FL + V-ZIF-8 NPs, RhB + V-ZIF-8 and HC + V-ZIF-8 NPs, HC + V-ZIF-8 and FL + V-ZIF-8 NPs into gelatin/ pHEAA hydrogels, the resultant RhB + V-ZIF-8/FL + V-ZIF-8/gelatin/pHEAA, RhB + V-ZIF-8/HC + V-ZIF-8/gelatin/ pHEAA, and HC + V-ZIF-8/FL + V-ZIF-8/gelatin/pHEAA hydrogels emitted yellow, magenta, and cyan colors, respectively, while the mixing of three V-ZIF-8 NPs led to white-emitting hydrogels. As shown in Figure 5b, the red, green, and blue colors of the OFM + V-ZIF-8/gelatin/pHEAA hydrogel presented its own characteristic peaks of 585, 535, and 460 nm. It should be noted that the adsorbed multiple OFM + V-ZIF-8 NPs in these fluorescent hydrogels did not interfere with each other; instead, they can simultaneously present the distinct primary colors of yellow, magenta, and cyan and the secondary color of white. The corresponding Commission International de L'Eclairage (CIE) chromaticity coordinates of OFM + V-ZIF-8/gelatin/pHEAA hydrogels showed a triangle of vertices, in which three primary colors and two secondary colors were located on the side, while white color was located at CIE 1931 coordinates (0.27 and 0.31) (Figure 5c).

From a practical viewpoint, fluorescent OFM + V-ZIF-8/ gelatin/pHEAA hydrogels can be fabricated into different shapes of a bicolor pattern of the universe and a four-color pinwheel pattern, with multiple colors being presented in different regions of the same hydrogels (Figure 5d). More challengingly, we used RhB + V-ZIF-8/gelatin/pHEAA hydrogels to create a 21*21 fluorescent QR code with the stored information of "1", and the resultant fluorescent QR code showed a clearly red color under 365 nm UV light, as well as can be recognized by the WeChat APP (Figure 5e).

3. CONCLUSIONS

In this work, we demonstrated a facile strategy for preparation of tough and multi-fluorescent hydrogels by incorporating both MOF and OFM NPs into gelatin/pHEAA hydrogels. The resultant OFM + V-ZIF-8/gelatin/pHEAA hydrogels exhibited a combination of extraordinary mechanical properties, including high strength (fracture stress of 2.4 MPa), extensibility (fracture strain of 14), and toughness (fracture energy of 14.10 MJ/m³). Meanwhile, OFM + V-ZIF-8/gelatin/ pHEAA hydrogels can emit the full-color fluorescence from primary RGB colors to any secondary color (even to white color) by simply changing the types and relative ratios of the single or multiple OFM + V-ZIF-8 NP concentration. Mechanical enhancement and tunable fluorescence in OFM + V-ZIF-8/gelatin/pHEAA nanocomposite hydrogels are attributed to multiple chemical crosslinking and physical interactions between V-ZIF-8 NP and the polymer network. Finally, the hydrogels can be fabricated into fluorescenceresponsive patterns, including bicolor Tai Chi, four-color pinwheels, and multiple colored QR codes. Our hydrogels hold great potential for developing tough and fluorescent hydrogels for imaging, sensing, and other optical applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.1c03034.

Materials and synthesis methods for V-ZIF-8 NPs, OFM + V-ZIF-8 NPs, gelation/pHEAA double network hydrogels crosslinked by different NPs; FTIR, TEM, PXRD, and ¹H NMR characterization of hydrogels; and mechanical tests for the hydrogels (PDF)

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Notes

The authors declare no competing financial interest.

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