Tunable, luminescent, and self-healing hybrid hydrogels of polyoxometalates and triblock copolymers based on electrostatic assembly†

Haibing Wei,† Shuming Du, Yang Liu, Hongxiang Zhao, Chongyi Chen, Zhibo Li, Jun Lin, Yang Zhang, Jie Zhang and Xinhua Wan*

Hybrid hydrogels based on electrostatic co-assembly of polyoxometalates and ABA triblock copolymers were readily prepared and exhibit excellent luminescence and self-healing performance.

Self-healing materials, which possess the ability to repair themselves after damage, are emerging as a novel class of smart materials.1 The supramolecular assembly through non-covalent bonds, such as π–π stacking, hydrogen bonding, and host–guest interactions, is considered to be the most promising way to construct healable materials, owing to their intrinsic and autonomic self-healing nature.2–6 Inspired by supramolecular self-healable hybrid nanocomposites in nature, such as nacre and bones, recent advances have resulted in synthetic organic–inorganic healable materials consisting of two constituents at the nanometer or molecular level, which not only resemble natural healable materials, but also can be endowed with exceptional integrated functions and tunable supramolecular adaptive characteristics.7,8 A remarkable high-modulus supramolecular self-healing hydrogel prepared using inorganic clay with a dendritic molecular binder at high water content can immobilize enzymes and transport biological catalytic activities.7 Incorporation of Fe3O4 nanoparticles into PEG-grafted chitosan produced a magnetic self-healing hydrogel.8

Polyoxometalates (POMs), as a type of nanosized inorganic transition-metal oxide clusters, possess diverse functionalities in catalytic, photoelectrical, magnetic, and biological fields.9 Introducing POMs into the self-healing materials would be promising to extend the application scope of POM materials. For instance, self-healing POM hydrogels could be injectable materials, i.e. the broken hydrogel fragments after injection can in situ reform an integral gel at the target position under physiological conditions, which may result in enhanced delivery efficiency of POM medical cargos or low toxicity and high luminescence efficiency for bio-imaging in the presence of POM luminescent probes.10 However, as far as we know, there still is no report on the POM-based self-healing materials, due to challenges in exploration of facile supramolecular approaches to hybridize POMs into the self-healing materials.

Recently, we have demonstrated that self-assembly is a powerful technique for constructing hierarchical POM nanomaterials with enhanced luminescence by co-assembly of Na9EuW10O36 (EuW10) with diblock copolymers.11 Herein, we report a facile method to prepare self-healable supramolecular luminescent hydrogels from macroanionic POMs and cationic-neutral-cationic ABA triblock copolymers. The supramolecular strategy is illustrated in Fig. 1a. We envisioned that the micelle networks should be constructed, driven by the electrostatic interaction between the cationic A block and the anionic EuW10.

To test the aforementioned idea, we first synthesized a series of novel ABA triblock copolymers poly[2-(2-guanidinoethoxy)ethyl methacrylate]-b-poly(ethylene oxide)-b-poly[2-(2-guanidinoethoxy)ethyl methacrylate] (PG9-b-PEO230-b-PG30; Scheme 1) with various block lengths of cationic PG segments with polydispersity indices...
The micelles of hybrid hydrogels from PG34-\(b\)-PEO230\(-\)b-PG\(_n\) and EuW\(_{10}\) were mixed together under vigorous stirring at a concentration of 20 wt%. The aqueous solutions of PG\(_{20}\)-b-PEO230-b-PG\(_n\) and EuW\(_{10}\) were mixed together under vigorous stirring at a charge stoichiometric point and appropriate solid concentrations above 5.0 wt%, and the hydrogels were formed spontaneously (Fig. S3, ESI†). Interestingly, the minimum gelation concentration (MGC) of the hydrogels is highly dependent on the length of the positively charged PG blocks of the copolymers. For the copolymer PG\(_n\)-b-PEO230-b-PG\(_n\) (\(n \geq 9\)), the MGC of the hybrid hydrogels decreases with an increased length of the cationic PG blocks, while the copolymer, PG\(_{20}\)-b-PEO230-b-PG\(_{10}\), did not cause gelation when mixed with the EuW\(_{10}\) solution even at a high concentration of 20 wt%.

Cryogenic transmission electron microscopy (cryo-TEM) (Fig. 1b and c) reveals that the hydrogels are composed of well-separated isotropic micelles with a small size distribution. The micelles of hybrid hydrogels from PG\(_{20}\)-b-PEO230-b-PG\(_{10}\), have an average radius of \(\sim 10\) nm, and those of PG\(_{34}\)-b-PEO230-b-PG\(_{34}\) with a shorter PG chain have a smaller average radius of less than 5 nm. Furthermore, a generalized indirect fourier transformation\(^{12}\) analysis of small-angle X-ray scattering (SAXS) measurement of the PG\(_{34}\)-b-PEO230-b-PG\(_{34}\)-EuW\(_{10}\) complex in aqueous dispersion indicates that the scattering objects, the micellar cores, have a globular, almost spherical, shape with a \(R_g\) value of about 10 nm (Fig. S4, ESI†), in good agreement with the cryo-TEM results. We reasonably postulate the possible structural model of the cross-linked network as shown in Fig. 1a: the visible micelles constitute the flower-like core–shell single one and the scars almost disappeared. The resulting hydrogel was strong enough to hold itself when suspended horizontally between two posts (Fig. 3) and slantwise (Movie S1, ESI†), demonstrating its high self-healing efficiency. Furthermore, the self-healing feature of the hydrogel was also confirmed by rheological measurements (Fig. 3c). After a large-amplitude force (\(\gamma = 50\%\), \(\omega = 2\) rad s\(^{-1}\)) was applied, the \(G'\) value decreased from 30 kPa to 0.4 kPa and the \(\tan \delta = 34\%\) of \(G'\) value increased from 0.15 to 4.0, indicative of the collapse of the hydrogel to a quasi-liquid state. By the removal of the large strain, \(G'\) fully recovered to its initial value (30 kPa) within 20 s and returned to its original gel state. Moreover, the recovery behavior was repeated for three cycles without any distinct degradation. This fast recovery observed in our hybrid hydrogels...
dominant fraction of through coupling with O–H vibrations. In the present work, the longer one can be attributed to EuW10 — 26.6 3.06/1.000 — 0.02
Gel-5 PG 34-PEO230-PG34 22.3 4.16/0.941 1.16/0.059 —
Gel-4 PG 25-PEO230-PG25 19.2 3.96/0.916 0.84/0.084 0.10
Gel-3 PG 20-PEO230-PG20 18.5 4.07/0.931 1.17/0.069 0.09
2.1 ms) with a much lower fraction of

Table 1 Summary of photophysical properties of the EuW10 crystal and the hydrogels based on EuW10 and copolymers with diverse block lengths

| Samples | Copolymer | \(\varphi_{PL}^a\) (%) | \(\tau_1\) (ms)/\(f_1\) | \(\tau_2\) (ms)/\(f_2\) | \(q^b\)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel-1</td>
<td>PG9-PEO230-PG9</td>
<td>15.5</td>
<td>3.67/0.908</td>
<td>0.76/0.909  —</td>
<td></td>
</tr>
<tr>
<td>Gel-2</td>
<td>PG14-PEO230-PG14</td>
<td>16.7</td>
<td>3.85/0.930</td>
<td>0.99/0.970  —</td>
<td></td>
</tr>
<tr>
<td>Gel-3</td>
<td>PG25-PEO230-PG25</td>
<td>18.5</td>
<td>4.07/0.931</td>
<td>1.17/0.069 0.09</td>
<td></td>
</tr>
<tr>
<td>Gel-4</td>
<td>PG35-PEO230-PG35</td>
<td>19.2</td>
<td>3.96/0.916</td>
<td>0.84/0.084 0.10</td>
<td></td>
</tr>
<tr>
<td>Gel-5</td>
<td>PG45-PEO230-PG45</td>
<td>22.3</td>
<td>4.16/0.941</td>
<td>1.16/0.059 —</td>
<td></td>
</tr>
<tr>
<td>EuW10</td>
<td>—</td>
<td>26.6</td>
<td>3.06/1.000  —</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>EuW10 (aq)</td>
<td>—</td>
<td>0.51</td>
<td>1.79/1.000  —</td>
<td>0.39</td>
<td></td>
</tr>
</tbody>
</table>

a Apart from determining 8 wt% EuW10 (aq) by the relative method with tryptophan as a standard, quantum yields were measured by an integrating sphere (\(\varphi_{ex} = 280\) nm). b The fluorescence decay intensity \(I(t)\) as a function of time \(t\) was fitted by the equation consisting of two exponential terms, \(I(t) = f_1 \exp(-t/\tau_1) + f_2 \exp(-t/\tau_2)\), where the amplitude of each exponential component \(f_i\) represents the fractional contribution of the fluorophore in a specific environment to the total fluorescence decay. c The number of water molecules coordinated to Eu3+ in the micellar core of the hydrogels associated with the total lifetime \(\tau_1\).

may be attributed to the disassociation and reformation of the coacervate core arising from quickly responsive and non-directional nature of electrostatic attraction.

It is known that in aqueous solutions, coordination with water leads to a severe quenching of the EuW10 luminescence, owing to radiationless deactivation of the \(D_0\) excited state through coupling with O–H vibrations. In the present work, the hydrogels show the typical emission spectra of EuW10 (Fig. S6, ESIF), similar to the EuW10 crystals, and the EuW10 emission of hybrid hydrogels in an aqueous milieu was greatly enhanced (Table 1). The absolute photoluminescence quantum yields of the hydrogels increase from 15.5% to 22.3% as the PG block lengths of the copolymers increase from 9 to 34, independent of the concentration and ionic strength (Table S2 and S3, ESIF). The hybrid hydrogels exhibit a high quantum yield of 22.3% which is close to that of the EuW10 crystals (26.6%).

According to the time-resolved fluorescent measurements, all hybrid hydrogels display double-exponential emission decays (Fig. S7, ESIF). As summarized in Table 1, hybrid hydrogels have a long lifetime \(\tau_1 \approx 3.67–4.12\) ms with a dominant fraction of \(f_1 > 0.9\) and a short lifetime \(\tau_2 \approx 0.76–1.17\) ms with a much lower fraction of \(f_2 < 0.1\). Similar to our previous reports, the longer one can be attributed to EuW10 species located in the hydrophobic core of hybrid micelles, while the shorter one, which is comparable to 1.79 ms of EuW10 in 8 wt% aqueous solution, could be associated with the free EuW10 molecules outside the micelles. It is noteworthy that the decay lifetime \(\tau_1\) of the hydrogels was even longer than that of the EuW10 crystal (3.1 ms), which is unusual among EuW10 hybrid materials. Meanwhile, the number of water molecules \(q\) coordinated to Eu3+ in aqueous solutions can be estimated by eqn (1):

\[
q = 1.05 \left(1/\tau_{H_2O} - 1/\tau_{D_2O}\right)
\]

where 1/\(\tau_{H_2O}\) and 1/\(\tau_{D_2O}\) are the reciprocal experimental lifetimes in H2O and D2O solutions in ms\(^{-1}\), respectively. For luminescent EuW10 species with super long lifetimes in hydrogels, the \(q\) values are less than 0.1, suggesting that there is almost no water molecules coordinated to the Eu3+ ion. Therefore, the lumiphore EuW10 confined within the hydrophobic cores effectively shielded the coordination with water molecules, contributing to the enhanced luminescence and prolonged decay lifetime.

In summary, we reported the facile preparation of hybrid luminescent hydrogels by assembling triblock copolymers with polyoxometalates through electrostatic interactions in an aqueous solution. The mechanical strength of the hydrogel is exceptionally high and can be easily tuned by altering the copolymer composition, concentrations, and ionic strengths. The hydrogels exhibit excellent self-healable properties. Owing to the hydrophobic nature of the coacervate core, the hybrid hydrogels exhibit significantly enhanced emission with comparably high quantum yields to the EuW10 crystals. Such a novel modular assembly strategy as well as the diversity of POMs offers us an opportunity in the realms of catalytic, electrochromic hybrid gels, etc.

This work was supported by the NNSFC (No. 51030001, No. 51373001, No. 21322404, No. 20834001), the Beijing Natural Science Foundation (No. 2122024), and the Open Research Fund of State Key Laboratory of Polymer Physics and Chemistry, CIAC, CAS (No. 110000R041).

Notes and references


This journal is © The Royal Society of Chemistry 2014


