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Synthesis of conducting polymer hydrogels with 2D building blocks and their potential-dependent gel–sol transitions†

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Conducting polymer hydrogels with unusual 2D building blocks were synthesized in one step via a combination of oxidative coupling polymerization and non-covalent crosslinking of an amphiphilic thiophene derivative. Chemicals with standard electrode potentials higher than 0.8 V triggered disbanding of the resulting conducting polymer hydrogels, indicating the occurrence of potential-dependent gel–sol transitions.

Electrically conductive hydrogels (ECHs), various combinations of conducting polymers¹ and aqueous gels,² have recently attracted great attention due to their huge potential for application in the chemical mimicry of neural networks, bio-recognition membranes, electro-stimulated drug release, nerve rehabilitation, *etc.*³ Embedding or grafting one of the conducting polymers as a discontinuous phase to a non-conductive host matrix,³ *e.g.*, ion-crosslinked PEDOT–PSS hydrogels,⁴ chitosan-grafted polyaniline hydrogels,⁵ *etc.*, is an effective way to synthesize various ECHs. However, discrete electron-transferring domains in the non-conductive host matrix would impair the performances of the resulting composite ECHs compared to those with conducting polymers as a continuous phase, *i.e.*, conducting polymer hydrogels (CPHs). Up to now, the synthesis of CPHs is still a great challenge due to the poor solubility of conducting polymers in aqueous solution, originating from the lack of hydrophilic groups and stiff chains.⁶ Recently, a polyaniline hydrogel⁷ and polythiophene counterpart⁸ have been reported elsewhere. Unfortunately, tedious chemical crosslinking was indispensable in either case for obtaining the 3D network of the corresponding hydrogel after monomer polymerization.

In this communication, we present a rational approach, illustrated in Fig. 1, to synthesize CPHs in one step, starting from sodium 4-(2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methoxybutane-1-sulfonate (EDOT-S), which is one of the thiophene derivatives used as an amphiphilic monomer, by a

combination of oxidative coupling polymerization and non-covalent crosslinking. A striking synergistic effect between the oxidants ammonium persulfate (APS) and FeCl₃ was achieved during the synthesis of the PEDOT-S hydrogel. Real time cryo-TEM, SEM and AFM images disclosed the unique sheet-like building blocks in the 3D assembly of the CPHs. Due to overoxidation, degradation of the backbones in the polymeric hydrogels was observed upon selective addition of chemicals with potentials higher than *ca.* 0.8 V, indicating the occurrence of chemical potential dependent gel–sol transitions.

The amphiphilic EDOT-S serving as the monomer was prepared according to the literature.⁹ The oxidizing agent used in our case was either APS or FeCl₃, or a mixture of both. APS is a non-crosslinking oxidant in the synthesis of conducting polymers. It is well known that APS can polymerize aniline, pyrrole, EDOT, *etc.*,¹⁰ via oxidative coupling and the corresponding conducting polymers in the form of a precipitate can be obtained due to both the stiffness of their backbones and strong π – π interactions among large conjugated units in their backbones.⁶ However, in our case, the conducting polymer in the form of a 3D network (namely a hydrogel) was obtained for the first time using only non-crosslinking APS as the oxidizing agent, when the amphiphilic EDOT-S was used as the starting monomer. This indicates that the structure of the monomer, *e.g.* the introduction of the hydrophilic ionic group to the hydrophobic monomer, plays a key role in the synthesis

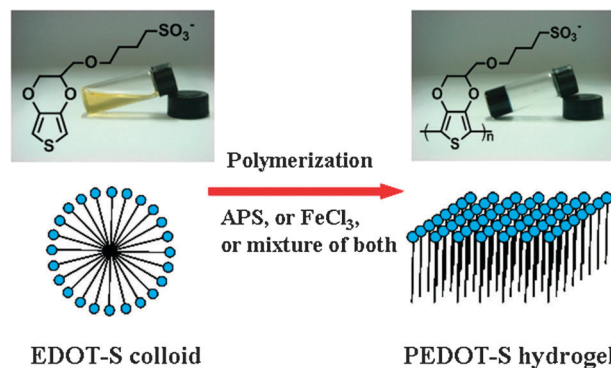


Fig. 1 A schematic diagram for synthesis of conducting polymer hydrogels: An EDOT-S colloidal solution with spherical micelles has converted into a PEDOT-S hydrogel with sheet-like building blocks upon addition of an oxidant (APS, or FeCl₃, or a mixture of both) to trigger the polymerization.

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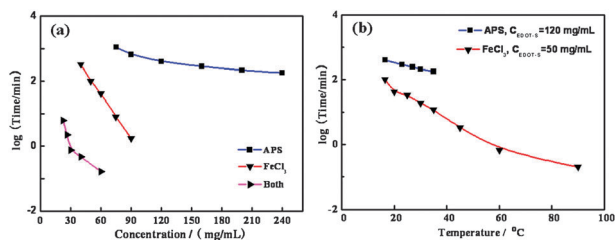


Fig. 2 The effects of various synthetic parameters, such as the type of oxidant, concentration of the monomer, reaction temperature, *etc.*, on the formation of PEDOT-S hydrogels: (a) room temperature (16.5 °C) curves of concentration *versus* gelation time and (b) curves of temperature *versus* gelation time.

of CPHs. This also gives us the inspiration for preparing other CPHs, starting from amphiphilic derivatives of aniline, pyrrole, *etc.*, with a similar structure to EDOT-S. In comparison with those made using APS as the oxidant, the PEDOT-S hydrogels can be obtained under conditions of either a lower monomer concentration or a higher reaction temperature, when FeCl₃ was used as the oxidant, as shown in Fig. 2. This is probably due to the multivalent metal ions (excessive Fe³⁺ in our case) offering an additional cross-linking force to the sulfonate groups attached to PEDOT-S backbones, evidenced from the fact that a small quantity of iron was observed in the XPS spectra of the dried hydrogels made with FeCl₃ (see the supporting information, Fig. SI1†). When the mixture of APS and FeCl₃ was used as the oxidant, a striking synergistic effect was achieved during the synthesis. Taking a monomer concentration of 60 mg mL⁻¹ as an example, when only APS was used no hydrogels were obtained with such a low monomer concentration, which means the gelation time is infinite; when only FeCl₃ was used, the gelation time was 2580 s. However, when the mixture of APS and FeCl₃ was used, the gelation time was only 10 s, which is incredibly fast for synthesizing CPHs and this was due to the synergistic effect. To the best of our knowledge, this is the fastest known synthesis in comparison with other reported synthetic strategies for various CPHs.

The internal 3D structure of the resulting PEDOT-S hydrogels was disclosed by SEM and AFM images of freeze-dried samples. For the samples using APS as the oxidant, when the hydrogel did not form ($C_{\text{EDOT-S}} < 75 \text{ mg mL}^{-1}$), the freeze-dried product shows a “fishbone-like” morphology (Fig. 3a) due to secondary instability formation perpendicular to the freezing direction.¹¹ When the hydrogel did form ($C_{\text{EDOT-S}}$ in the range 75–240 mg mL⁻¹), the freeze-dried product shows an unusual sheet-like morphology (Fig. 3b) with an area to thickness ratio much larger than 1000, with the quasi-2D sheets serving as the building blocks to form 3D hydrogels. An AFM image (see Fig. SI2†) further reveals that these quasi-2D sheets were composed of multi-layers. For the samples using FeCl₃ or a mixture of APS and FeCl₃ as the oxidant, the unusual quasi-2D sheet-like building blocks were similarly observed, as seen in Figs 3c and d, respectively. Polymeric chains, 0D quantum dots, or 1D nanostructures serving as the building blocks of a number of hydrogels were usually observed.² Sheet-like 2D nanostructures, except for some inorganic materials such as graphene, graphene oxide, and clay,¹² serving as the building units in the hydrogels were

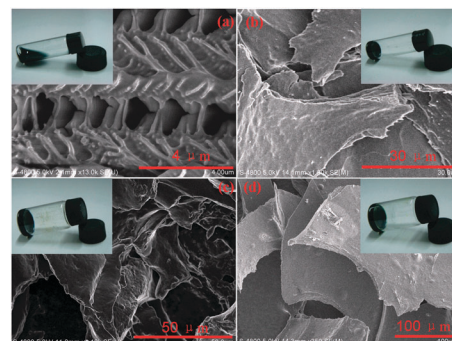


Fig. 3 SEM images of the resulting PEDOT-S products (see each inset) synthesized with different oxidants: (a) & (b) using APS as the oxidant; (c) using FeCl₃ as the oxidant; (d) using a mixture of APS and FeCl₃ as the oxidant.

hardly ever seen. To the best of our knowledge, this is the first example of using organic 2D nanostructures as the building units in hydrogels.

To disclose the formation mechanism of such unusual sheet-like building blocks during the synthesis of the PEDOT-S hydrogels, a real time cryo-TEM investigation was conducted. When an EDOT-S solution with a monomer concentration of 240 mg mL⁻¹ was mixed with APS, spherical micelles, which were very similar to those observed before addition of oxidant (see Fig. SI3†), were clearly recognized, indicating that the EDOT-S monomer possesses an excellent capability for micellization due to its amphiphilic molecular structure. In the presence of oxidant, these EDOT-S spherical micelles gradually gathered and fused together to form a lamellar structure and ultimately evolved into the large PEDOT-S sheets (see Fig. SI4†). Simultaneously, changes in color of the mixture from straw-yellow to jet-black were observed, indicating that polymerization was taking place during the evolution of the EDOT-S micelles. It should be emphasized that the π - π interactions are negligible unless the number of aromatic rings is three or more,¹³ and thus the EDOT-S (1 aromatic ring in each molecule) with negligible π - π stacking easily forms spherical micelles, in which the overlapping of ring planes of the monomers never occurs due to the geometry (see Fig. SI5†). As the polymerization continues, the non-negligible π - π stacking among gradually growing PEDOT-S macromolecules has converted the spherical micelles into sheet-like nanostructures, in which overlapping of the ring planes of the macromolecules easily occurs (see Fig. SI6†).

Intriguingly, it was found that the resulting PEDOT-S hydrogel exhibits chemical potential-dependant gel-sol transitions upon treatment with a series of oxidants (for the standard electrode potentials of these oxides see Table SI1†). As shown in Fig. 4a, after one of the oxidants with a chemical potential higher than *ca.* 0.8 V, such as APS, H₂O₂, Ce(SO₄)₂, K₂Cr₂O₇, HNO₃, was added, the black hydrogels were irreversibly turned into the sols with different colors over a period of time. However, when one of the oxidants with a chemical potential lower than *ca.* 0.8 V, such as AgNO₃, FeCl₃, CuSO₄, was added, no similar gel-sol transitions were observed for the original PEDOT-S hydrogels. To explore such a chemical potential-dependant gel-sol transition, UV spectroscopy was used to investigate the change in the PEDOT-S hydrogel upon

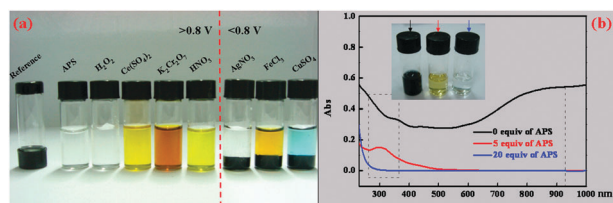


Fig. 4 (a) Chemical potential-dependent gel-sol transitions of the resulting PEDOT-S hydrogels. When chemicals with a potential higher than *ca.* 0.8 V were added, the investigated hydrogels disappeared, while when chemicals with a potential lower than *ca.* 0.8 V were put in, the investigated hydrogels were retained. (b) UV spectra of the PEDOT-S hydrogels treated with different amounts of APS.

addition of a strong oxidant, as shown in Fig. 4b. It can be seen that the broad peak at *ca.* 900 nm, which is typical of p-doped polythiophenes,¹⁴ disappeared first upon addition of APS. This indicates the instability of doped PEDOT-S that is induced by strong oxidants. The peak located around 300–400 nm, which refers to the π - π^* transition of PEDOT-S,¹⁴ blue-shifted with increasing amounts of APS. This represents a decrease in the conjugation length in the delocalized π -bond along the PEDOT-S chains. When 20 equiv. of APS was added, the PEDOT-S was not seen in the spectrum, indicating the complete destruction of the conjugated structure.

The irreversible gel-sol transition of the resulting PEDOT-S hydrogels is ascribed to the overoxidation of PEDOT-S (see Fig. S17[†]). It was reported that either polythiophene¹⁵ or PEDOT¹⁶ can be ring-opened *via* overoxidation when strong oxidants were applied. Similarly, in our case, the disappearance of the p-doped peak in the UV spectra corresponds to the ring-opening process of the thiophene rings with positive charges. Once these rings were depleted, the uncharged rings in the PEDOT-S chains underwent the oxidative doping and subsequent ring-opening process again, resulting in a decrease in the conjugation length, which is in accordance with the blue shift of the peak representing the π - π^* transition. If a large amount of strong oxidants were put in, the degradation reaction completed and hardly any macromolecules were collected after dialysis.

In conclusion, the PEDOT-S hydrogels with unusual 2D building units were successfully synthesized by using different oxidants. The striking synergistic effect of the oxidants was obtained when a mixture of APS and FeCl₃ was used, which has provided the fastest known way to make CPHs. Preliminary investigation shows that the conductivities of these conducting polymer hydrogels are in the range 10⁰–10² S m⁻¹, dependent on the monomer concentration and oxidant type (see Table S12[†]). The resulting PEDOT-S hydrogels presented unique chemical potential-dependent

gel-sol transitions upon addition of different chemicals. The rheological properties of these CPHs are currently under investigation, but we believe that these hydrogels might have great potential for application in a number of technologies, such as chemical mimicry of neural networks, electro-stimulated drug release, sensors, *etc.*

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