Facile fabrication of conducting polymer hydrogels *via* supramolecular self-assembly

Tingyang Dai,[a] Xiujuan Jiang,[a] Shouhu Hua,[a] Xiaoshu Wang[b] and Yun Lu*[a]

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We describe a simple and versatile method to fabricate conducting polymer hydrogels *via* supramolecular self-assembly between polymers and multivalent cations; the as-prepared hydrogels are potentially applicable in the fields of electrosensors, chemical release and artificial muscles.

Conducting polymers have been attracting increasing attention since they cover a wide range of functions from insulators to metals originating from their unique π-conjugated systems.[1,2] Gels of conducting polymers, cross-linked with chemical bonds[3] or physical nodes (crystallites or aggregates),[4] have been intensively investigated in the past decade because the materials exhibit the mechanical and swelling properties of gels added to the specific transport properties of conducting polymers.[5] Nowadays, the most successful conducting polymer in commercial applications is probably poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate), known as PEDOT-PSS, due to its remarkable advantages over other conducting polymers, such as a high transparency in the visible range, excellent thermal stability, and processability in aqueous solution.[6] PEDOT-PSS hydrogels have been prepared by physically crosslinking the negatively-charged colloidal particles of PEDOT-PSS with multivalent cations *via* supramolecular self-assembly,[7] and applied in supercapacitors and biosensors.[8,9] However, the conventional fabrication of PEDOT-PSS hydrogels involves the preparation of PEDOT-PSS films first, and then the treatment of the films with aqueous solutions containing multivalent cations.[7–9] This two-step procedure is almost impossible to be scaled up for producing bulk amounts of conductive hydrogels, because PEDOT-PSS films disintegrate easily in aqueous solutions.[8] Moreover, as-prepared hydrogels, in the form of films with thickness of only several microns,[9] find difficulty for application in areas such as artificial muscles and electromechanical actuators,[10] which is likely the most important applications for conducting polymer gels. In this communication, we present a novel and simple method for the fabrication of PEDOT-PSS hydrogels *via* supramolecular self-assembly. 3,4-Ethylenedioxythiophene (EDOT) monomers are polymerized in PSS aqueous solution under a static condition with Fe^{3+} ions acting as both the oxidant and the ionic crosslinker. The gelation process happens simultaneously with the polymerization process. Such a one-step procedure can be easily scaled up and is versatile for the fabrication of conducting polymer hydrogels.

The synthesis of PEDOT-PSS hydrogel, which contains a substantial amount of water and exhibits a highly swollen macroscopic appearance (Fig. 1(a)), is accomplished using a mixture of EDOT, poly(sodium 4-styrenesulfonate) (NaPSS) and $Fe(NO_3)_3{\cdot}9H_2O$.[11] In a typical experiment, 100 μL of EDOT (0.9 mmol) was added into 15 ml of 0.1 M NaPSS (1.5 mmol) aqueous solution. After stirring for 30 min, 15.3 g $Fe(NO_3)_3{\cdot}9H_2O$ (38 mmol) in 5 ml of water was added. The resulting system was stirred for 1 min to ensure complete mixing and then the reaction was allowed to proceed without agitation for 24 h at room temperature. Finally, the product was purified in a large amount of distilled water for at least 1 week in order to wash out low molecular weight components of the systems. Fe^{3+} ions in excess amount play a key role in the gelation process, since Fe^{3+} ions not only promote the

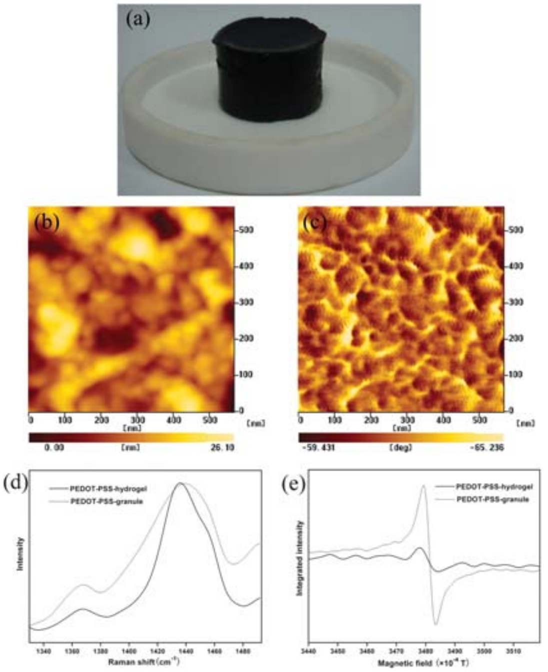

Fig. 1 (a) Macroscopic appearance of a saturated sample of PEDOT-PSS hydrogel. (b,c) Topography and corresponding phase images of PEDOT-PSS hydrogel. (d,e) Raman spectra and ESR of PEDOT-PSS hydrogel and granules. Hydrogels were freeze-dried before AFM, Raman and ESR measurements.

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[a] *Department of Polymer Science and Engineering, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, PR China. E-mail: yunlu@nju.edu.cn; Fax: 86-25-83317761; Tel: 86-25-83686423*
[b] *Centre for Materials Analysis, Nanjing University, Nanjing, 210093, PR China*

polymerization of EDOT as an oxidant, but also electrostatically interact with negatively-charged PSS as an ionic crosslinker. To confirm the importance of Fe^{3+} ions, ammonium peroxydisulfate (APS) was used to replace $Fe(NO_3)_3{\cdot}9H_2O$ as the oxidant, and only granules could be obtained as the resulting product. Further, on addition of aqueous $Fe(NO_3)_3$ solution, PEDOT-PSS precipitates out immediately from its dispersion (Baytron-P, commercially available from Bayer AG, Germany), implying that Fe^{3+} ions have the function of crosslinking the polymer. Similar gelation phenomena can also be induced using other multivalent cations with oxidizing capacity, such as Ce^{4+} ions, as both the oxidant and the crosslinker. Anyway, this type of ionic crosslinking is well known in systems of conventional ionic polymers.[12] Elemental analysis shows that a dry sample of as-prepared PEDOT-PSS hydrogel has an iron content of 0.46 wt%. Because of the excess amount of Fe^{3+} ions added into the reaction systems (with Fe^{3+}/ EDOT molar ratio higher than 40 : 1), the iron content in the product is almost exclusively contributed by the Fe^{3+} ions incorporated in the network, although Fe^{2+} ions (the product of the redox reaction) may also exist. Herein, it should be pointed out that most of the Fe^{3+} ions in the hydrogels have been leached in the purifying process.

The morphology of a freeze-dried PEDOT-PSS hydrogel, imaged using atomic force microscopy (AFM, SPI-3800, Seiko Instruments Inc.) in the tapping mode, is shown in Fig. 1(b) and (c). It can be observed from the topography image (Fig. 1(b)) that the material is an assembly of spherical grains, directly showing that the hydrogel is prepared by physically crosslinking the PEDOT-PSS particles. Interestingly, in the corresponding phase image (Fig. 1(c)), a three-dimensional network structure is detected on the surface of the sample. For the PEDOT-PSS system, the bright phase corresponds to PEDOT while the dark phase refers to PSS.[13] Therefore, the bright/dark interlaced image indicates that, at the nanometer scale, a phase separation takes place in PEDOT-PSS hydrogel and a conducting network of PEDOT is formed. As such phase separation has not been detected either in the literature where films of PEDOT-PSS were crosslinked with multivalent cations[7] or in our experiment that PEDOT-PSS granules were prepared with stirring,[14] we believe that the static condition we have employed in the polymerization (gelation) process is mainly responsible for the observed phenomenon. In general, during the synthesis process of PEDOT-PSS dispersion (Baytron-P), the mechanical energy, arising from vigorous stirring or shaking, could be transformed into interfacial energy between the two phases of PEDOT-PSS granules and the surrounding aqueous solution.[15] So the dispersion is characterized by a positive Gibbs energy, and is actually a metastable state of PEDOT-PSS. In our preparation of PEDOT-PSS hydrogels, however, no mechanical energy is injected and the reaction takes place spontaneously and continuously. Thereby, the PEDOT-PSS system may reach a more stable state, with a nanoscalar network structure,[15] through spontaneous phase separation. Research is now under way to investigate the detailed mechanism for such phase separation.

The conformation of the polymer chains in both PEDOT-PSS hydrogel and granules[14] is characterized *via* Raman spectroscopy (labRAM HR800, using 532 nm laser as the excitation source) and electron spin resonance (ESR, Bruker EMX 10/12) measurements. From Raman spectra (Fig. 1(d)), an obvious difference is observed for the strong band located between 1400 and 1500 cm^{-1}, and the hydrogel exhibits a narrower band at a lower position. In ESR measurements (Fig. 1(e)), the integrated ESR intensity of the hydrogel is much lower than that of the granules. Both of the results suggest that, comparing with the PEDOT-PSS granules prepared under stirring, PEDOT-PSS hydrogel possesses a more expanded-coil conformation in the polymer chains.[16] It has been reported that mechanical shear is likely to make the polymer chains more coiled in solutions.[17,18] Therefore, it is reasonable to deduce that the static condition used in the preparation of PEDOT-PSS hydrogel induces the expansion of the polymer chains, which results in improved π–π interchain stacking, elongation of the effective conjugation length and a longer mean free path.[19] Accordingly, PEDOT-PSS hydrogel displays high electrical conductivity: a conductivity of 4.1×10^{-3} S cm^{-1} at its saturated state and a compressed dry pellet conductivity of 4.3 S cm^{-1} (measured using the four-probe technique[20] at room temperature), which is more than an order of magnitude higher than that of PEDOT-PSS granules (0.4 S cm^{-1}).

The more expanded-coil conformation of PSS also makes the PSS chain itself have more chances to interact with Fe^{3+} ions. Consequently, PEDOT-PSS hydrogels can be prepared even when the amount of negatively-charged PSS is less than that of positively-charged PEDOT. From this viewpoint, the as-prepared PEDOT-PSS hydrogel is actually a Fe^{3+}-crosslinked PSS network containing a PEDOT component. Hydrogels synthesized with different EDOT/PSS ratio present an evolvement in microscale morphology, from a relatively uniform integrative structure (Fig. 2(a) and (b)) to small pieces of connected films (Fig. 2(c) and (d)), and finally to network structures composed of connected feather-like films with the size of several microns (Fig. 2(e) and (f)). Although the

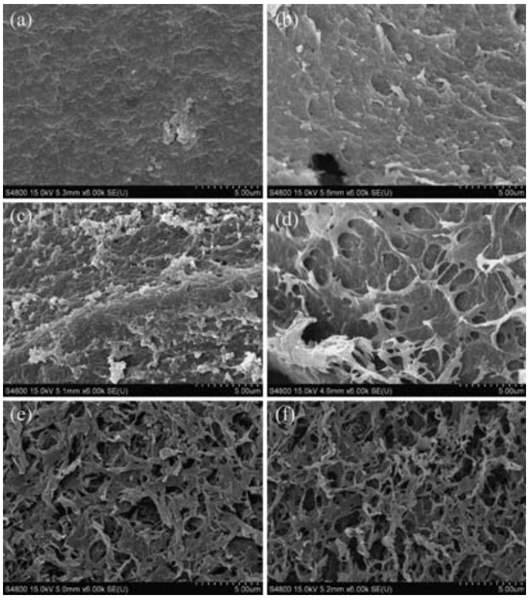

Fig. 2 SEM images of PEDOT-PSS hydrogels prepared with (a) 50 μL, (b) 100 μL, (c) 200 μL, (d) 400 μL, (e) 600 μL and (f) 800 μL of EDOT. Other conditions: PSS: 1.5 mmol; $Fe(NO_3)_3{\cdot}9H_2O$: 15.3 g. Samples were freeze-dried before SEM measurements.

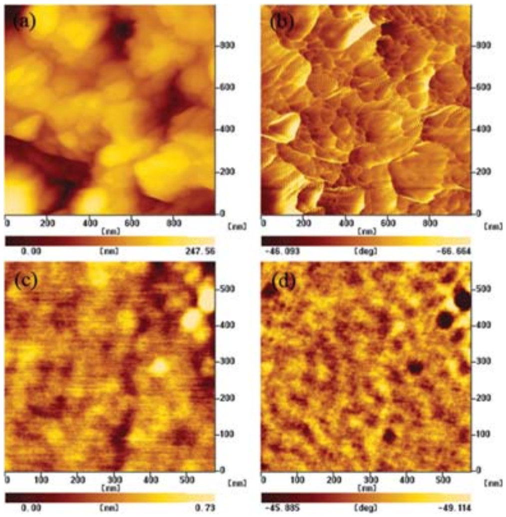

Fig. 3 Topography (a,c) and corresponding phase images (b,d) of PEDOT-PSS hydrogels prepared with 800 μL EDOT. Other conditions: PSS: 1.5 mmol; $Fe(NO_3)_3·9H_2O$: 15.3 g. (a,b) were obtained from a freeze-dried sample, while (c,d) were obtained from a sample dried at 60 °C in the atmosphere.

mechanism for the morphological transformation is still unknown, a possible driving force might be the spatially-repulsive effect[21] of the excess formed PEDOT.

A dramatic shrinkage of swollen hydrogels, together with the exudation of the water component, is detected in response to a given stimulus. For example, a piece of hydrogel prepared with EDOT/PSS molar ratio of 4.8 : 1 undergoes a shrinkage with volume ratio of about 80 : 1 when dried at 60 °C in the atmosphere. During this process, the shrinkage of both the connected PEDOT-PSS particles (Fig. 3(a,c), topography images) and the nanoscalar networks (Fig. 3(b,d), phase images) is directly observed in AFM measurements. Such stimuli-responsive properties, on both the macroscopic and the microscopic levels, endow the materials with potential applications for chemical release and artificial muscles.[10,22] The swelling–shrinking behavior of the hydrogels in response to the change in ionic strength, pH value as well as electric fields is currently being investigated in our lab.

The gelation procedure for preparing PEDOT-PSS hydrogels, utilizing the supramolecular self-assembly between polymers and multivalent cations, is versatile for the fabrication of different conducting polymer hydrogels. For instance, polypyrrole (PPy) and sulfonated polyaniline (SPAn),[23] as the conducting polymer and the negatively-charged poly-electrolytic dopant, respectively, are employed to replace PEDOT and PSS. Hydrogels of PEDOT-SPAn, PPy-PSS and PPy-SPAn (Fig. 4) can all be prepared, using Fe^{3+} ions as both the oxidant and the ionic crosslinker.

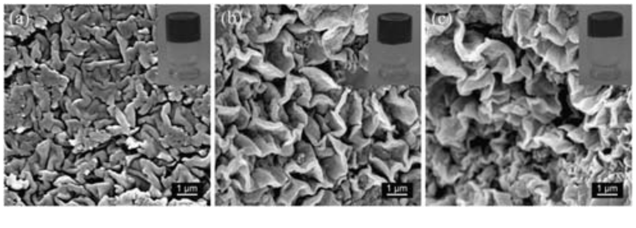

Fig. 4 SEM images of the hydrogels of (a) PEDOT-SPAn, (b) PPy-PSS and (c) PPy-SPAn. Insets: corresponding macroscopic images of the hydrogels.

In summary, we have demonstrated an effective approach for the synthesis of conducting polymer hydrogels. Under the static condition, the polymer chains show a more expanded-coil conformation and are capable of interacting with multivalent cations to form supramolecular networks. Gelation takes place at the same time with the polymerization process, and this ingenious method makes it possible to easily fabricate conducting polymer hydrogels in one step. As-prepared stimuli-responsive hydrogels may be applied in the fields of electrosensors, chemical release and artificial muscles. Significantly, the present work may provide a profound understanding for the supramolecular self-assembly in systems containing conducting polymers, and give valuable hints for achieving facile fabrication of conducting polymer materials applicable for electronic industry.

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