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Electronic Supplementary Information

Electronic conductive hydrogel synthesis from a hydrogelator and a conducting polymer

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Materials and Methods

NaPPDT was synthesized as shown in the literature.¹ Ammonium persulfate (KPS, 99% Tokyo Chemical Industry Co., Ltd. (TCI)), aniline, (99%, Wako Pure Chemical Industries, Ltd. (Wako)), and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) aqueous solution (PAMPS, average M_w 2,000,000, 15 wt. %, Sigma-Aldrich Co. LLC.) were used without further purification. All other solvents were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. Water was deionised with an Elix UV 3 Milli-Q integral water purification system (Nihon Millipore K.K).

Water-soluble polyaniline complex (**wsPANI**) was prepared by the oxidative polymerization of aniline with KPS in the presence of PAMPS. The mixture of aniline 800 mg and 15% PAMPS aq. 10.68g in 4.52 g 1M HCl aq. was stirred for 30 min at room temperature and then stirred for 10 min in the ice bath (0~5°C). To this mixture, APS 980mg in 16.00g 1M HCl was added in the ice bath for 30 min and then stirred at room temperature for 1 h (the colour of mixture turned from blue to green). The obtained reaction mixture was dialyzed by use of Fisherbrand[™] regenerated cellulose dialysis tubing (molecular weight cut off: 3500 Da, Fisher Scientific) in pH 4 HCl aq. for 1 week with repeated changes

of HCl aq. twice a day to remove the residues of polymerization. Water was removed from the dialyzed solution and then the residue was dried in vacuo to yield a dark green film like solid of **wsPANI** (782 mg, monomer conversion 98%).

wsPANI: ¹H-NMR (500 MHz, D₂O, TMS, δ , ppm): 8.18 (t, 1H, *J* = 5.4 Hz), 7.21 (s (br), 1H), 3.63 (d, 2H, *J* = 6.0 Hz), 3.24 (d, 2H, *J* = 4.1 Hz), 2.12 (m, 2H), 1.53 (m, 2H) 1.24 (m, 24H) , 0.86 (t, 3H *J* = 7.3 Hz). Elemental anal. calcd for C₂₆H₅₂N₂O₇: C, 61.87; H, 10.38; N, 5.55. Found: C, 61.80; H, 10.31; N, 5.51.

The composite hydrogels were prepared by mixing of **NaPPDT** aqueous solution or hydrogel and **wsPANI** aqueous solution at room temperature as follows. Pale yellow solid **NaPPDT** was placed in a vial with a rubber seal (mighty vial, no. 01; Maruemu Corporation) containing water at a specific concentration (wt%), and the vial was capped. The vial was then heated in a dry bath at 90 °C until the **NaPPDT** solid was dissolved, at which point the **NaPPDT** aqueous solution was left to stand for 1 h at room temperature and then **NaPPDT** aqueous solution or gel are prepared. To this NaPPDT aq. or gel, **wsPANI** aqueous solution (5.0 wt%) was added and shook using a vortex genie (Scientific Industries, Inc) at room temperature. Then the mixed composite was left for 3 h before measurements.

The gelation tests were performed using vial inversion method in a vial. The gelation was determined by visual observation after inversion of the vial. If the mixture did not drop at the vial inversion, the mixture form gel.

¹H-NMR and ¹³C-NMR spectra were acquired using an AVANCE 500 (500 MHz, Bruker BioSpin K. K.) spectrometer. Elemental analysis was performed with a JM10 elemental analyzer (J-SCIENCE LAB CO., Ltd.).

Thixotropic behaviour was evaluated using the vial inversion method. The prepared hydrogel in the vial was shaken and mechanically collapsed using a vortex genie (Scientific Industries, Inc). The obtained sol was then allowed to set for a given time at room temperature, and the recovery of the gel state from the sol state was determined by visual observation after inversion of the vial.

Scanning electron microscopy (SEM) images were recorded using an SU-8000 scanning electron microscope (Hitachi High-Technologies Corporation) at 1.0 kV; the SEM sample (xerogel of hydrogel) was freeze-dried and placed on a conductive tape on the SEM sample stage. Pt, as a conductive material, was used as a coating (10nm-thick) on the sample.

Rheological measurements of the frequency sweep were performed at 25 °C using an MCR-301 rheometer (Anton Paar Japan K.K.) with a parallel plate (8 mm diameter) at a gap of 0.50 mm and γ of 0.01 %. Rheological measurements of the strain sweep were performed at 25 °C using an MCR-301 rheometer with a parallel plate (8 mm diameter) at a gap of 0.50 mm and a constant angular frequency of 1 rad s⁻¹. For the rheological measurements, the hydrogel sample was applied onto the parallel plate and sample stage and then any overflow gel was swept away. Step-shear measurements were carried out by repeatedly applying a normal strain (strain amplitude 0.01% and frequency 1 Hz) and a large strain (shear rate 3000 s⁻¹ for 0.1 s).

Measurements of absorbance of a polymer or hydrogel sample in 100 µm thickness on the slide

glass cell with a light path length of 10 mm were performed with a measurement system consisting of spectrometer HR4000 (Ocean Optics, Inc.), UV-VIS-NIR light source DH-200-BAL (Mikropack GmbH), and variable attenuator FVA-UV (Ocean Optics, Inc.) controlled by PC software OPwave (Ocean Photonics). The measurement system was constructed by Ocean Photonics.

Electronic conductivity of the composite hydrogel was performed with a four-probe method using an interdigitated array electrode (ALS Co., Ltd.), a digital multimeter 34401a (KEYSIGHT TECHNOLOGIES) and (ADC CORPORATION), a digital multimeter GDM 8255 (Good Will Instrument Co., Ltd.) and a DC power supply U8001 A (30V/3A, KEYSIGHT TECHNOLOGIES). After an ionic current of the composite hydrogel was settled down, electronic conductivity of the hydrogel was measured.

Infrared spectroscopy was performed using an FT/IR-620 (JASCO Corporation) and the ATR method (ZnSe prism).

Figs. S1 and S2



Fig. S1 Dynamic rheological properties of the composite hydrogels: (a) Frequency sweep and (b) strain sweep. These results confirmed the existence of stable gel state (G' > G'') and indicated that the composite hydrogels possessed a lower G value (the composite hydrogels becomes softer material than **NaPPDT** 1.0 wt% hydrogel in spite of having higher concentration of polymers).



Fig. S2 Thixotropic hysteresis loop of the **NaPPDT** hydrogel and composite hydrogel; (a, b) **NaPPDT** 1.0 wt% hydrogel, (c, d) **wsPANI** 5.0 wt%/ **NaPPDT** 1.0 wt% (2/1, w/w) composite hydrogels. The test was conducted with 1^{st} cycle: 0.001 s⁻¹ - 5.0 s⁻¹ - 0.001 s⁻¹ (120 s), 2^{nd} cycle: 0.001 s⁻¹ - 20 s⁻¹ - 0.001 s⁻¹ (120 s), 3^{rd} cycle: 0.001 s⁻¹ - 100 s⁻¹ - 0.001 s⁻¹ (120 s), 4^{th} cycle: 0.001 s⁻¹ - 0.001 s⁻¹ (120 s), with 1 min intervals between cycles.

Figs. S3 and S4



Fig. S3 The UV-vis absorption bands of **wsPANI**, **NaPPDT** and **NaPPDT/wsPANI** composite hydrogel (100 μm thickness on the slide glass).

The absorption band of **wsPANI** ranging from 600 nm to 850 nm is a typical band of doped state of polyaniline derivatives which is attributed to an emeraldine oxidized state of **wsPANI**.¹ It is observed that the doping state of **wsPANI** was kept in **NaPPDT/wsPANI** composite hydrogel by comparing the exitence of the bands ranging from 600 nm to 850nm in both materials, which was not observed in the spectrum of **NaPPDT**.



Fig. S4 IR spectra of the composite hydrogel in the region of sulfonyl stretching. To obtain information about the interaction of the components, the infrared (IR) spectrum of xerogels of hydrogels in the region of the sulfonyl was measured (Fig. S4). In Fig. S4, whereas the absorptsion peaks of the composite xerogel and dried **wcPANI** was the same, those of **NaPPDT** xerogel was different. This might reflect that the extent of sulfonic group in **wcPANI** was much larger than **NaPPDT** and peaks attributed to **NaPPDT** were hidden in the peaks of **wsPANI**.

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