

Temperature, Ionic Strength and pH Induced Electrochemical Switch of Smart Polymer Interfaces

Jianhua Zhou, Geng Wang, Jianqiang Hu, Xianbo Lu and Jinghong Li*

Department of Chemistry, Key Lab of Bioorganic Phosphorus Chemistry & Chemical Biology,

Tsinghua University, Beijing 100084, China; E-mail: jhli@mail.tsinghua.edu.cn

1. Experimental Section

Preparation of smart polymer-modified electrodes Au-disc electrodes were polished with wet alumina powder (from $\phi = 1 \mu\text{m}$ down to $0.05 \mu\text{m}$) on a polishing cloth, and then washed ultrasonically with ethanol and water respectively. In a typical process, *in-situ* electrochemical polymerization was performed in an aqueous solution which contained 1.0 M *N*-isopropylacrylamide or sodium acrylate (Aldrich, for P(NIPAm-co-AAc), 8 mol-% of AAc against NIPAm), and $\text{Na}_2\text{S}_2\text{O}_8$ (0.01 M), cycling the potential between -0.35 and -1.35 V at 100 mV s^{-1} (or 50 mV s^{-1}) for 60 cycles. The reaction solution was deoxygenated by bubbling nitrogen gas for 30 min at room temperature. After the polymerization, the electrodes were washed with double-distilled water to remove the monomers.

Electrochemical measurements A standard three-electrode cell was used for the electrochemical measurements. The potentials were reported vs. Ag/AgCl reference electrode. All experiments were carried out at room temperature unless otherwise noted. Cyclic voltammetry (CV) and electrochemical impedance (EIS) measurements were performed using CHI 630B (CHI Inc., USA) and PARSTAT 2273 Advanced electrochemical system (Princeton Applied Research, USA), respectively.

All electrochemical measurements were carried out in the presence of 5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ (1:1) mixture as a redox probe (0.1 M KClO_4 used as supporting electrolyte). CV measurements were performed in a potential range from

-0.1 to 0.5 V at the scan rate of 50 mV s⁻¹.

EIS measurements were performed at a bias potential of 0.240 V, in the frequency range from 100 kHz to 100 mHz, using an alternating voltage of 10 mV. The impedance spectra were plotted in the form of complex plane diagrams (Nyquist plots). The data were simulated by Echem Software ZSimpWin 3.20d. The circuit includes the electrolyte resistance between the working and the reference electrodes (R_s), Warburg impedance (Z_w), resulting from the diffusion of ions from the bulk of the electrolyte to the interface, electron transfer resistance (R_{et}), and the constant phase element Q (instead of the double layer capacitance, C_{dl}) to take the frequency dispersion into account.

2. ATR-FTIR Characterization

Attenuated total internal reflection fourier transform infrared (ATR-FTIR) spectra of the polymer brushes on electrodes were carried out using Perkin Elmer Spectrum one. The spectra were taken at a resolution of 4 cm⁻¹. The spectrum was consistent with the literature.¹⁻³ For PNIPAm, the N-H stretch at ~3310 cm⁻¹ and the C=O stretch at ~1640 cm⁻¹ confirmed the presence of amide groups in the polymer layer, and the characteristic doublet at 1385 and 1360 cm⁻¹ indicated the presence of the isopropyl group (see Fig. S1). Poly(acrylic acid) brushes were prepared by the same method for comparison. At pH 7, the carboxylic functional groups of PAA were partially ionized, the characteristic stretching frequencies included the carbonyl stretch (C=O) at 1723 cm⁻¹, CH₂ stretching at 1456 cm⁻¹, the C-O stretch at 1264 cm⁻¹, and the symmetric and antisymmetric stretching frequencies of the carboxylate ion (COO⁻) at 1420 and 1550 cm⁻¹, respectively. Comparing the spectrum of the copolymer P(NIPAm-co-AAc) with that of the homopolymer PNIPAm and PAA, the bands at 1546 and 1641 cm⁻¹ in the P(NIPAm-co-AAc) spectrum were attributed to amide stretching, which is found in the PNIPAm spectrum. The bands at 1728 and 1426 cm⁻¹ arose from carbonyl stretching of the acrylic acid carboxyl groups in PAA.

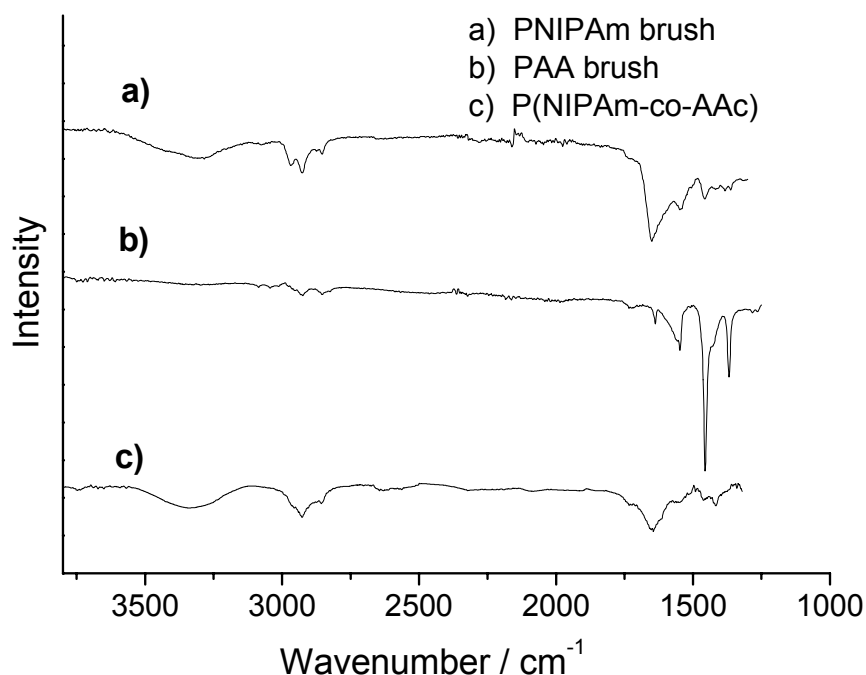


Fig. S1 In situ ATR-FTIR of spectra (a) PNIPAm brush, (b) PAA brush, and (c) P(NIPAm-co-AAc) brush on Au electrodes, at pH 7.

3. Thermo-, Ionic- and pH Sensitive Behavior of P(NIPAm-co-AAc) Brush Interface Investigated by Cyclic Voltammetry

Fig. S2 shows the cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-/4-}$ on the P(NIPAm-co-AAc) modified electrode at various environmental conditions. The redox label, $\text{Fe}(\text{CN})_6^{3-/4-}$, exhibited a quasi-reversible wave (peak-to-peak separation, $\Delta E_p = 302$ mV) at 20°C , $c_{\text{NaCl}} = 0$ M, pH 2.0 due to the attachment of P(NIPAm-co-AAc) brush on the electrode (curve a). When the temperature or the concentration of NaCl was switched to 50°C or 2.5 M, an obvious decrease of the peak currents and an increase of ΔE_p value were observed (curve b and c), suggesting that the collapse of P(NIPAm-co-AAc) chains at the interface insulated the electrical communication between redox label and electrode surface, and then controlled the permeation of ions or molecules (e.g. $\text{Fe}(\text{CN})_6^{3-/4-}$). Also, the redox response of $\text{Fe}(\text{CN})_6^{3-/4-}$ was completely depleted while the pH value was raised from pH 2.0 to 8.2 (curve d), revealing that the ionic repulsion among the fully ionized COO^- groups expanded the

polymer chain to form a rigid structure with more negative charge on the surface, and repulsed $\text{Fe}(\text{CN})_6^{3-/4-}$ from the interface. These results indicated that the electron transfer process at P(NIPAm-co-AAc) modified electrode could be greatly affected by environmental conditions, such as temperature, ionic strength and pH.

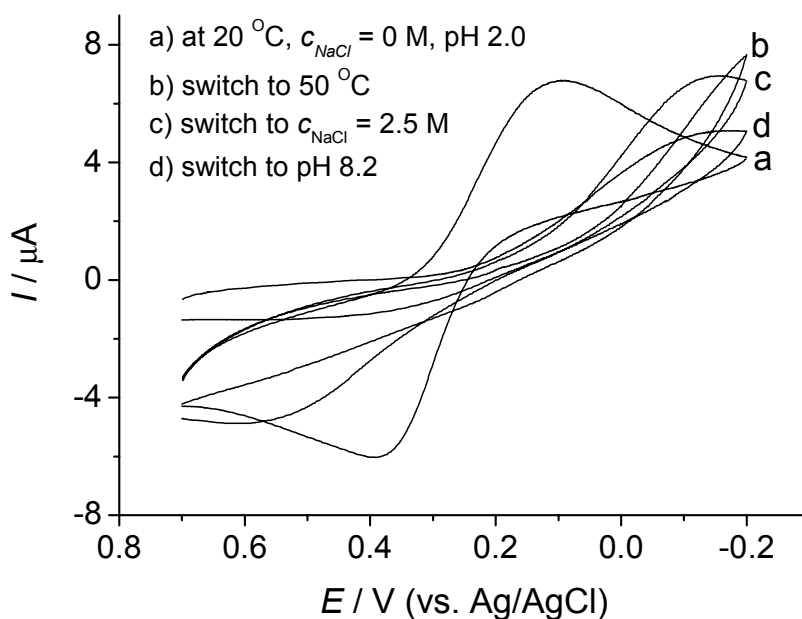


Fig. S2 Cyclic voltammograms of P(NIPAm-co-AAc) modified Au electrode in 0.1 M KClO_4 and 5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ aqueous solution with a scan rate of 50 mV s^{-1} ; (a) at $20 \text{ }^\circ\text{C}$, $c_{\text{NaCl}} = 0 \text{ M}$, pH 2.0, (b) at $50 \text{ }^\circ\text{C}$, $c_{\text{NaCl}} = 0 \text{ M}$, pH 2.0, (c) at $20 \text{ }^\circ\text{C}$, $c_{\text{NaCl}} = 2.5 \text{ M}$, pH 2.0, (d) at $20 \text{ }^\circ\text{C}$, $c_{\text{NaCl}} = 0 \text{ M}$, pH 8.2. Electrode area: $8 \times 10^{-2} \text{ cm}^2$.

References

- 1 Y. V. Pan, R. A. Wesley, R. Luginbuhl, D. D. Denton, B. D. Ratner, *Biomacromolecules*, 2001, **2**, 32.
- 2 L. J. Kirwan, P. D. Fawell, W. V. Bronswijk, *Langmuir*, 2003, **19**, 5802.
- 3 C. M. Schilli, M. Zhang, E. Rizzardo, S. H. Thang, Y. K. Chong, K. Edwards, G. Karlsson, A. H. E. Müller, *Macromolecules*, 2004, **37**, 7861.

Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2006