Temperature, ionic strength and pH induced electrochemical switching of smart polymer interfaces†

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A reversible electrochemical switching has been displayed at smart polymer brush interfaces, which was responsive to temperature, ionic strength and pH stimuli, independently or simultaneously.

Stimuli-responsive polymer interfaces, which switch their physical and chemical properties in response to external stimuli, have great potential in many technologically important areas such as drug delivery,[1] controlled permeation membrane,[2] surface patterning,[3] temperature-induced switching,[4] actuate microdevices constitution,[5] separation,[6] and so on. As typical examples, poly(*N*-isopropylacrylamide) (PNIPAm) and poly(acrylic acid) (PAA), which are easily synthesized, as well as chemically and mechanically robust, attract extensive research interest for application in the engineering of smart surfaces because of their excellent responding ability to environmental changes in temperature, ionic strength, pH and solvent.

Although reversible superhydrophilic and superhydrophobic switches of responsive surfaces in air has been reported,[7] it is still rare to study the electrochemical properties of sensitive solid/polymer brush/liquid interfaces, which leads an effective way to illustrate the interfacial properties, such as surface charge density, ion or molecule permeability, electronic properties, hydration and bioadhesion. Through reversibly controlling the conformation of attached polymer chains in aqueous solutions by modulating the environmental conditions, the electrochemical signal would regularly alter, revealing in real time the physicochemical or biological properties of the stimuli-responsive interfaces.

Furthermore, due to their water-soluble and biocompatible properties, intelligent polymers (*e.g.* PNIPAm and PAA) might be ideal materials to bridge the gap between biological machines and multi-functional actuators.[8] However, it is still a big challenge to devise an efficient approach for fabricating multi-sensitive smart solid/polymer/liquid interfaces, which is an important step towards the utilization of surface-confined smart polymers as building blocks for biomimetics. In this communication, stable intelligent interfaces based on PNIPAm, PAA and poly(*N*-isopropylacrylamide-co-acrylic acid) [P(NIPAm-co-AAc)] brushes were fabricated through electrochemically induced free-radical polymerization (EIFRP),[9] and the control of the polymer interface properties, which responded in aqueous solution independently or simultaneously to various external stimuli such as temperature, salt concentration and pH (shown in Fig. 1), was investigated in detail by *in-situ* electrochemical methods, *i.e.* electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The results showed that these switchable interfaces exhibited fast electrochemical switching behavior, excellent reversibility and multi-functionalization.

The thermo-, ionic- and pH sensitive interfaces were fabricated through an *in-situ* electrochemical induced polymerization process, which was performed in an aqueous solution containing 1.0 M *N*-isopropylacrylamide or sodium acrylate (Aldrich, for P(NIPAm-co-AAc), 8 mol% of sodium acrylate against NIPAm), and $Na_2S_2O_8$ (0.01 M), cycling the potential between -0.35 and -1.35 V (*vs.* Ag/AgCl) at 100 mV s^{-1} for 60 cycles. As the polymerization proceeded, the resulting polymers assembled on the electrode surfaces, which were demonstrated by *in-situ* attenuated total internal reflection Fourier transform IR spectra (see Fig. S1 in ESI†). CV measurements were also run to verify the formation of polymeric membranes on the electrodes. Fig. 2 shows the cyclic voltammograms of 5 mM $Fe(CN)_6^{3-/4-}$ in 0.1 M $KClO_4$ aqueous solution for a bare gold electrode and gold electrodes modified with polymer brushes. It can be seen that the redox response of $Fe(CN)_6^{3-/4-}$ changed due to the formation of polymer layer assemblies. More specifically, the peak currents in curve (b) (PNIPAm brush modified electrode), curve (c) (PAA brush modified electrode), and curve (d) (P(NIPAm-co-AAc) brush modified electrode) were much lower than that in curve (a)

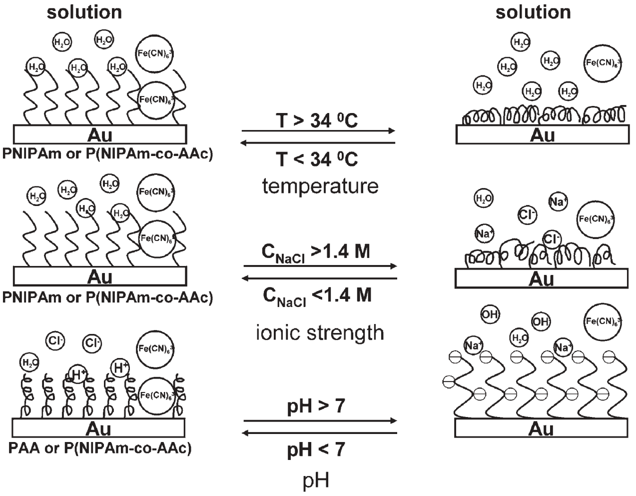

Fig. 1 Schematic illustration of temperature, ionic strength and pH induced switchable PNIPAm, PAA and P(NIPAm-co-AAc) brush interfaces.

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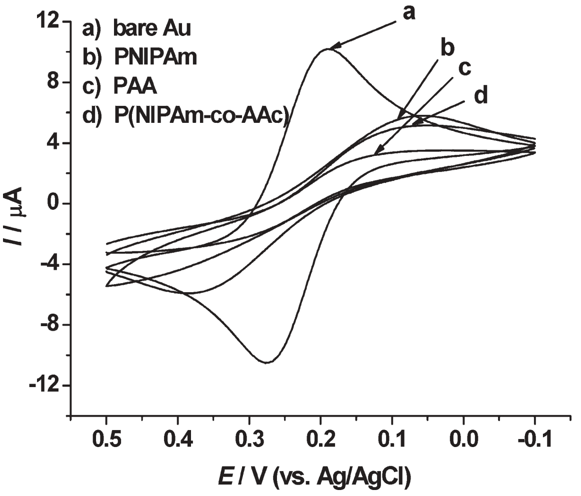

Fig. 2 Cyclic voltammograms of (a) bare Au electrode, (b) PNIPAm modified Au electrode, (c) PAA modified Au electrode and (d) P(NIPAm-co-AAc) modified Au electrode in 0.1 M $KClO_4$ and 5 mM $Fe(CN)_6^{3-/4-}$ aqueous solution with a scan rate of 50 mV s^{-1}. Electrode area: 8 × 10^{-2} cm^2.

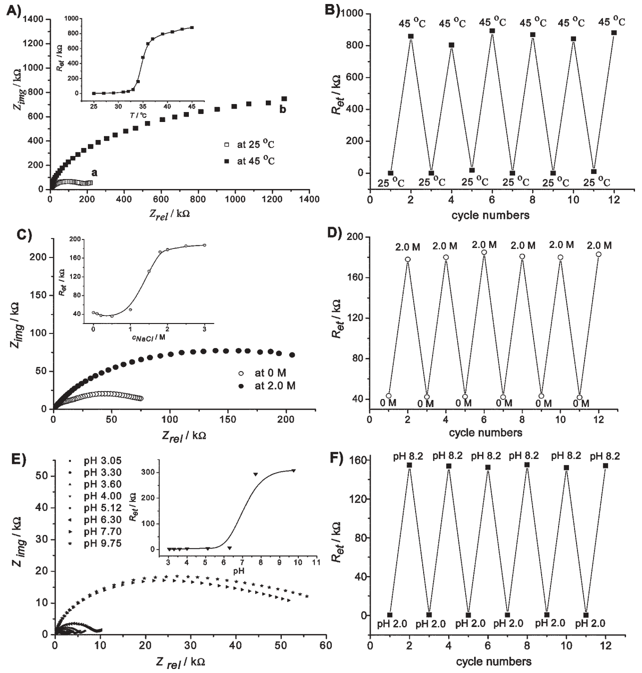

Fig. 3 (A) Impedance spectra of PNIPAm brush interface, at 25 and 45 °C, $c_{NaCl} = 0$ M. Inset: response interfacial ETR of $Fe(CN)_6^{3-/4-}$ at the brush interface *vs.* temperature; (B) interfacial ETR variation upon switching the temperature; (C) impedance spectra of PNIPAm brush interface, at 0 and 2.0 M of NaCl, at 20 °C. Inset of (C): interfacial ETR of $Fe(CN)_6^{3-/4-}$ at the brush interface *vs.* concentration of NaCl; (D) Interfacial ETR variation upon switching the concentration of NaCl; (E) impedance spectra of the PAA brush interface at different pH. Inset: response interfacial ETR of $Fe(CN)_6^{3-/4-}$ at the brush interface *vs.* pH; (F) interfacial ETR change upon switching pH at 2.0 and 8.2.

(bare Au electrode), and the electron transfer processes became slower, as was evident from the increase of peak-to-peak potential separation value. The reason was that the non-conducting polymer membranes assembled on the electrodes retarded the electron transfer between the redox species and the electrodes.[10]

As is known, linear PNIPAm precipitated in water in response to an increase of temperature and salt concentration.[11] It is reasonable to suppose that the Au electrode/PNIPAm brush/water interface fabricated by our method is dual-responsive and its electrochemical properties could be well controlled. EIS is an excellent technique to investigate interfacial electrical properties of any type of solid/liquid interface.[12] Fig. 3(A) shows the Nyquist plots of the PNIPAm brush modified electrode in 5 mM $Fe(CN)_6^{3-/4-}$ at 25 °C (curve (a)) and 45 °C (curve (b)), respectively. The semicircle diameter corresponded to the electron transfer resistance (ETR, R_{et}) of $Fe(CN)_6^{3-/4-}$ at the electrode surface. The low interfacial ETR ($R_{et} \approx 100$ kΩ) at 25 °C revealed that the polymer was in an expanded coil state, whereas the high interfacial ETR ($R_{et} \approx 890$ kΩ) at 45 °C indicated that the insulating polymer brush was in a collapsed globule conformation.[13] A plot of interfacial ETR of $Fe(CN)_6^{3-/4-}$ at the brush surface *vs.* temperature is given in the inset of Fig. 3(A). The phase transition temperature of the polymer was estimated to be about 34 °C. A similar phase transition behavior induced by the ionic strength of NaCl in the solution is shown in Fig. 3(C). $Fe(CN)_6^{3-/4-}$ exhibited low interfacial ETR in the absence of NaCl in solution, while it displayed a high interfacial ETR when the concentration of NaCl was increased to 2.0 M. Interfacial ETR of $Fe(CN)_6^{3-/4-}$ at a PNIPAm modified electrode *vs.* concentration of NaCl is plotted in the inset of Fig. 3(C). The critical concentration of NaCl, at which the phase transition of the polymer brush occurred, was about 1.4 M.[14] By switching the temperature between 25 and 45 °C, or the concentration of NaCl between 0 and 2.0 M, interfacial ETR showed "fast switching" and excellent reversibility (see Fig. 3(B), (D)). This reversibility remained even after the samples had been under ultrasonic irradiation for 30 min, indicating that the polymer film was very stable. The resulting "ON" and "OFF" cycles of R_{et} can be interpreted by the competition between intermolecular and intramolecular hydrogen bonding below and above the phase transition,[11] which controlled the interfacial properties and the permeation of ions or molecules (*e.g.* $Fe(CN)_6^{3-/4-}$). This meant that the responsive polymer interfaces could convert environmental information effectively into an electrochemical signal, and this phenomenon may find applications in bioelectronics.[3]

Through grafting PAA, as a pH sensitive polymer,[15] onto a conducting substrate, a pH responsive solid/polymer/liquid interface could be fabricated. Fig. 3(E) shows the Nyquist plots of $Fe(CN)_6^{3-/4-}$ at a PAA brush modified Au electrode at different pH. At pH 3.05, the R_{et} of $Fe(CN)_6^{3-/4-}$ was about 1.8 kΩ. Along with the increase of pH, the interfacial ETR substantially ascended to about 300 kΩ (at pH 9.75), with a dramatic increase between pH 6.30 and 7.70 (see inset of Fig. 3(E)). The increase of the interfacial ETR was attributed to the ionization of carboxylate groups, which enhanced the negative charge density of the surface, and then repelled $Fe(CN)_6^{3-/4-}$ from the interface.[15] When the pH was repeatedly cycled between 2.0 and 8.2, the variation of R_{et} was recorded (see Fig. 3(F)). The origin for such changes was that, at low pH, the carboxylate groups were hardly ionized and the PAA brush was at a relaxed conformation. While at high pH, the carboxylate groups were fully ionized, and the ionic repulsion among COO^- groups expanded the polymer chain to form a rigid

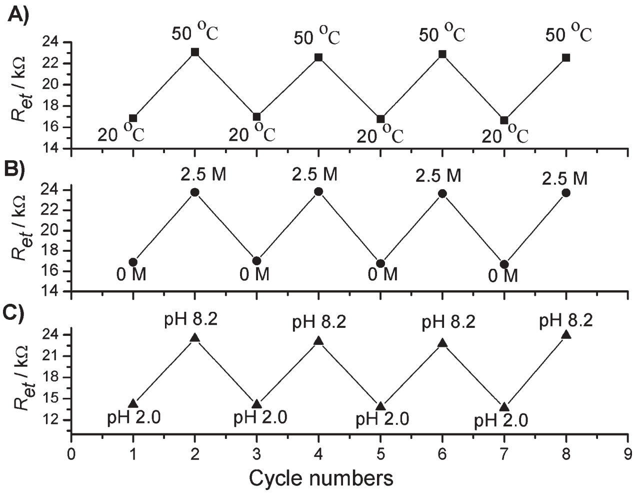

Fig. 4 Environmental condition induced switching at a P(NIPAm-co-AAc) brush interface as a function of (A) temperature, (B) concentration of NaCl, (C) pH.

structure with more negative charge on the surface.[16] The stable PAA brush interface demonstrated that the interfacial charge density, as well as ion permeability, can be tuned by pH, and this excellent structure–property relationship may have potential applications in protein immobilization, surface functionalization, layer-by-layer assembly, and controlled release.

The above-mentioned PNIPAm and PAA brush interfaces were responsive to both temperature and ionic strength, or pH stimuli. However, for some applications, simultaneous response to several factors, may be required. Here, a multi-sensitive interface simultaneously responsive to temperature, salt concentration and pH was simply achieved through copolymerization of NIPAm and AAc at an Au electrode surface. As shown in Fig. 4, when switching the temperature between 20 and 50 °C (at C_{NaCl} = 0 M, pH 5.6), concentration of NaCl between 0 M and 2.5 M (at T = 20 °C, pH 5.6), or pH between 2.0 and 8.2 (at T = 20 °C, C_{NaCl} = 0 M), interfacial ETR of $\mathrm{Fe(CN)_6}^{3-/4-}$ at P(NIPAm-co-AAc) brush modified gold electrode can be all repeatedly cycled between low and high values, showing that the states presenting different interfacial properties were switchable, which was in accordance with that obtained in CV (see Fig. S2 in ESI†). This phenomena can be explained by the reversible change in hydrogen bonding between the two components (NIPAm and AAc) and water, and the ionization of carboxylate groups in different environmental conditions.[17] The results also exhibited excellent reversibility, and a quick transformation as a single cycle measurement lasted only a few minutes. This reversibility still remained after the samples had been laid aside without special protection for months, suggesting that the interface was stable. The fast switching, excellent reversibility, and good stability of the interface showed that multi-sensitive interfaces could be built by combining two signal responsive components, and such multi-sensitive behavior of intelligent polymers could be used to design multi-responsive intelligent interfaces in biomimetics as a functional component.

In conclusion, we have demonstrated that temperature, ionic strength and pH induced switchable smart polymer interfaces with good stability and excellent reversibility could be fabricated *via* electrochemical induced free-radical polymerization of PNIPAm, PAA or P(NIPAm-co-AAc). Real-time electrochemical measurements, *i.e.* EIS and CV, indicated that the interfacial electrochemical properties can be intelligently switched through varying external stimuli independently or simultaneously. The multi-sensitive P(NIPAm-co-AAc) interface further illustrated that such polymer-based smart interfaces may have great potential in biomimetics as multi-functional components, biological actuators, controlled permeation membrane, separation, immobilized biocatalysts, interfacial engineering, responsive filters, and so on.

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