

Supporting Information

Dynamic electrical behavior of thermo-responsive polymer in well-defined poly(*N*-isopropylacrylamide)-grafted semiconductor devices

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Experimental Procedures

Materials

N-Isopropylacrylamide (NIPAAm) was kindly provided by KJ Chemicals (Tokyo, Japan) and purified by recrystallization in toluene/hexane. Tris(2-(*N,N*-dimethylamino) ethyl) amine (Me₆TREN) was purchased from Tokyo Chemical Industries (Tokyo, Japan). Copper (I) chloride (CuCl), α -chloro-*p*-xylene, dehydrated toluene, dimethylformamide (DMF), acetone, and methanol were purchased from Wako Pure Chemical Industries (Osaka, Japan). The FET sensor used in this study was 5 mm x 6 mm of silicon based metal-oxide-semiconductive FET (MOSFET, Toppan Co. Ltd.) whose 2 mm square of Ta₂O₅ gate

electrode was extended from MOSFET device.

Immobilization of ATRP initiator onto the Ta₂O₅ surface

ATRP initiator (CMPETMS) was immobilized onto the surface of the gate insulator of FET sensor (Ta₂O₅) by silane coupling reaction. The surface of FET sensor was cleaned by oxygen plasma irradiation (intensity: 400 W, oxygen pressure: 0.1 mmHg, duration: 180 s) in a dry plasma cleaner (PC-1100) (SAMCO, Kyoto, Japan). The cleaned FET sensors were placed into a separable flask, in which the relative humidity was 60%, for 2 h. Toluene solution containing CMPETMS (1.2v/v%) was poured into the separable flask, and the solution was stirred for 18 h at 25 °C. The ATRP initiator immobilized FET sensors were washed with toluene and acetone, and dried in a vacuum oven for 2 h at 110 °C.

Modification of thermo-responsive polymer on the gate insulator of FET sensor by ATRP

NIPAAm monomer (9.51 g, 84.0 mmol) was dissolved in DMF/water 1:1 mixed solvent (30 mL/30 mL) and the oxygen in the solution was removed by Argon gas bubbling for 1 h. CuCl (83.2 g, 0.84 mmol) and Me₆TREN (225 μL, 0.84 mmol) were added to the solution under argon atmosphere. The solution was stirred for 15 min to obtain CuCl/Me₆TREN catalyst system. The prepared ATRP solution was poured into a separable flask containing the ATRP initiator immobilized FET sensors, and α-chloro-*p*-xylene (22.2 μL, 0.168 mmol), which acts as an unbound sacrificial ATRP initiator, was added to the solution under an argon atmosphere in a globe box. The ATRP reaction was proceeded for 18 h at 25 °C. After the ATRP reaction, the PNIPAAm grafted FET sensors were washed with acetone, methanol, EDTA solution, and water. After washing, the PNIPAAm grafted FET

sensors were dried in a vacuum oven for 3 h at 100 °C. The reaction solution containing the free PNIPAAm was dialyzed against water for 5 days using dialysis membrane (MWCO: 14,000), and the polymer was recovered by freeze-drying. Number-averaged molecular weight (M_n) polydispersity index (PDI) of obtained PNIPAAm were determined by gel permeation chromatography (GPC) (Tosoh, Tokyo, Japan) using DMF containing 50 mM LiCl as a mobile phase. A calibration curve was prepared by poly(ethylene glycol) standards.

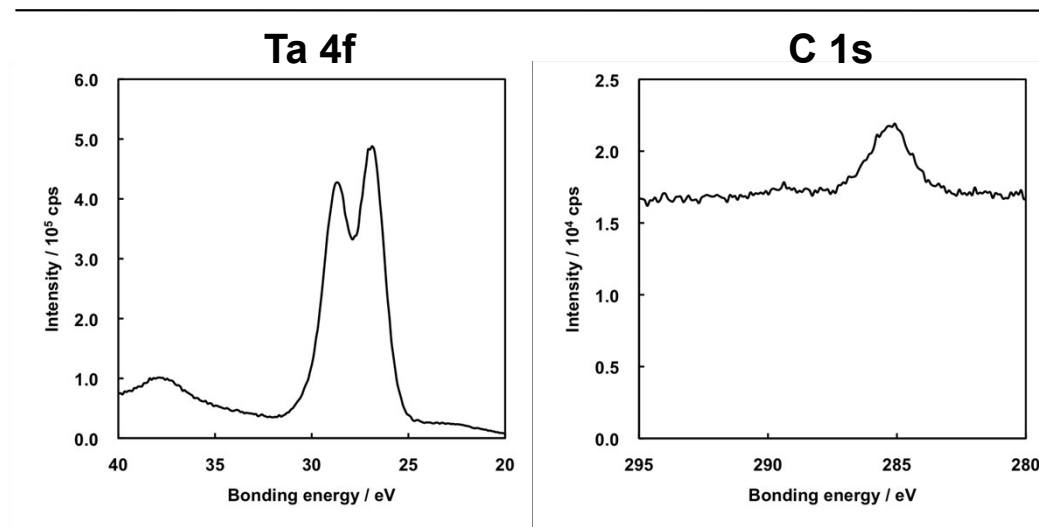
Elemental analyses by X-ray photoelectron spectroscopy

Elemental analyses were performed on the surfaces of the unmodified FET sensor, ATRP initiator immobilized FET sensor, and PNIPAAm grafted FET sensor by X-ray photoelectron spectroscopy (XPS) (K-Alpha, Thermo Fisher Scientific, Waltham, MA). Excitation X-rays were produced from a monochromatic Al K α X-ray source at a takeoff angle of 90° (**Figure S1**).

Quantitative estimated amount of grafted PNIPAAm

PNIPAAm was modified onto the surface of glass cover slips through the same procedure as FET sensor and the amount of grafted PNIPAAm was estimated by ATR/FT-IR (Nicolet 6700) (Thermo Fisher Scientific, Waltham, MA). The strong Si-O absorption due to glass substrates appeared at 1000 cm⁻¹ and the absorption of the amide carbonyl derived from PNIPAAm on glass substrates appeared at around 1650 cm⁻¹. The amount of PNIPAAm was determined from the peak intensity ratio (I_{1650}/I_{1000}), using a calibration curve which was prepared according to the previous studies (the calibration curve shown as **Figure S2**).^{S1} The amount of grafted PNIPAAm prepared in this study was determined to be $11.7 \pm 2.8 \mu\text{g cm}^{-2}$

Non-grafted FET



PNIPAAm grafted FET

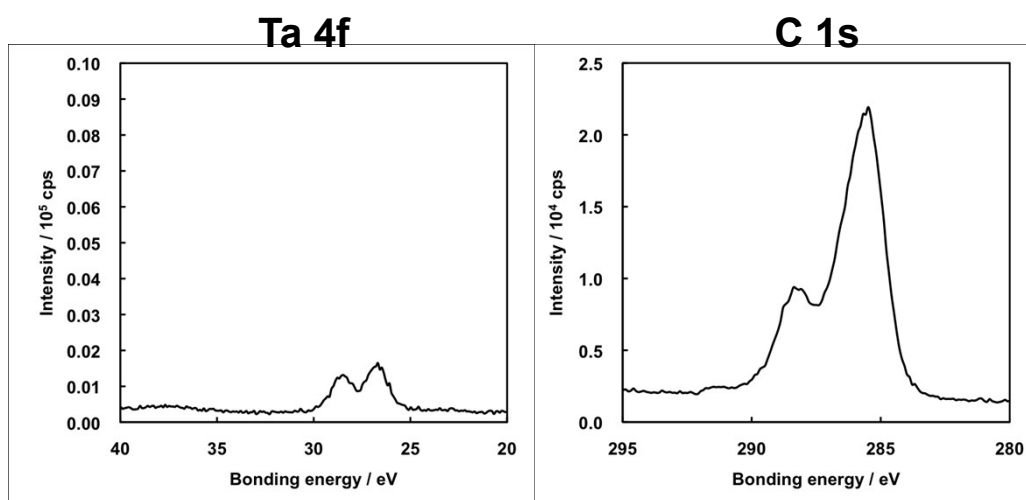


Figure S1 XPS spectra for Ta 4f and C 1s of the non grafted FET and PNIPAAm grafted FET.

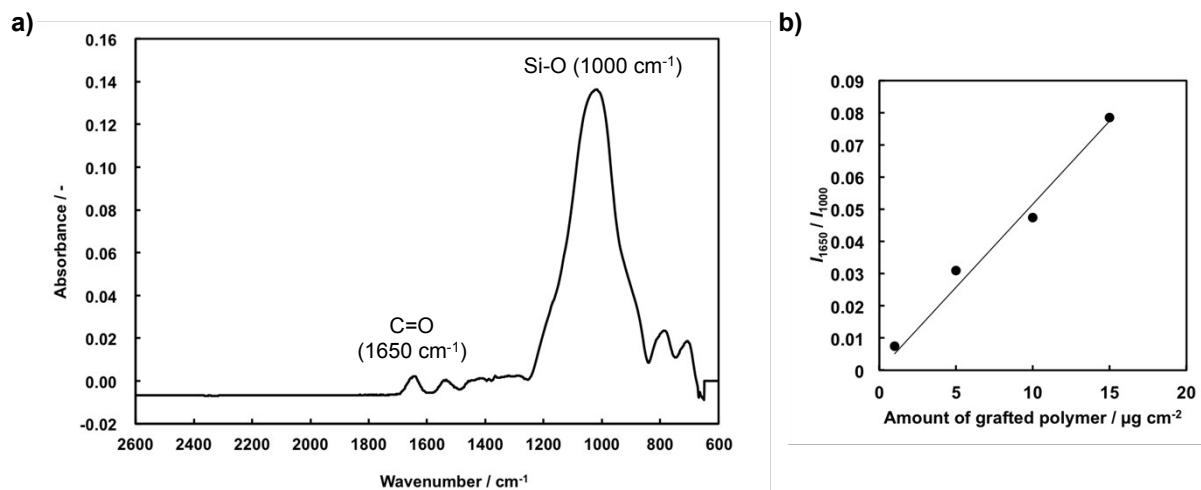


Figure S2 (a) The absorbance spectrum for PNIPAAm-grafted glass substrate. (b) Calibration curve for determining the amount of grafted PNIPAAm on a glass substrate.

Thickness measurement of PNIPAAm surface by AFM

The thickness of the grafted PNIPAAm film was measured by an atomic force microscopy (AFM) (Nanoscope, Veeco, Santa Barbara, CA) in air, using tapping mode measurement (silicon cantilever, scan rate: 0.5 Hz, tip velocity: 10.0 mm s⁻¹). Part of the PNIPAAm film was cleaved from the glass substrate by scratching with a scalpel blade. The thickness of PNIPAAm film modified on the Ta₂O₅ gate was approximately 70 nm (**Figure S3**).

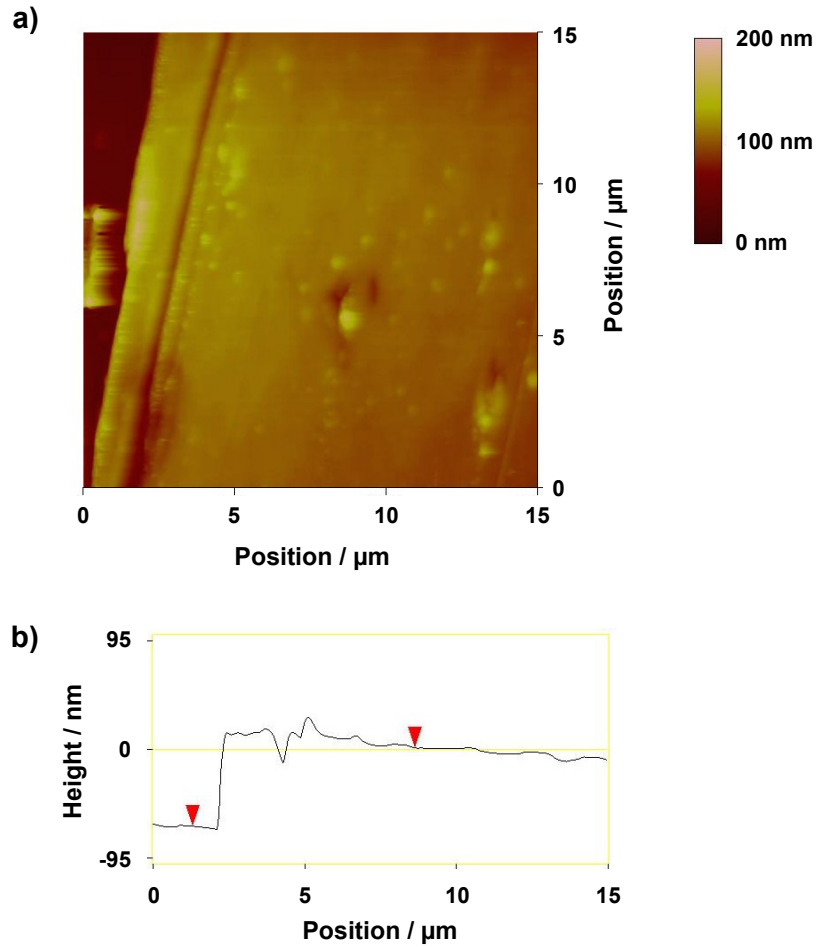


Figure S3 (a) AFM image of PNIPAAm modified on the Ta₂O₅ gate surface of FET device, and (b) the cross-section analysis.

Electrical measurement of PNIPAAm-FET

The electrical characteristics of PNIPAAm-FET responding to temperature change was measured using semiconductor parameter analyzer (B1500A, Keysight technologies). The drain current (I_D)-gate voltage (V_G) curve was measured in PNIPAAm modified FET and non-modified FET at the V_G sweep range of -3 to 3 V and the constant drain voltage (V_D) of 2 V. (**Figure S4**). Ag/AgCl with 3.3 M KCl was used as the reference electrode, which was connected with the measurement solution with the FET devices through the salt bridge. Water was utilized as the measurement solution. The change in surface potential (ΔV_{out}) at the

gate was measured at a constant I_D (700 μA) using the source follower circuit^{S3} shown in **Figure S5**; thus, the detected ΔV_{out} was regarded as the change in the source-gate voltage (ΔV_S), which was equal to $-\Delta V_T$. Using this system, the surface potential of the FET can be monitored in real time.

Also, the electrical properties of FET devices are supported for understanding the effect of temperatures on the V_G - I_D electrical characteristic, as follows. The V_G - I_D characteristic of an ISFET operating in a saturation region is given as Equation (S1):^{S3,S4}

$$I_D = \frac{1}{2}\beta(V_G - V_{T_ISFET})^2 \quad (\text{S1})$$

and β can be defined as

$$\beta = \mu \frac{C_{OX}W}{L} \quad (\text{S2})$$

where W and L are the channel width and length, respectively, and μ is the mobility of the electrons in the channel.

Moreover, the mobility $\mu(T)$ and the $V_{T_ISFET}(T)$ shift with the temperature are given by Equations (S1) and (S2):^{S3,S4}

$$\mu(T) = \mu_0 \left(\frac{T}{T_0} \right)^{-m} \quad (\text{S3})$$

$$V_{T_ISFET}(T) = V_{T_ISFET}(T_0) + \alpha(T - T_0) \quad (\text{S4})$$

and α can be defined as

$$\alpha = \frac{\partial V_{T_FET}}{\partial T} + \frac{\partial E_{ref}}{\partial T} + \frac{\partial \phi}{\partial T} \quad (\text{S5})$$

where T and T_0 are temperature of solution and room temperature. μ_0 is mobility of 25°C, m is a constant, with typical values between -1.4 and -2.2,^{S4} depending on the doping concentrations of silicon. α in Equation (S3) is the temperature coefficient of threshold

voltage of ISFET. α consists of temperature characteristics of V_{T_FET} , E_{ref} , and ϕ . Considering Equations (S1), (S2), (S3) and (S4), the V_G - I_D characteristic for ISFET operating in saturation region containing temperature characteristic is calculated with:

$$I_D = \frac{1}{2} \mu(T) \frac{C_{OX} W}{L} (V_G - V_{T_ISFET}(T))^2 \quad (S6)$$

Thus, the drain current of an ISFET is affected by $\mu(T)$ and $V_{T_ISFET}(T)$.

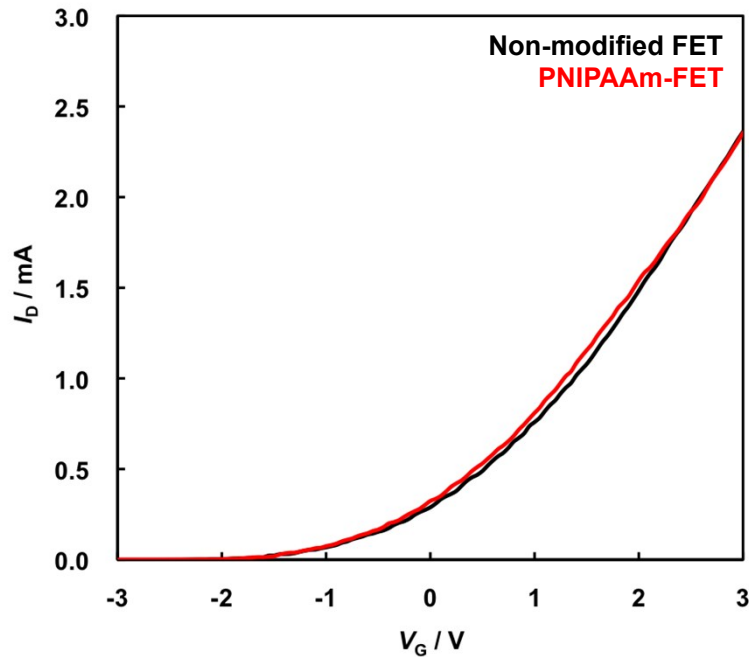


Figure S4 The I_D - V_G property for PNIPAAm modified FET was rarely different from that of non-modified FET.

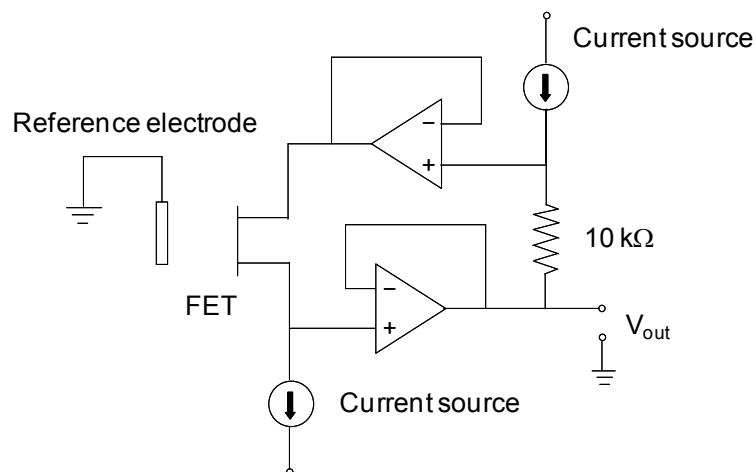


Figure S5 Electrical circuit (source follower circuit) for measuring surface potential of FET sensor.^{S2}

Impedance and capacitance measurement of PNIPAAm-Ta₂O₅

The substrate for measuring capacitance or impedance was prepared as follows. 10 mm Φ of a thin film of Ta₂O₅ was prepared by sputtering (thickness: approximately 50 nm), following the sputtering of Cr as an adhesive layer (thickness: approximately 15 nm) on 10 x 24 mm of sputtered Cr/Au (thickness: approximately 15 nm/50 nm) glass substrate as an electrode. PNIPAAm was grafted on the surface of Ta₂O₅ through the same procedure as described above. All electrochemical measurement was carried out by immersing Ta₂O₅ part of the electrode in ultrapure water with connecting to the grand intermediated with 3.3 M KCl salt bridge. Capacitance and impedance was evaluated using LCR meter (E4980A, Keysight technologies). Capacitance of Ta₂O₅ electrode was measured at 200 kHz of frequency and 0 V of bias voltage, and impedance analysis was carried out at the range of frequency from 20 Hz to 2 MHz.

To evaluate the effect of the PNIPAAm modification on the electrochemical properties of the interface, impedance and capacitance for the non-grafted Ta₂O₅ interface and the PNIPAAm grafted Ta₂O₅ were measured at each temperature. The results with respect to the capacitance measurement are shown in **Figure 3** in the manuscript. Regarding the impedance measurement, **Figures S6(a)** and **(b)** shows Nyquist plots for the non-grafted Ta₂O₅ interface and PNIPAAm grafted Ta₂O₅ interface, respectively (Bode plots for these interfaces shown as **Figure S7**). For the both interfaces, the Nyquist plots showed the circular profile at high frequency region and the linear profile at low frequency region, indicating that the both interfaces can be described by the equivalent circuit composed of capacitance, resistance and Warburg impedance (**Figure S6(c)**). As temperature increased, the real of impedance at intersection of X axis which was indicated as the combining of solution

resistance and charge translocation ($R_{sol} + R_{ct}$) became small. This is attributed to becoming progressively smaller value of R_{ct} associated with the decrease of the insulation resistance connected with Warburg impedance in series. As for the PNIPAAm grafted Ta_2O_5 interface, the shift of the Nyquist plot between 35 °C and 40 °C was smaller than those of other temperature intervals. Considering PNIPAAm become hydrophobic/collapsed state above 32 °C, this result suggested that the electrochemical properties of the PNIPAAm grafted Ta_2O_5 interface did not changed by temperature change above the LCST of PNIPAAm, which is because PNIPAAm chain became completely collapsed state. The temperature range where the electrical change was observed in the impedance measurement was higher than that in the case of FET measurement was higher. This is because the swelling-deswelling behavior of the densely grafted PNIPAAm chain become broaden compared with the free PNIPAAm chain in water, which was reported by Annaka *et al.*^{S5}

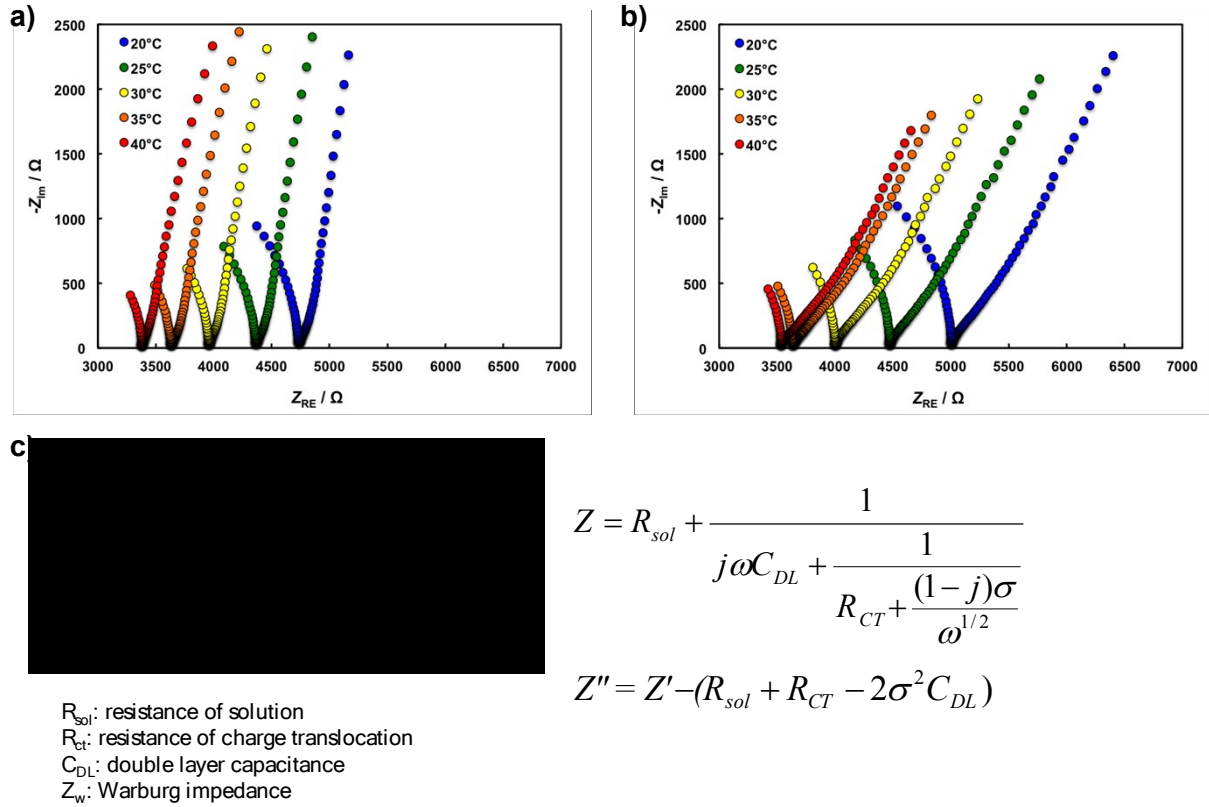


Figure S6 Nyquist plots of (a) Ta₂O₅ interface and (b) PNIPAAm grafted Ta₂O₅ interface. Frequency was scanned from 20 Hz to 2 MHz during the impedance measurement. (c) Equivalent circuit for the interface.

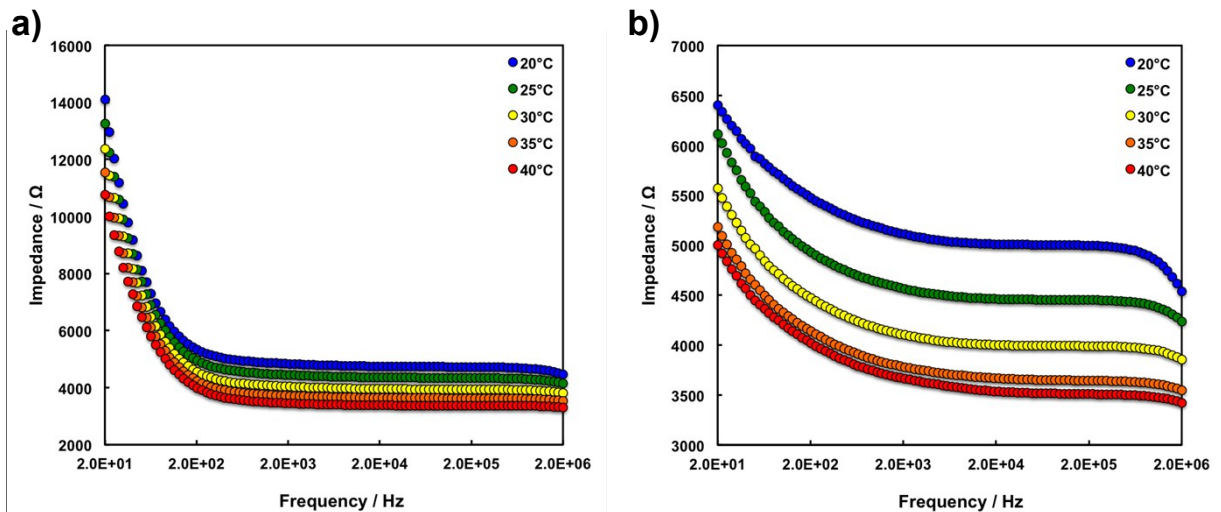


Figure S7 Bode plots of (a) Ta₂O₅ interface and (b) PNIPAAm grafted Ta₂O₅ interface. Frequency was scanned from 2 Hz to 2 MHz during the impedance measurement.

References

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