

Electronic Supplementary Information

Organic/inorganic hybrid electrochromic devices based on photoelectrochemically formed polypyrrole/TiO₂ nanohybrid films

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Experimental

Absorbance by the TiO₂ film was qualitatively estimated by spectroelectrochemical measurements. The experiment was performed with the method described previously.¹⁻³ The TiO₂ film electrode was set to a three electrode cell with a quartz window, and placed in an absorption spectrometer (JASCO, V-670). Pt and Ag/AgCl electrodes were employed as counter and reference electrodes, respectively. Absorption spectra were observed after bias application into the TiO₂ film in 0.1 M KCl aqueous solution with a series of pH for 5 min. The solution pH was adjusted by adding HCl into the KCl solution, and was identical prior to and after the spectroelectrochemical experiments. The bias was applied from +0.2 V with -0.1 V steps following the measurement of the reference line after 15 min. stabilization at +1.0 V vs. Ag/AgCl. N₂ gas was employed prior to and during the optical experiments in order to avoid O₂ contamination.

Results

Fig. S1 shows cyclic voltammograms of a TiO₂ electrode in 0.1 M KCl aqueous solution with a series of pH. The current density increased with decrease in the solution pH at the same applied voltage, clearly indicating the larger number of electronic states available to accept electrons. This also suggests that the same number of electronic states is available at more positively applied bias as the solution pH decreases.

These electronic states were monitored spectroelectrochemically. The difference spectra of the TiO₂ film, immersed in 0.1 M KCl with pH 4, under electrical bias application are shown in Fig. S2. Gradual increase in absorbance in the whole visible wavelength range was observed with negative bias applications. This absorbance change originates from the presence of Ti³⁺ species, created by cathodic current flow to the TiO₂ electrode.⁴ In contrast, negative absorbance change was observed at ~380 nm; this change is probably explained by

the band edge unpinning or the presence of an accumulation layer.⁴ Following these bias dependent spectral changes, we chose a wavelength of 380 nm to monitor polypyrrole color change, since absorbance change of the TiO₂ is minimal.

Absorbance increase behavior with the negative bias application was compared by modifying pH in the electrolyte solution. Fig. S3 shows absorbance increase, monitored at 800 nm, as a function of the applied bias in the electrolyte with a variety of pH. As the solution pH decreases, the absorbance change at the identical applied bias increases and the onset potential shifts positively, in agreement with the previous report.^{5, 6} These data suggest that a density of electron acceptor states inside the TiO₂ film at the identical applied bias increases with the solution pH decrease. Thus, an electron can be conducted inside the TiO₂ film at relatively positive potential by employing the aqueous electrolyte with low pH.

References

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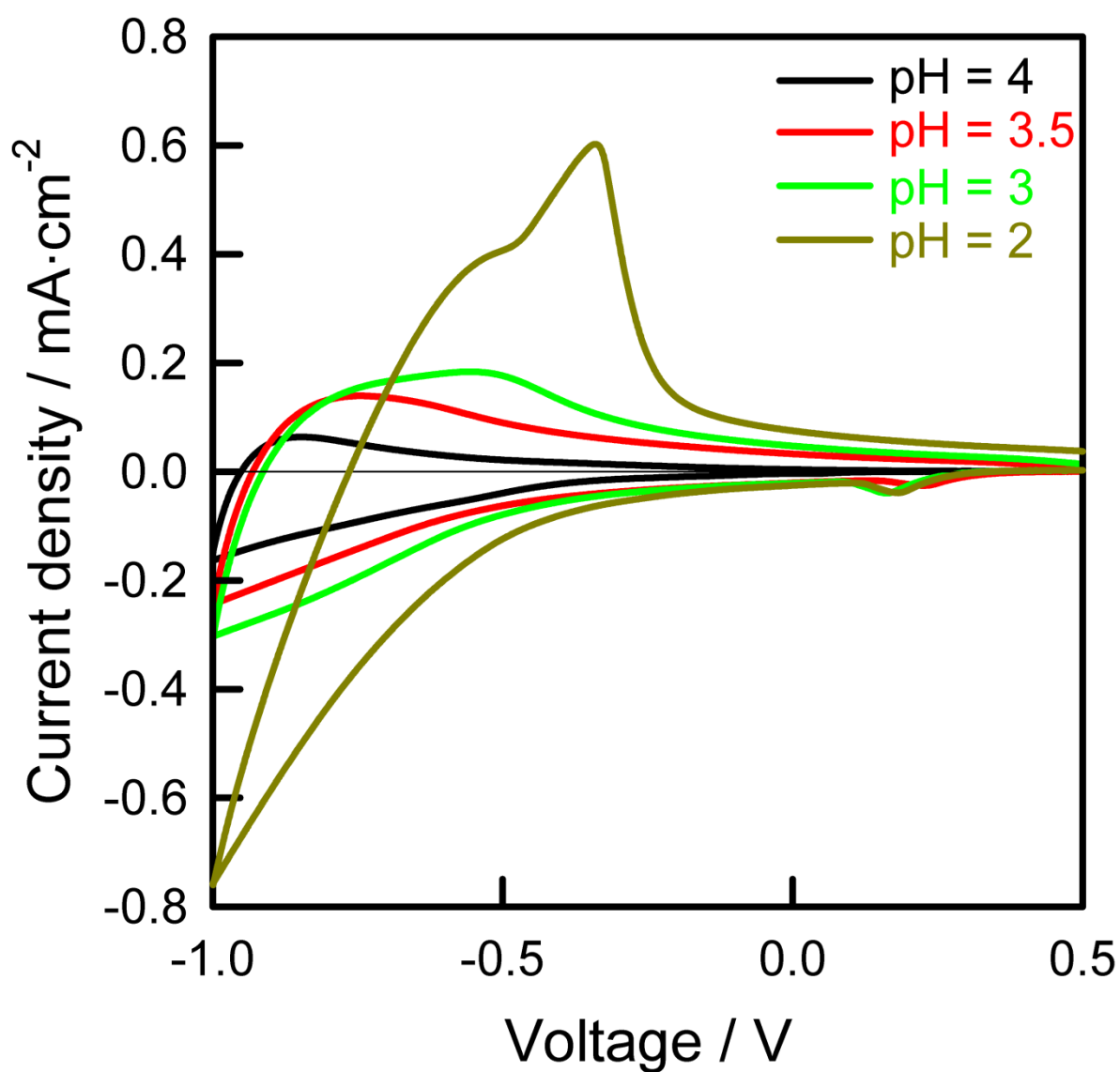


Fig. S1 Cyclic voltammograms of nanocrystalline TiO₂ electrode in 0.1 M KCl aqueous solution with a series of pH. The scan rate is 20 mV s⁻¹.

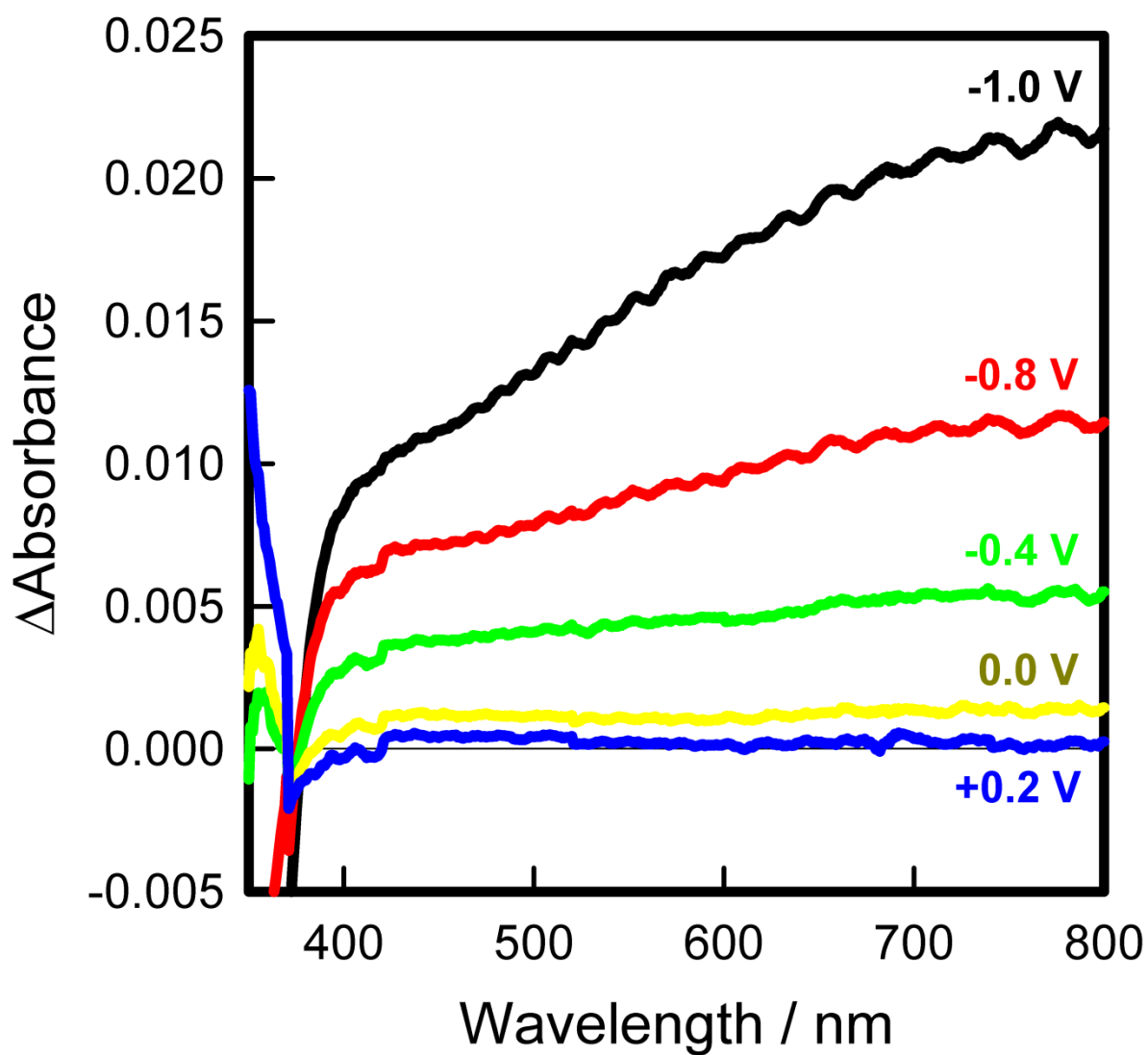


Fig. S2 Absorbance difference spectra of a TiO_2 film in 0.1 M KCl aqueous solution with pH 4 under electrical bias application.

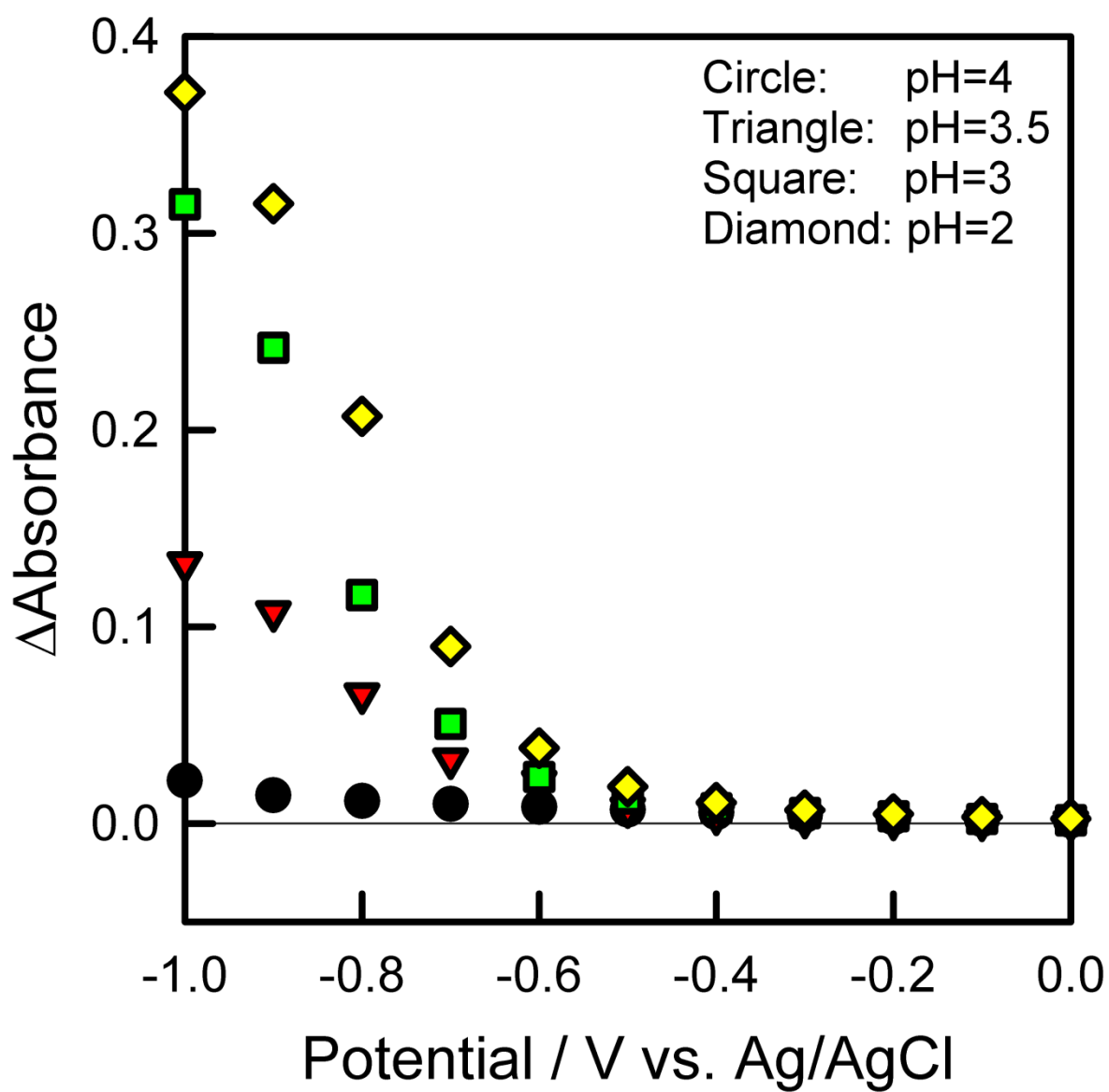


Fig. S3 Absorbance difference of a TiO₂ film in 0.1 M KCl aqueous solution with a series of pH, monitored at 800 nm, under electrical bias application.