

## Enhanced sensitivity for visualization and quantification of weak friction force using composites of layered polydiacetylene and dry liquid

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### Abstract

The composite device of the polydiacetylene (PDA)-coated paper substrate and dry liquid (DL) was designed and prepared for detection of weak friction force smaller than 1 N. The PDA/DL composite device showed the response cascades with disruption of DL, outflow of the interior liquid, and stimuli-responsive color changes. The applied friction forces with writing brush in calligraphy were colorimetrically quantified using the device.

### 1. Introduction

PDA is obtained by polymerization of diacetylene (DA) monomers. PDA is applied to sensors based on the color-change properties with the application of external stimuli, such as thermal and mechanical stresses. A DA monomer, 10,12-pentacosadienic acid (PCDA), forms layered crystal structure. In our previous works, stronger friction forces, such as writing pressure and brushing force in the range of 0.9–30 N, were visualized and quantified using the PDA-coated paper substrates.<sup>1,2)</sup> However, the color change was not induced by weaker friction force because the self-organized molecules are not dynamically moved by such stress. Response cascade via the integration of stimuli-responsive materials is an effective strategy to achieve the response in weaker stress.<sup>3)</sup> The original applied stress is converted to other ones and the color change can be eventually induced by the converted stresses. Here we used DL, a free-flowing powder consisting of solid-particle-stabilized liquid droplets, for the stimuli conversion.<sup>4)</sup> The composite device of the PDA-coated substrate and DL exhibited the enhanced sensitivity to weaker friction force (Fig. 1).

### 2. Experiment

DL containing 20 wt-% aqueous solution of branched polyethyleneimine (PEI,  $M_n$  300) with the droplet size 105–250  $\mu\text{m}$  was dispersed on the PDA-coated paper. The red color intensity ( $x$ ) of the device was measured on the photographs after the application of friction force 0.02–0.7 N.

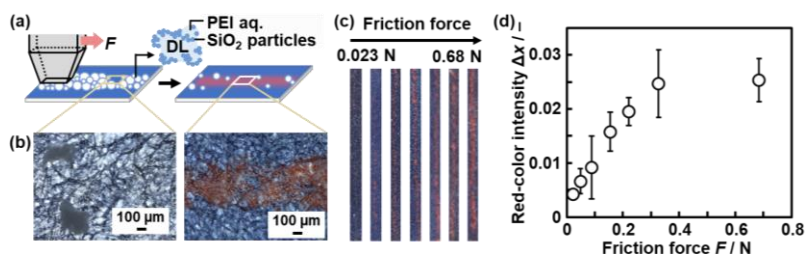


Fig. 1. PDA/DL device. (a) Schematic illustration. (b) Photographs before and after the application of friction force. (c,d) Photographs (c) and relationship (d) between  $F$  and  $\Delta x$ .

### 3. Results and discussion

The color of PDA with DL changed by the application of friction force (Fig. 1b). The applied friction force ( $F$ ) and red-color intensity ( $\Delta x = x - x_0$ ) had a linear correlation in the range of  $F = 0.02\text{--}0.3$  N (Fig. 1b, c).

The application of friction force leads to disruption of DL and outflow of the interior PEI aqueous solution. Then, the color change of PDA is induced by the shortening the effective conjugation length through the intercalation of PEI in the interlayer space and subsequent motion of the layered structure (Fig. 2a). The X-ray diffraction (XRD) pattern showed the shift of the peak corresponding to the interlayer distance (Fig. 2b). The interlayer interaction was changed from the intermolecular hydrogen bond between the dimerized carboxy groups to the electrostatic interaction between the carboxylate anion and ammonium cation on the Fourier-transform infrared (FT-IR) spectra (Fig. 2c).

The sensitivity, colorimetric response to the applied friction force, was tuned by the intercalation of the guests, such as nickel ion ( $\text{Ni}^{2+}$ ), in the layered PDA (Fig. 3a). The larger and smaller DLs showed the higher and lower sensitivities to the same strength of the applied stress, respectively (Fig. 3b).

Writing pressure in calligraphy was visualized using the PDA/DL device. The relationship between the accumulated work and  $\Delta x$  as the calibration curve was prepared for the quantification (Fig. 4a). The differences in the applied friction forces with writing brush in sweep and upward brushstroke motions were visualized and quantified by the color changes (Fig. 4b).

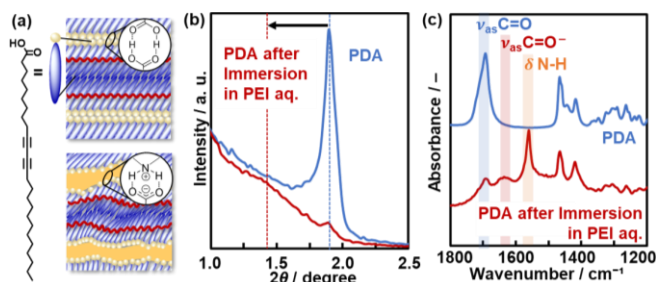


Fig. 2. Color-change mechanisms with the intercalation of PEI. (a) Schematic illustrations of layered PDA. (b) FT-IR spectra. (c) XRD patterns.

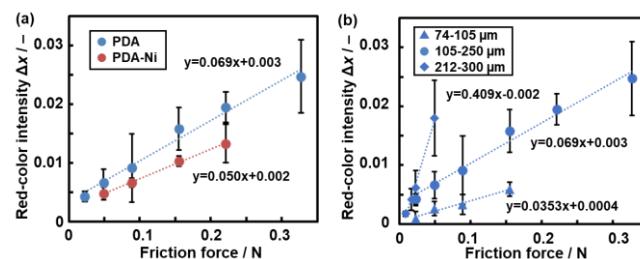


Fig. 3. Relationship between  $F$  and  $\Delta x$  for PDA/DL with and without the intercalation of  $\text{Ni}^{2+}$  (a) and for PDA/DL fabricated with the different sizes (b).

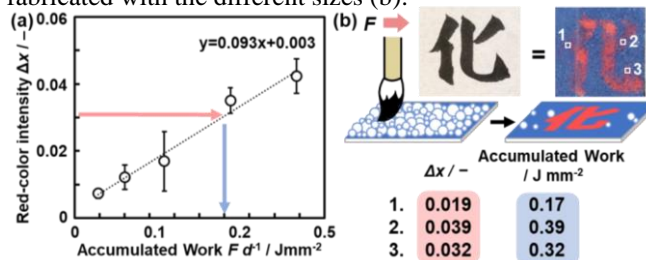


Fig. 4. Application of the PDA/DL device. (a) Relationship between  $F d^{-1}$  and  $\Delta x$ . (b) Schematic illustration for visualization and quantification of writing pressure in calligraphy.

### 4. Conclusions

In summary, weak friction force below 0.3 N was visualized and quantified using the PDA/DL composite device with the tunable sensitivity. The device has potentials as colorimetric friction force sensors.

### References

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