

Supporting Information

Chirality Detection by Raman Spectroscopy: The Case of Enantioselective Interactions between Amino Acids and Polymer- Modified Chiral Silica

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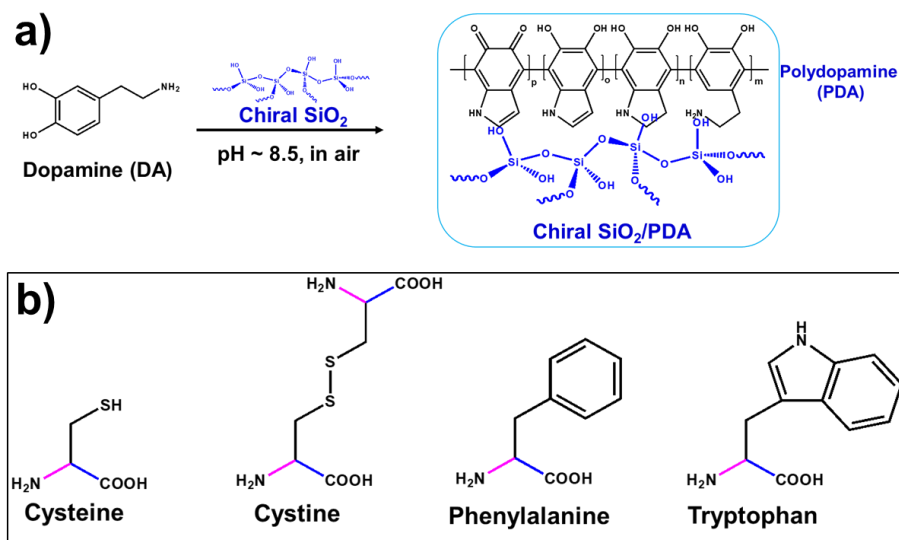
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The enantioselective interactions between amino acids and polymer-modified chiral SiO₂ could be easily reveal by Raman spectroscopy, which were further developed into Raman-based enantiomeric discrimination for organics and chirality detection of inorganic nanomaterials.

Experimental section

Synthesis of D-, L- and DL-SiO₂: The synthesis procedures are given in our previous work (seeing Reference 9: Angew. Chem., Int. Ed. 2012, 51, 5862-5865). Briefly, using linear polyethylenimine (PEI) polymer and D-tartaric acid (tart) enantiomer (D-tart) as the raw materials, D-PEI/tart complexes were prepared. After mixing D-PEI/tart with tetramethoxysilane (TMOS) in aqueous solution with a stirring of 2 hours, PEI/tart@SiO₂ powders were produced. SiO₂ was obtained by the removal of PEI and tart via a high-temperature treatment (600 °C, 3 hours) in air. By replacing D-tart with L-tart (or DL-tart), D-SiO₂ (or DL-SiO₂) was similarly prepared.

Synthesis of D-, L- and DL-SiO₂/PDA: The synthesis of chiral SiO₂/PDA is schematically shown in Scheme S1a. 0.050 g of D-SiO₂ powders were soaked in 10 mL Tris-HCl buffer solution (pH~8.5) containing 0.030 g dopamine hydrochloride with stirring for 24 hours in air. After centrifugation, washing (using water and ethanol) and drying, the white D-SiO₂ powders turned into brown D-SiO₂/PDA powders (about 0.045 g). By replacing D-SiO₂ with L- (or DL-) SiO₂, L- (or DL-) SiO₂/PDA powders were also prepared using the procedure above.



Scheme S1. (a) Schematic description of the molecular structures of chiral SiO₂ and PDA, and the formation of chiral SiO₂/PDA (Note: the molecular structure of PDA is drawn according to Reference 16: ACS Appl. Mater. Interfaces 2018, 10, 7523-7540). (b) Molecular structures of cysteine (Cys), cystine, phenylalanine and tryptophan.

Characterizations: TEM images were obtained on the FEI Tecnai G2 F20 instrument. The TG-DTA analysis was carried out on an Exstar 6000 instrument (Seiko Instruments Inc.). XPS spectra were collected on a Thermo ESCALAB 250XI equipment. Electronic circular dichroism (CD) and UV-Vis absorption spectra were acquired on the JASCO-820 spectropolarimeter with a DRCD-466L unit (DRCD: solid-state diffuse reflectance circular dichroism). SiO₂ (or SiO₂/PDA) powders were first ground with KCl powders in a mortar and then subjected to CD measurement. Raman spectra were recorded on a Jobin Yvon confocal laser Raman system (SuperLabRam II) equipped with a laser at 633 nm.

To assess the Raman enantio-discrimination ability of SiO₂ or SiO₂/PDA, four kinds of chiral molecules were selected, which included cysteine, cystine, phenylalanine and tryptophan (their molecular structures are shown in Scheme S1b). And the sample treatments before Raman measurements are conducted as follows: 1) about 1.5 mg of SiO₂ (or SiO₂/PDA) with a given handedness tag (D-, L- or DL-) were dispersed in 1 mL of water by ultrasonic treatment; 2) 0.1 mL of the above dispersion was taken out and mixed with 0.1 mL of a specific enantiomer solution with a given concentration; 3) after overnight mixing, the above mixture was dropped on a flat aluminium foil and dried in air for the following Raman test.

The influences of excitation laser wavelengths (including 532 nm, 633 nm and 785 nm) on the enantio-discrimination were probed by collecting the Raman spectra of “D-SiO₂/PDA and D-Cys” and “D-SiO₂/PDA and L-Cys”. The Raman test under 532 nm and 785 nm were conducted on a Raman microscope (Thermo DXR2xi, U.S.A.). It is found that laser of 532 nm with high energy may destruct the samples and no characteristic Raman scattering signals of Cys or cystine appeared (seeing Figure S9). A longer wavelength will produce weak Raman scattering signals, and the discrimination performance under 785 nm excitation is lower than that under 633 nm. Therefore, the laser of 633nm was selected for Raman measurement.

To check the discrimination performance in the case of that cysteine were added into juice, the as-used juice is the product of “Water soluble C100 Fruit Juice” which is

supplied by the company of Nongfu Spring (China).

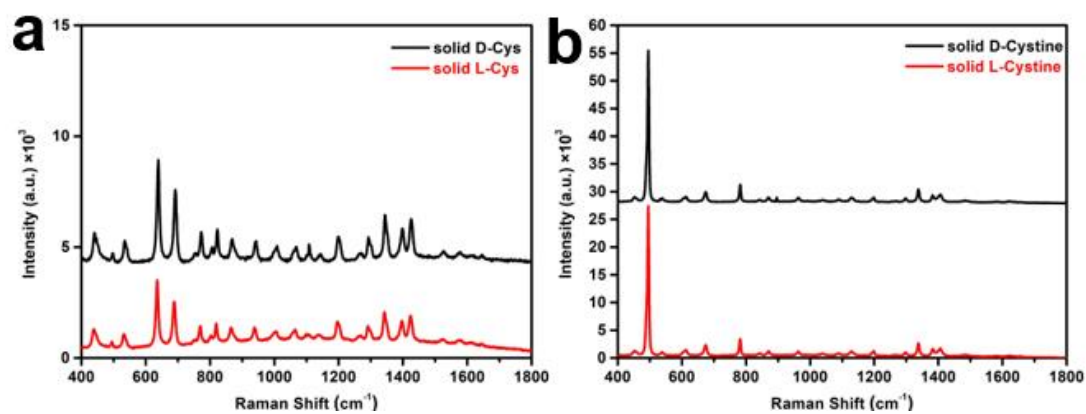


Figure S1. Raman spectra for solid powders of pure a) Cys and b) cystine enantiomers (black lines for D-form enantiomers and red for L-form ones).

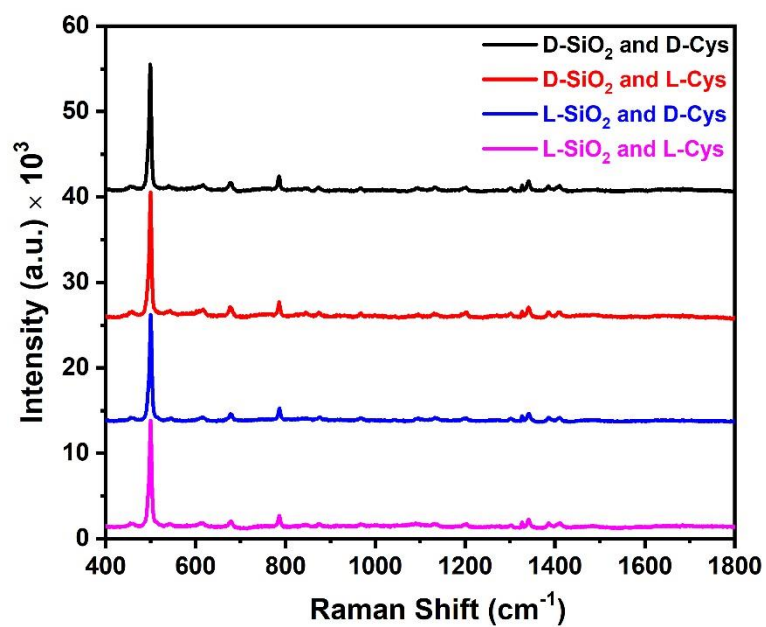


Figure S2. Typical Raman spectra for “D-SiO₂ and D-Cys” (black), “D-SiO₂ and L-Cys” (red), “L-SiO₂ and D-Cys” (blue) and “L-SiO₂ and L-Cys” (pink).

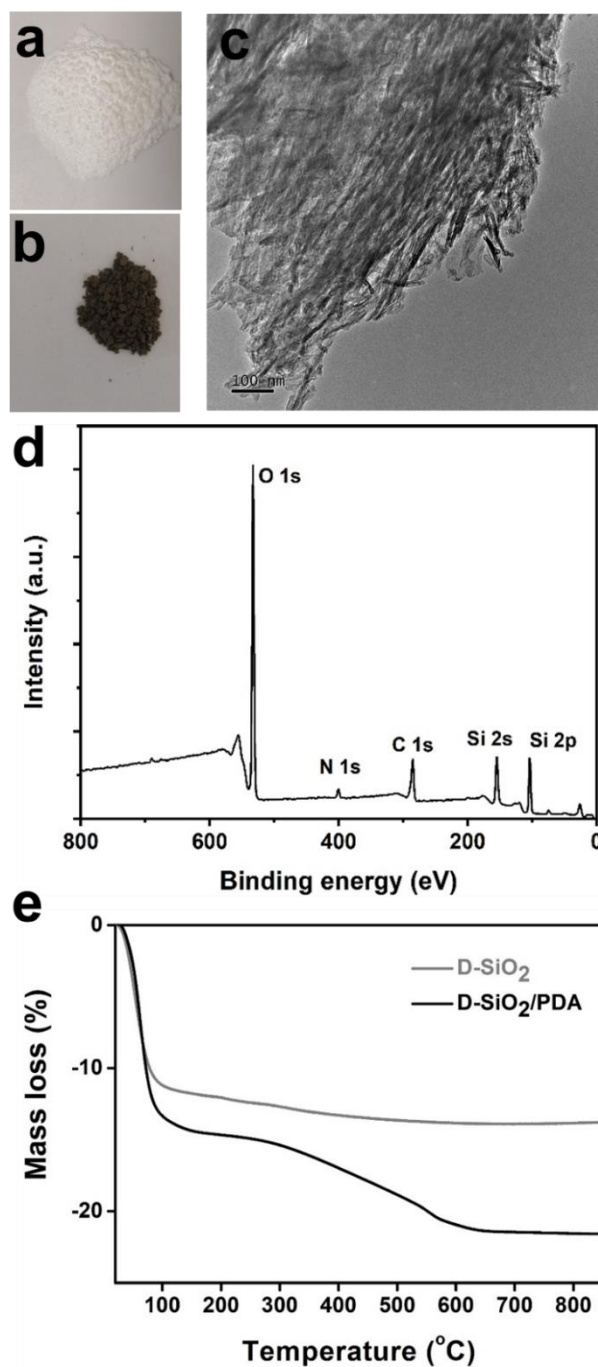


Figure S3. Photos of (a) D-SiO₂ and (b) D-SiO₂/PDA powders. (c) TEM image and (d) XPS spectrum of D-SiO₂/PDA. (e) TG-DTA curves of D-SiO₂/PDA (black line) and D-SiO₂ (gray line).

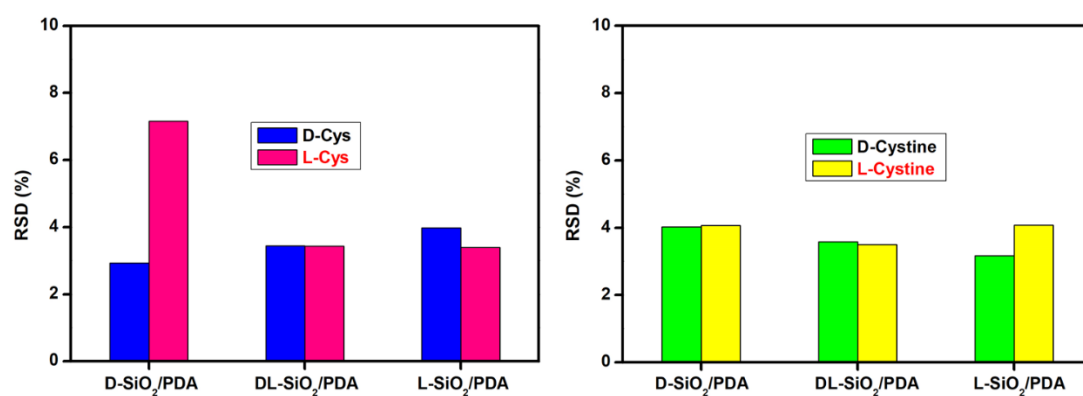


Figure S4. RSD values for different coupled mixtures of “SiO₂/PDA and Cys” (left) and “SiO₂/PDA and Cystine” (right) (the handedness tags of SiO₂/PDA, Cys and Cystine are shown). (Note: Each RSD value was calculated based on 30 Raman spectra.)

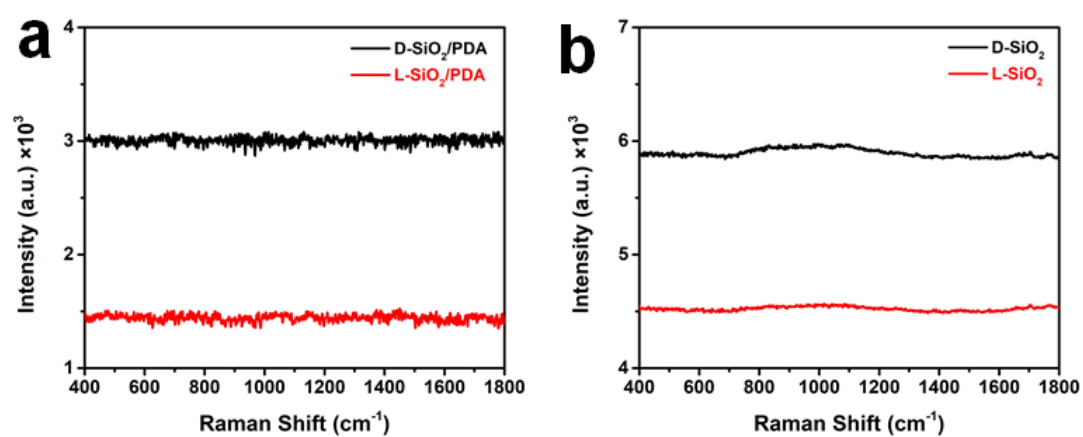


Figure S5. Raman spectra for a) D-SiO₂/PDA (black) and L-SiO₂/PDA (red); b) D-SiO₂ (black) and L-SiO₂ (red) powders.

$$\text{DI (D-SiO}_2\text{/PDA)} = \frac{I_{498}(\text{D-SiO}_2\text{/PDA and D-cystine})}{I_{498}(\text{D-SiO}_2\text{/PDA and L-cystine})}$$

$$\text{DI (L-SiO}_2\text{/PDA)} = \frac{I_{498}(\text{L-SiO}_2\text{/PDA and L-cystine})}{I_{498}(\text{L-SiO}_2\text{/PDA and D-cystine})}$$

$$\text{DI (DL-SiO}_2\text{/PDA)} = \frac{I_{498}(\text{DL-SiO}_2\text{/PDA and D-cystine})}{I_{498}(\text{DL-SiO}_2\text{/PDA and L-cystine})}$$

Figure S6. Equations for the calculation of DI of three types of SiO₂/PDA toward cystine enantiomers.

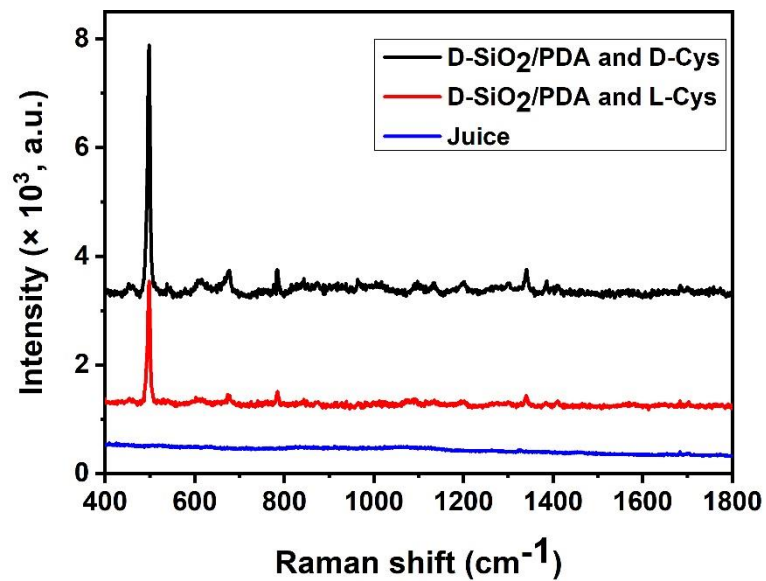


Figure S7. Raman spectra of “D-SiO₂/PDA and D-Cys” (black line), “D-SiO₂/PDA and L-Cys” (red line), and juice (blue line) in the case of that D-Cys and L-Cys were added into the juice.

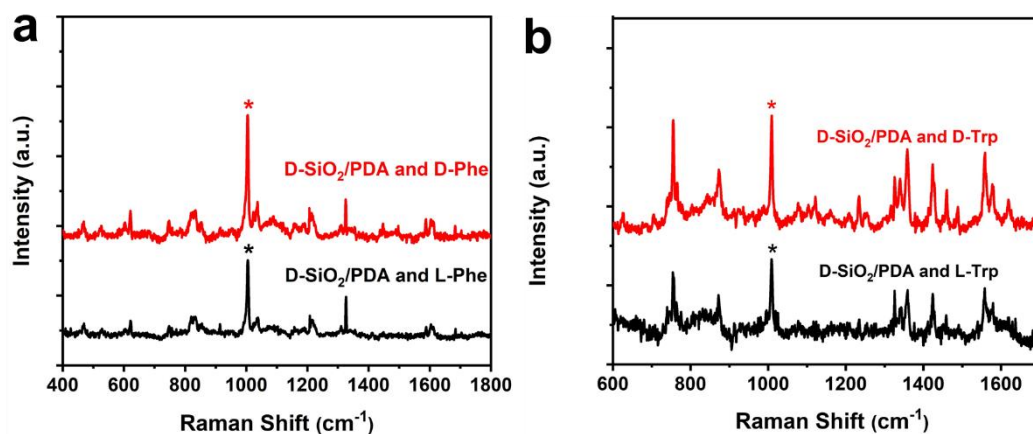


Figure S8. Representative Raman spectra for (a) “D-SiO₂/PDA and Phe”, (b) “L-SiO₂/PDA and Trp” (the black lines for the mixtures containing L-Phe or L-Trp while the red ones for D-Phe or D-Trp). Similar to the equation (1) in Table 1, the DI of D-SiO₂/PDA toward Phe and Trp is calculated based on the signal intensities around 1006 cm⁻¹ and 1010 cm⁻¹ (marked with asterisk symbols) , respectively.

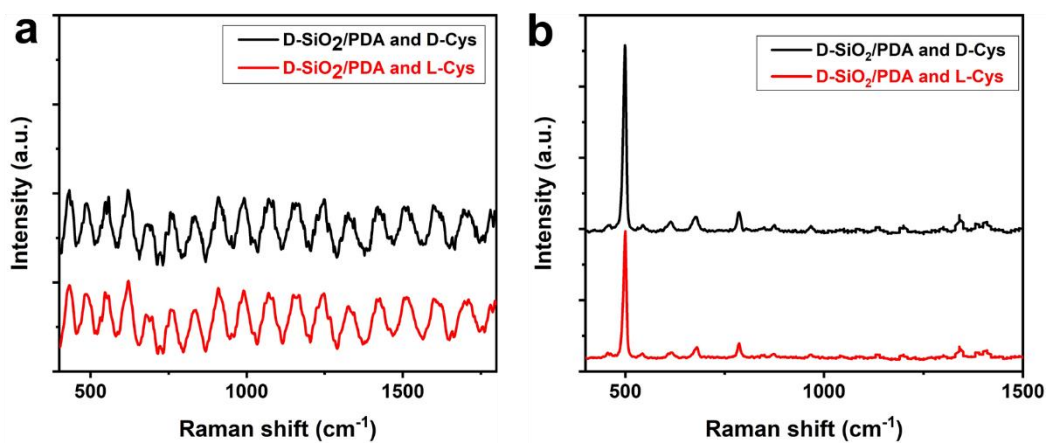


Figure S9. Raman spectra of “D-SiO₂/PDA and D-Cys” (black lines) and “D-SiO₂/PDA and L-Cys” (red lines) under a) 532 nm and b) 785 nm laser excitation.