Electronic Supplementary Information for:

Title: Surface-Enhanced Photochromic Phenomena by Phenylalanine Adsorbed on Tungsten Oxide Nanoparticles: A Novel Approach for “Label-Free” Colorimetric Sensing

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EXPERIMENTAL DETAILS

Chemicals

Sodium tungstate(VI) dihydrate ($Na_2WO_4 \cdot 2H_2O$), concentrated hydrochloric acid (Analytical Reagent, Wako Pure Chemical, Osaka, Japan), and a dialysis membrane tubing (3500 Da molecular cut-off; Spectrum Laboratories, CA, USA) were used to prepare tungsten(VI) oxide (WO_3) nanocolloids. L-Phenylalanine (Phe) was purchased from Tokyo Kasei Kogyo Co., Ltd (Tokyo, Japan). The water used for sample preparation was first distilled and then passed through a Milli-Q system (Millipore, USA), resulting in the specific resistivity of 18.2 MΩcm.

Preparation of WO_3 colloid aqueous solution

The preparation procedure of WO_3 colloid solution is based on the techniques reported by Zou *et al* [S1]. Conc. HCl (9.7 mL, 0.7 M) was added drop by drop to a Na_2WO_4 solution (90 mL, 0.027 M) under magnetic stirring. A transparent aqueous colloid solution was obtained, which was then closed in a dialytic membrane pipe and dialyzed in a 1000 mL beaker containing Milli-Q water for a period of 8 hours. The deionized water was periodically replaced until Cl ions could not be detected by ion chromatography analyzer (PIA-1000, Shimadzu, Japan) equipped with an anion-exchange column (Shim-pack IC-AC, Shimadzu, Japan). The concentration of tungsten component in the WO_3 colloid aqueous solution was determined by inductively coupled plasma-atomic emission spectrometry (Liberty Series II, Varian, USA). The as-prepared WO_3 colloid solutions were stable for at least one month at room temperature, yielding excellent processability, and refrigerated at 4ºC until used in the experiments. However, under strongly acidic conditions ($pH < 2$), the WO_3 colloid solution had poor stability, probably due to the coagulation of the WO_3 particles. The dried WO_3 colloids were analyzed by X-ray diffraction (RINT-2500, Rigaku, Japan) with Cu-Kα radiation (40 kV, 100 mA) from $2\theta = 5^\circ$ to 60° with scan speed of $5^\circ min^{-1}$. The XRD pattern was indexed to a $WO_3 \cdot 2H_2O$ layered structure in accordance with the JCPDS card No. 18-1419 (see Fig. S1). The band gap energy of the as-prepared WO_3 colloid particles was determined as to be 3.2 eV, corresponding to an indirect band gap of crystalline $WO_3 \cdot 2H_2O$ (see Fig. S2). From TEM measurement with a JEM-2100 instrument (JEOL, Japan), the resulting products are composed of almost spherical particles with diameters over the range 8-26 nm (see Fig. S4(a) and (c)).

Adsorption experiments of Phe on the WO_3 colloid surface

A typical experiment would consist of first mixing the WO_3 colloid aqueous solution, water, and hydrochloric acid or sodium hydrate. Then, the Phe aqueous solution would be added and stirred for 10 min at room temperature. It was preliminarily established that this time is sufficient for the establishment of adsorption equilibrium. The pH values of the Phe/WO_3 binary aqueous solution were periodically checked with a F-14 pH meter (Horiba, Japan) equipped with a 6366-10D glass electrode (Horiba, Japan). After filtration using 0.2 micro membrane filter (Ekikuro Disk, Shimadzu, Japan), the concentration of Phe was determined by high performance liquid chromatography (HPLC) on a CTO-20A (Shimadzu, Japan) system equipped with a guard column and a MIGHTYSIL RP-18 GP AQUA (250 nm L × 4.6 mm I.D., 5 μm) column (Kanto Reagents, Japan) with UV (λ=254 nm) detection, using water (100%) adjusted to ion strength (0.1 M) with sodium sulfate as an eluent at 1 mL/min and 25°C. We chose optimal conditions for Phe and plotted the calibration curve. The accuracy of determination of Phe within the studied concentration range was 3%. The values of adsorption of Phe, Δ[Phe] (mol dm^{-3}), could be determined from the difference between the initial and equilibrium concentrations. In the Phe/WO_3 binary system, Δ[Phe] value can be written as

$$\Delta[\mathrm{Phe}] = [\mathrm{Phe}]_{\mathrm{ad}} \frac{S}{V} \qquad \text{(S1)}$$

where S and V denote the total surface area of the WO_3 colloid (calculated from BET specific area value (11.8 m^2 g^{-1})) and the volume of the aqueous phase, respectively.

Photochromism measurements of the Phe/WO_3 binary aqueous solution

At first, the Phe aqueous solution was added to the aqueous solution containing WO_3 colloids and sodium sulfate. Then, the Phe/WO_3 binary aqueous solution was injected into a single compartment cell (1.0 cm path-length) with two quartz window. Afterward, the binary solution was bubbled with N_2 gas due to eliminate the oxygen, and then the cell was tightly sealed. Black lights (4W × 4, λ_{max} = 365 nm) were used as the excitation source. Photochromism of the Phe/WO_3 binary aqueous solution was measured by using an UV-vis spectrometer (UV-1600, Shimadzu, Japan).

Reference

[S1] Y. He, Z. Wu, L. Fu, C. Li, Y. Miao, L. Cao, H. Fan, B. Zou, *Chem. Mater.*, 2003, **15**, 4039-4045.

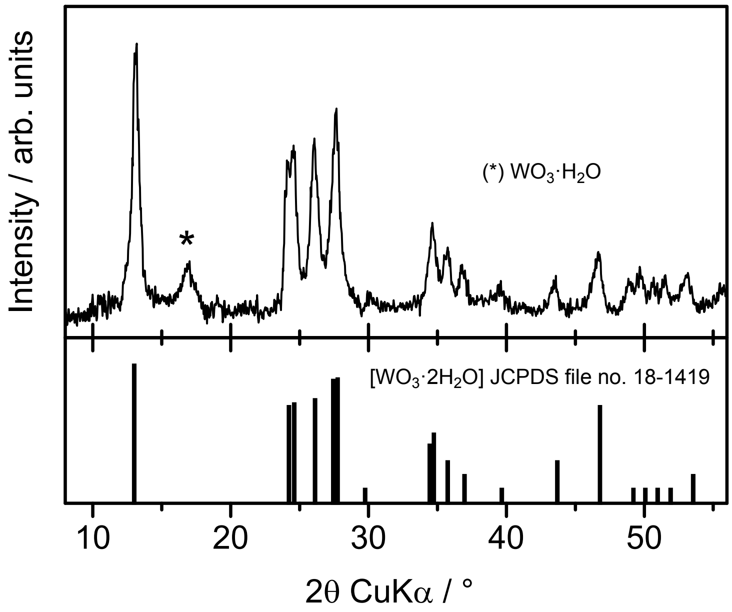

Figure S1 Powder XRD pattern of dried WO_3 colloids prepared in this study (which can be indexed to $WO_3 \cdot 2H_2O$, JCPDS No. 18-1419, and the peak marked with (*) belongs to the 020 reflection of $WO_3 \cdot H_2O$, JCPDS No. 18-1418).

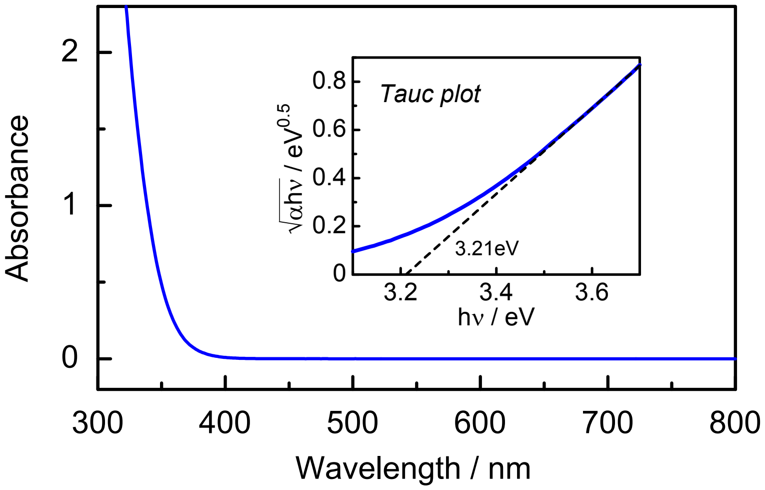

Figure S2 UV-Vis absorption spectrum of as-prepared WO_3 colloid solution. The inset shows the corresponding Tauc plot around the absorption edge for estimating the optical band gap energy.

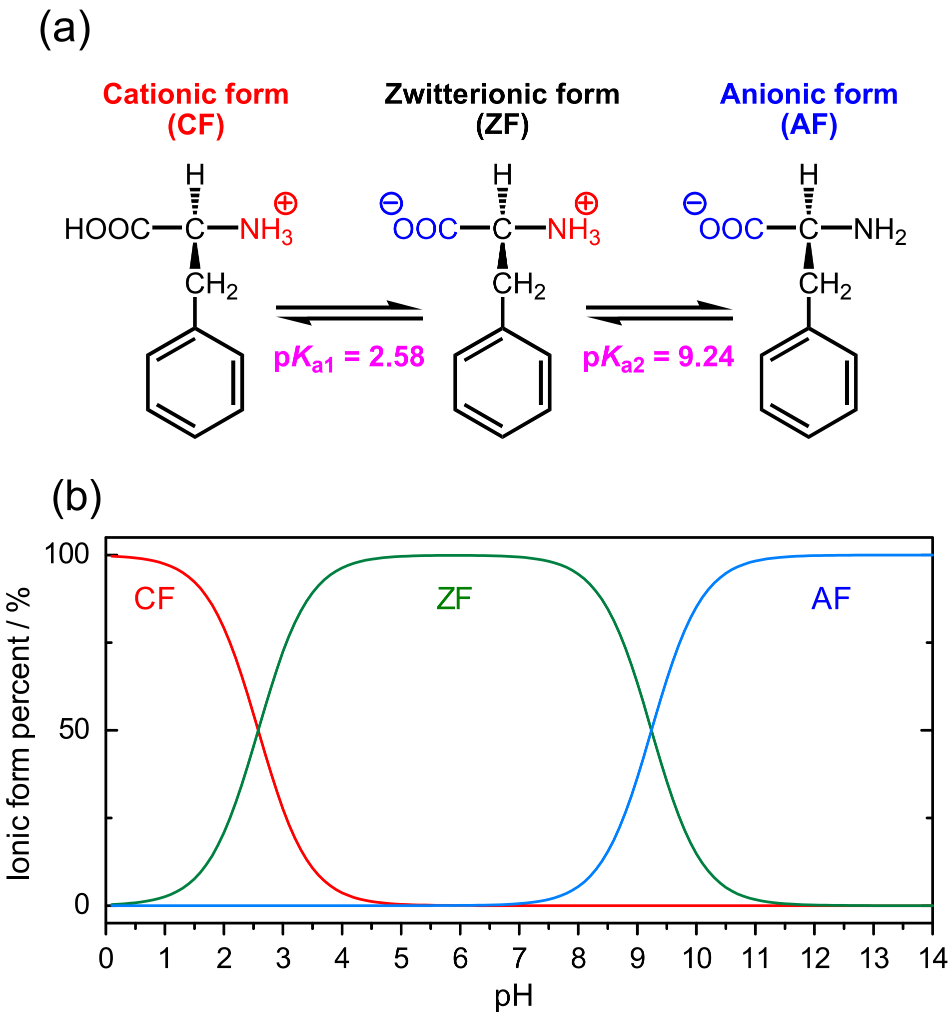

Figure S3 (a) Dissociation equilibria of L-phenylalanine forming cationic form (CF), zwitterionic form (ZF), and anionic form (AF). (b) Calculated ionic forms of L-phenylalanine as a function of pH values; CF (red line), ZF (green line), and AF (blue line).

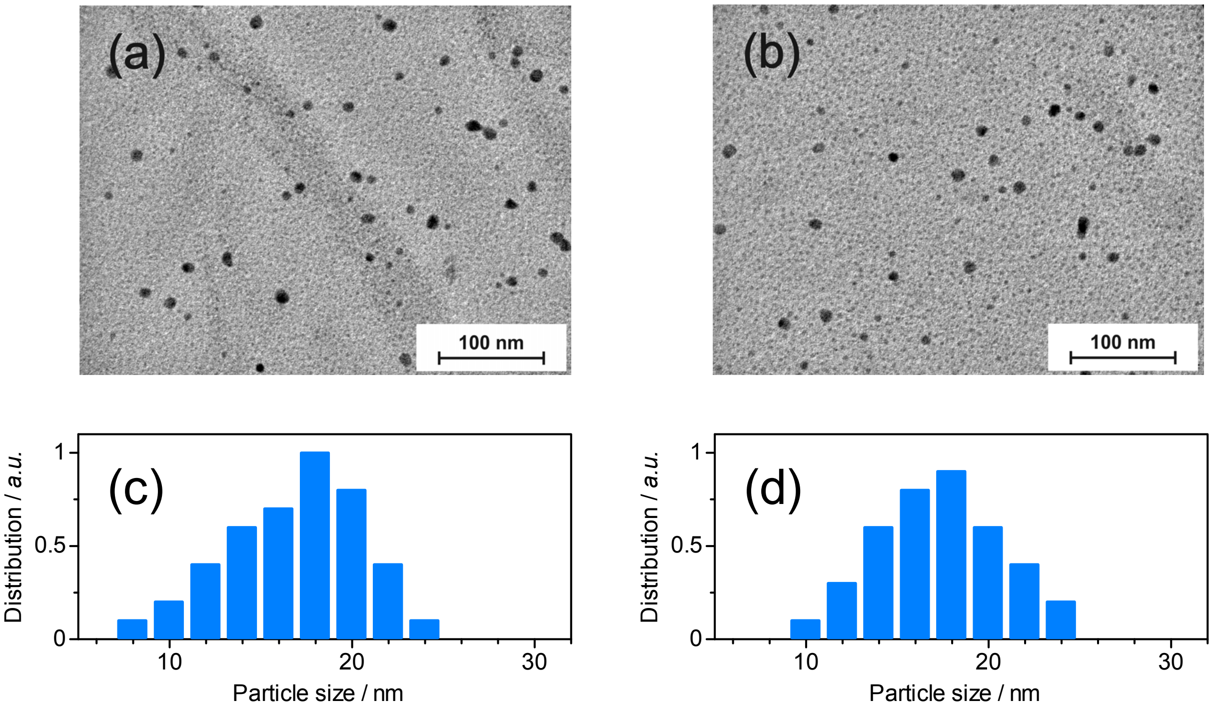

Figure S4 [(a) and (b)] TEM images of the WO_3 colloid, [(c) and (d)] corresponding particle size distribution histograms before and after the addition of the Phe, respectively

Table S1 Saturated concentrations (*a*), adsorption constants of cationic form (CF), zwitterionic form (ZF), and anionic form (AF) of L-phenylalanine onto the WO_3 colloid surface (K'_{CF}, K'_{ZF}, and K'_{AF}, respectively).

pH	a / moldm^{-2}		K'_{CF} / dm		K'_{ZF} / dm		K'_{AF} / dm	
		Average		Average		Average		Average
2.20	2.68×10^{-8}	**2.54×10^{-8}**	5.48×10^{-4}	**5.33×10^{-4}**	5.11×10^{-6}	**5.01×10^{-6}**	not obtained	---------
3.00	2.50×10^{-8}		5.40×10^{-4}		5.02×10^{-6}		not obtained	
4.20	2.58×10^{-8}		5.21×10^{-4}		4.92×10^{-6}		not obtained	
5.80	2.40×10^{-8}		5.23×10^{-4}		4.99×10^{-6}		not obtained	