## **Supporting Information**

## Displacement Reactions Between Environmentally and Biologically Relevant Ligands on TiO<sub>2</sub> Nanoparticles: Insights into the Aging of Nanoparticles in the Environment

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## **Experimental Details and Additional Experimental Data**

*Reagents and Sample Preparation.* TiO<sub>2</sub> nanoparticles (vendor reported size 21nm,  $\geq$ 99.5%) were purchased from Aldrich. Solutions of citric acid, (CA,  $\geq$ 99.5%, Sigma-Aldrich), ascorbic acid (AA, ACS grade, VWR), humic acid (HA, technical grade, Sigma-Aldrich), and bovine serum albumin (BSA,  $\geq$  98%, Sigma-Aldrich) were prepared with 25 mM 4-(2-hydroxyethyl)-1piperazineethanesulfonic acid (HEPES, Fisher Scientific) to maintain a stable pH. Sodium hydroxide (NaOH, 1N; Fisher Scientific;) and hydrochloric acid (HCl, 1N; Fisher Scientific) were used to adjust pH to 7.5. The ionic strength was maintained by sodium chloride (NaCl, Fisher Scientific). All the solutions were made in Milli-Q water.

*Nanoparticle Characterization.* The crystallinity of TiO<sub>2</sub> NPs was determined by Powder X-ray diffraction running at 40 kV, 4 mA for Cu K $\alpha$  ( $\lambda$  = 1.5418 Å) (Bruker D8 Advance diffractometer). The morphology and size of nanoparticles (Figure S1) were characterized by transmission electron microscope (FEI Tecnai G2 Sphera TEM) operating at 200 kV. Additionally, scanning electron

microscope (Zeiss Sigma 500 SEM) is employed to show the profile of a thin film of  $TiO_2$  nanoparticles shown in Figure S2.



**Figure S1.** Characterization of  $\text{TiO}_2$  NPs powder. (a) The TEM image shows the morphology of  $\text{TiO}_2$  NPs. (b) The X-ray diffractogram shows that rutile and anatase crystalline phases are present in the of  $\text{TiO}_2$  NPs. The blue and black lines represent the diffraction pattern of rutile and anatase, respectively.



**Figure S2.** SEM images of TiO<sub>2</sub> nanoparticles on Si wafer, (a) top view; (b) side view. The scale bars shown in the images are 1  $\mu$ m.

*Analysis of 2DCOS.* Two-dimensional correlation spectroscopy (2D-COS) was used to analyze the displacement reactions of CA-, AA- and BSA-coated TiO<sub>2</sub> NPs with HA. In this work, the time after introducing humic acid was used as the external perturbation for the structural changes of HA and its complexation on TiO<sub>2</sub> nanoparticles surfaces during the displacement process. Based on Noda and Ozaki's work,<sup>1</sup> the variation in a discrete set of dynamic spectra is represented by

$$\tilde{y}(v,t) = \begin{cases} y(v,t) - \bar{y(v)}, \ T_{min} \le t \le T_{max} \\ 0, \ others \end{cases}$$
(Eq. 1)

where v is the spectral variable (wavenumber in FTIR spectra); t is a perturbation variable.  $\bar{y}(v)$  is the time-averaged reference spectrum. The synchronous ( $\Phi$ ) and asynchronous ( $\Psi$ ) 2D correlation spectral maps can be calculated from discrete dynamic spectra by

$$\widetilde{\boldsymbol{y}}(v) = \begin{bmatrix} y(v,t_1) \\ y(v,t_2) \\ \vdots \\ y(v,t_m) \end{bmatrix}$$
(Eq. 2)

$$\Phi(v_1, v_2) = \frac{1}{m-1} \widetilde{\boldsymbol{y}}(v_1)^{\mathsf{T}} \widetilde{\boldsymbol{y}}(v_2)$$
(Eq. 3)

$$\Psi(v_1, v_2) = \frac{1}{m-1} \widetilde{\boldsymbol{y}}(v_1)^{\mathsf{T}} \boldsymbol{N} \widetilde{\boldsymbol{y}}(v_2)$$
 (Eq. 4)

where m is equally spaced point in t between  $T_{min}$  and  $T_{max}$ , and the Hilbert- Noda transformation matrix (N) is given by:

$$\mathbf{N} = \frac{1}{\pi} \begin{bmatrix} 0 & 1 & \frac{1}{2} & \frac{1}{3} & \cdots \\ -1 & 0 & 1 & \frac{1}{2} & \cdots \\ -\frac{1}{2} & -1 & 0 & 1 & \cdots \\ -\frac{1}{3} & -\frac{1}{2} & -1 & 0 & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{bmatrix}$$
(Eq. 5)

*QCM TiO*<sup>2</sup> *Characterization*. X-ray photoelectron spectroscopy confirms a Ti (IV) oxide and the presence shoulder with a binding energy around 532eV in Figure S3b indicates that the TiO<sup>2</sup> surface on the sensor is partially hydroxylated.



**Figure S3.** Binding energy of  $TiO_2$  sensor. High resolution scans in the (a) Ti 2p region and (b) O 1s region.

QCM Overtones. Frequency and dissipation changes following BSA adsorption and subsequent.



**Figure S4.** Shifts in frequency and dissipation for the displacement process of BSA by HA onto a  $TiO_2$  coated surface with QCM–D. Blue and red lines represents changes in frequency and dissipation, respectively. Data are shown for overtones 5,7, 9, and 11.

*Additional Displacement Studies.* In these experiments, HA adsorption was followed by AA, or CA or BSA. FTIR spectra are shown in Figure S5 and a proposed mechanism is shown in Figure S6.



**Figure S5.** Displacement reactions on HA pre-coated  $TiO_2$  NPs through ATR-FTIR by AA (a), CA (b), and BSA (c).



Figure S6. A schematic representation of displacement reactions of HA pre-coated  $TiO_2$  surface by AA (a), CA (b), and BSA (c), respectively. HA is represented here as a macromolecular structure.

## References

 I. Noda and Y. Ozaki, in *Two-Dimensional Correlation Spectroscopy – Applications in Vibrational* and Optical Spectroscopy, John Wiley & Sons, Ltd, 2005, DOI: 10.1002/0470012404.ch3, pp. 39-

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