

Surface Traps of TiO₂ Nanosheets and Nanoparticles as Illuminated by
Spectroelectrochemical Photoluminescence

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SUPPORTING INFORMATION

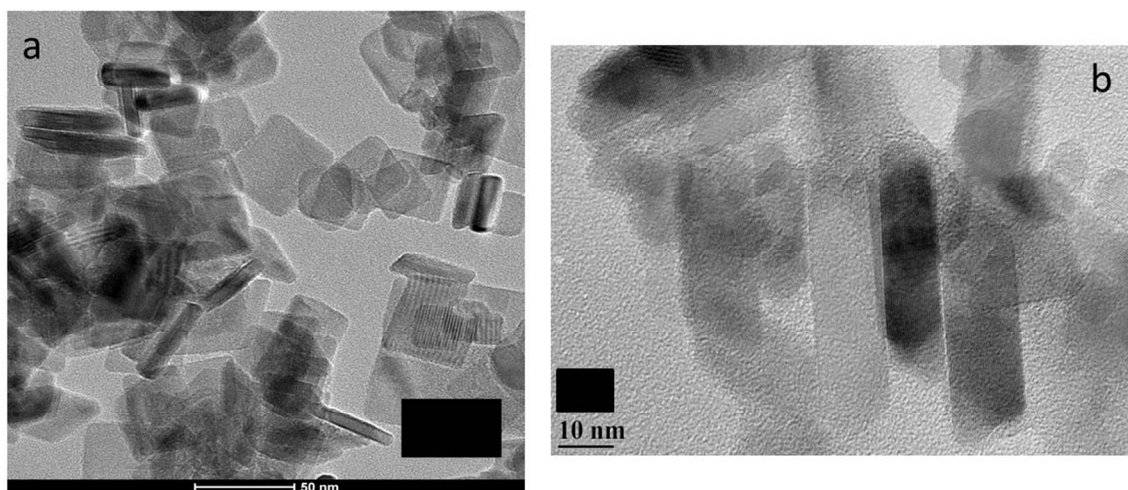


Figure S1. Transmission electron micrographs of TiO₂ nanosheets (a) and commercial Dyesol TiO₂ nanoparticles (b). The scale bars are 50 nm and 10 nm for the nanosheets and nanoparticles, respectively.

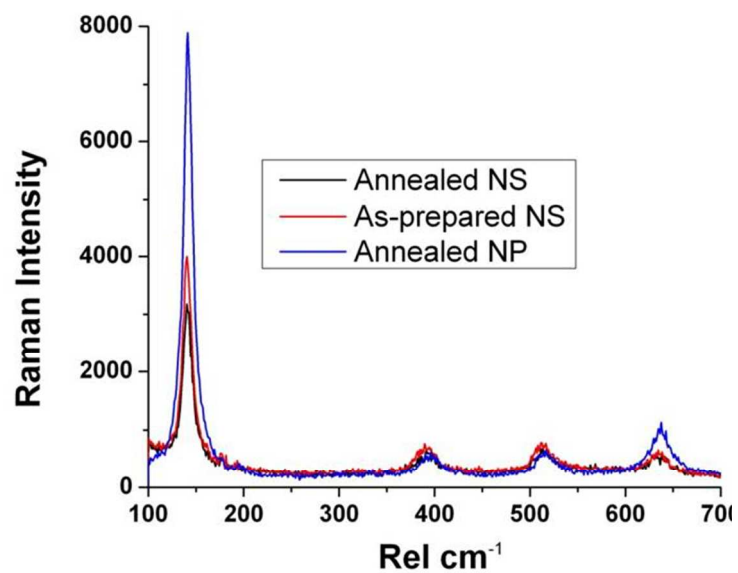


Figure S2. Raman spectra of annealed and unannealed TiO₂ nanosheets (NS) and annealed commercial TiO₂ nanoparticles (NP).

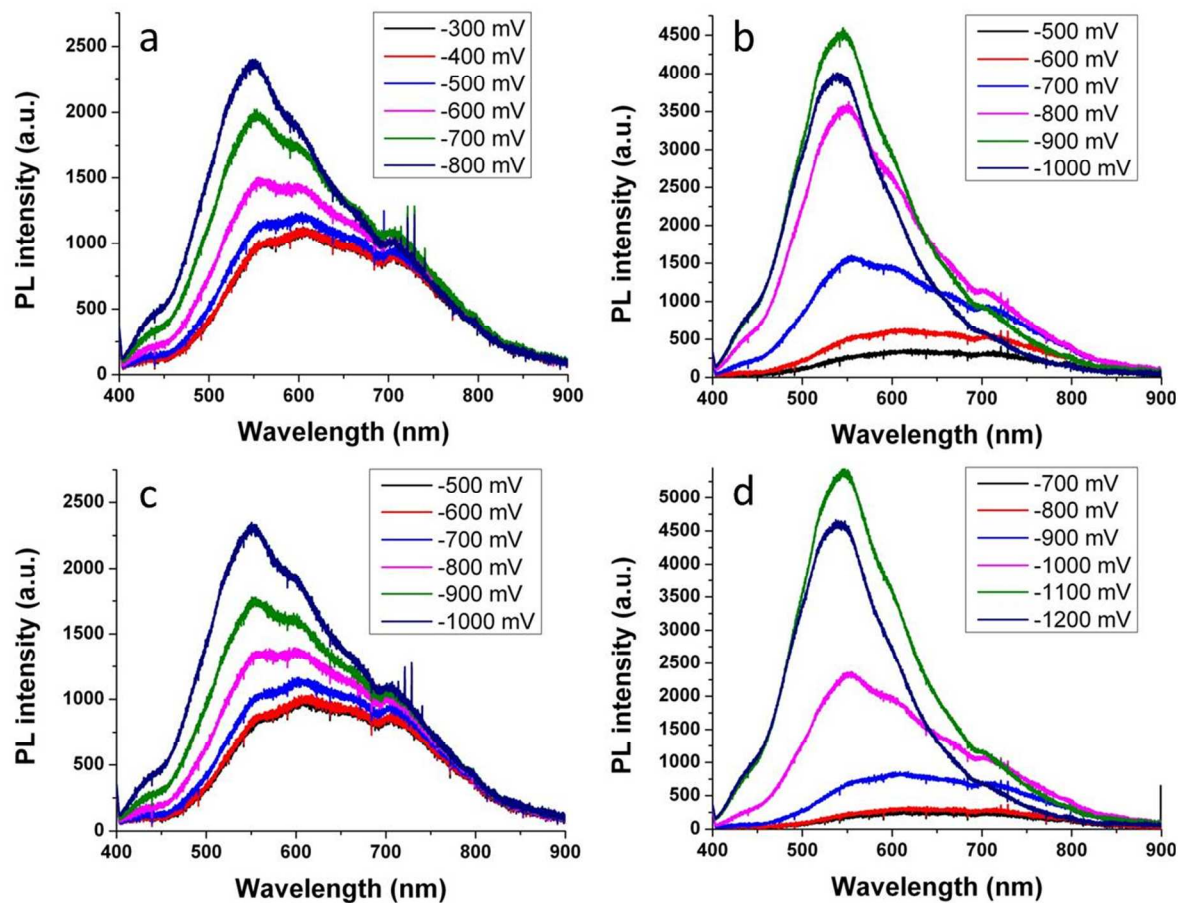
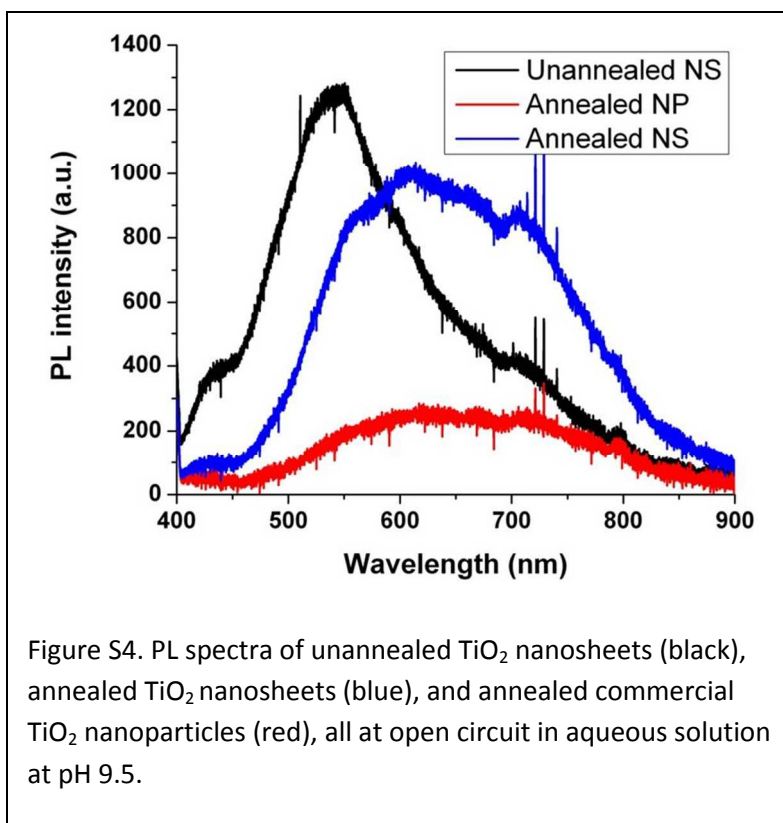


Figure S3. SEPL spectra of (a)TiO₂ nanosheets at pH 6.1, (b) TiO₂ nanoparticles at pH 6.1, (c) TiO₂ nanosheets at pH 9.5 (d) TiO₂ nanoparticles at pH 9.5, all in aqueous electrolyte with 0.2 M NaClO₄.



Data Analysis by non-negative matrix factorization:

The data matrix, \mathbf{D} , was constructed from columns containing the spectra measured at each voltage and pH, resulting in a matrix with the dimensions of m wavelengths by n voltages. For the analysis of the samples in aqueous media at different pH, the spectra (columns) for all the voltages at all the pH conditions were concatenated into a single \mathbf{D} matrix for the nanoparticle sample, resulting in a 10636 (wavelengths) \times 94 (voltages) matrix. The spectra for the nanosheets at all voltages and pH values were likewise concatenated into a single 10636 \times 91 matrix. The set of three component spectra, shown in Figure 2a (2b) therefore results from the global analysis of the nanosheet (nanoparticle) spectra at all pH's and all voltages. Separate data matrixes were constructed for the nanoparticles in acetonitrile (10636 \times 39) and also for nanosheets in acetonitrile (10636 \times 39).

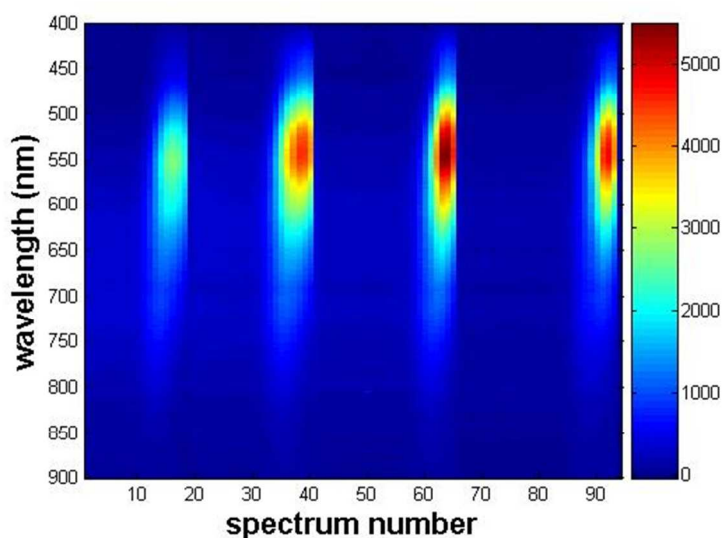


Figure S5 Data matrix for nanoparticle aqueous sample. Each column is a spectrum. The spectrum numbers increase within each pH as voltage is made more negative, and the four bright features in the two-dimensional data are for increasing pH on going from left to right.

The data matrix, **D**, was factored into component spectra and loading matrices,

$$\mathbf{D} = \mathbf{RC}$$

Where **R** is an $m \times n$ matrix containing the spectra of m wavelengths in its n columns, and **C** is an $i \times n$ matrix containing the loadings of the i components at the n different voltages. The factorization was done by two different methods: principal components analysis followed by non-orthogonal basis rotation to minimize negative values of component spectra and loadings¹, and non-negative matrix factorization (NMF).² The results presented here are from the NMF but both approaches to factorization gave nearly identical results.

For the four data sets (nanosheets in water, nanoparticles in water, nanosheets in acetonitrile, and nanoparticles in acetonitrile), the number of components was determined to be three, based on an examination of the residuals of the model of the data. The residuals are the difference between the measured data and the modeled **D** matrix that results from putting the factored **R** and **C** back into equation 1. If not enough components are used, then the data cannot be accurately reproduced, if too many components are used, then experimental noise is mistaken for a component.

Figure S6 shows the residuals from factoring the data from Figure S5 into two components. It is not possible to model the data with two components, so systematic error is obvious in the residuals.

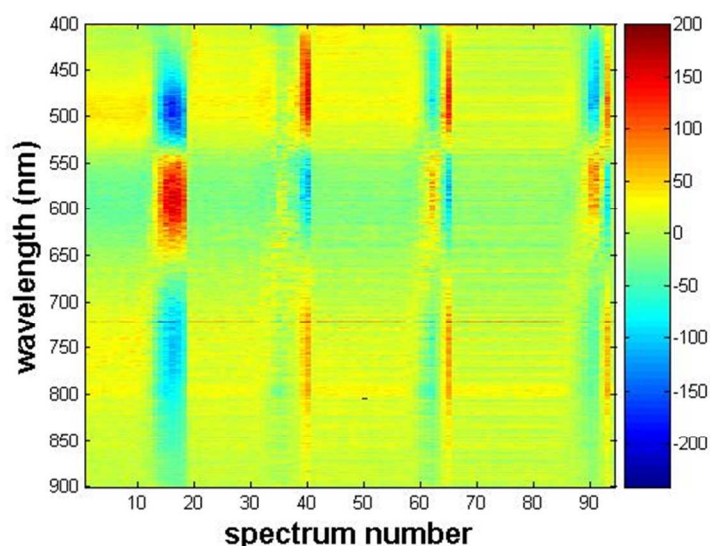


Figure S6. Residuals resulting from factoring the data matrix into two components. Note the systematic error from using too few components.

The factorization of the data into three components reduces the residuals to approximately 1% of the magnitude of the data set, and eliminates the obvious systematic error. Therefore, three components were used for the factorization of this data set.

After factorization, the component spectra were normalized to 1, and the component loadings were divided by the corresponding normalization factor.

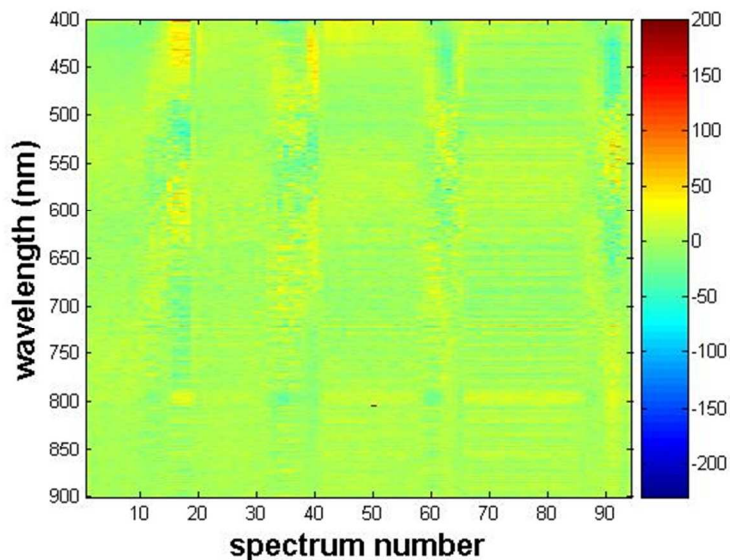


Figure S7. Residuals from modeling the data in Figure S5 with three components. Note that the systematic error is corrected.

When a fourth component was added to the model, the solution became unstable. A unique fit to the data with low residuals was obtained only in the three-component case.

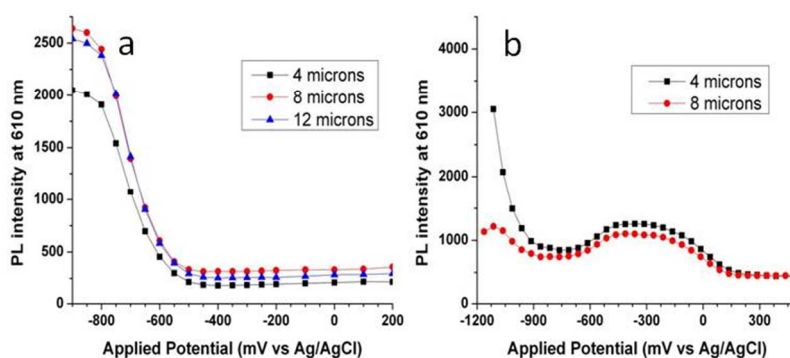


Fig. S8 PL intensity at 610 nm versus potential for a NP film in (a) water and (b) acetonitrile for several different film thicknesses. The increased intensity at more negative potentials for the thinner film in (b) is photoluminescence from the conductive glass substrate.