

Electronic Supplementary Information

Energy band alignment at the heterointerface between a nanostructured TiO₂ layer and Au₂₂(SG)₁₈ clusters:

Relevance to metal-cluster-sensitized solar cells

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Electronic structure of nanostructured TiO₂ film

The chemical state of the nanostructured TiO₂ anatase

Characterization of the TiO₂ substrate was conducted by means of an XPS analysis. The areas of interest are the Ti2p and O1s core-level spectra. First, we clarify the impact of Ar ion etching on the surface chemistry by comparing the Ti2p and O1s spectra before and after the treatment. The aforementioned spectra are shown in Figures S1a and b. Well-separated spin-orbit components Ti2p_{1/2}–2p_{3/2} with a splitting value of 5.7 eV are observed in the spectra (Figure S1a). The symmetric Ti2p_{1/2} and Ti2p_{3/2} peaks were centered at the binding energies of 464.7 and 459 eV, respectively. It is important to note that the peak intensity decreases significantly after Ar ion etching, suggesting some chemical changes in the material. These changes in the structure can be understood only after a deconvolution analysis of Ti2p core-level spectra. In the Ti2p spectrum, there are noticeable peaks that appear at low binding energies after an Ar⁺ treatment. These peaks can be attributed to the lower oxidation states of Ti³⁺ and Ti²⁺. Ar-induced reduction of transition-metal oxides was previously reported and has been widely studied ¹⁻³. With regard to the O1s spectrum, a minor shift towards a higher binding energy was recorded after etching (Figure S1b). Such changes can be ascribed to the appearance of Ti³⁺ as a result of sputter damage ³.

Peak fitting and deconvolution were conducted for TiO₂ after cleaning in the vicinity of the Ti2p and O1s core-level emissions shown in Figures S1c and d. The analysis indicated the presence of three oxidation states of titanium, which could be assigned to Ti²⁺, Ti³⁺ and Ti⁴⁺. Ti⁴⁺ and Ti³⁺ are referred to as the bulk configuration of TiO₂, while Ti²⁺ is rather a product of sputter damage to the film surface⁴. The observed value of the spin-orbital splitting also confirms the existence of the Ti⁴⁺ oxidation state⁴. The chemical state of the TiO₂ substrate was confirmed through an analysis of the O1s core-level spectra. Figure S1d presents the XPS spectra recorded near the O1s core-level emissions. Peak fitting and deconvolution were performed for the O1s core-level emission in the spectrum interval of 534 to 528 eV. The O1s spectrum was decomposed into two components. The fitting parameters are summarized in Table S1. The main compound centered at the binding energy of 530.4 originates from the Ti⁴⁺ oxidation state⁵. The peak at the binding energy of 531.5 eV can be assigned to the lower oxidation states of Ti³⁺ and Ti²⁺⁴. The analysis results of the O1s core-level spectrum are in line with data pertaining to the Ti2p spectrum.

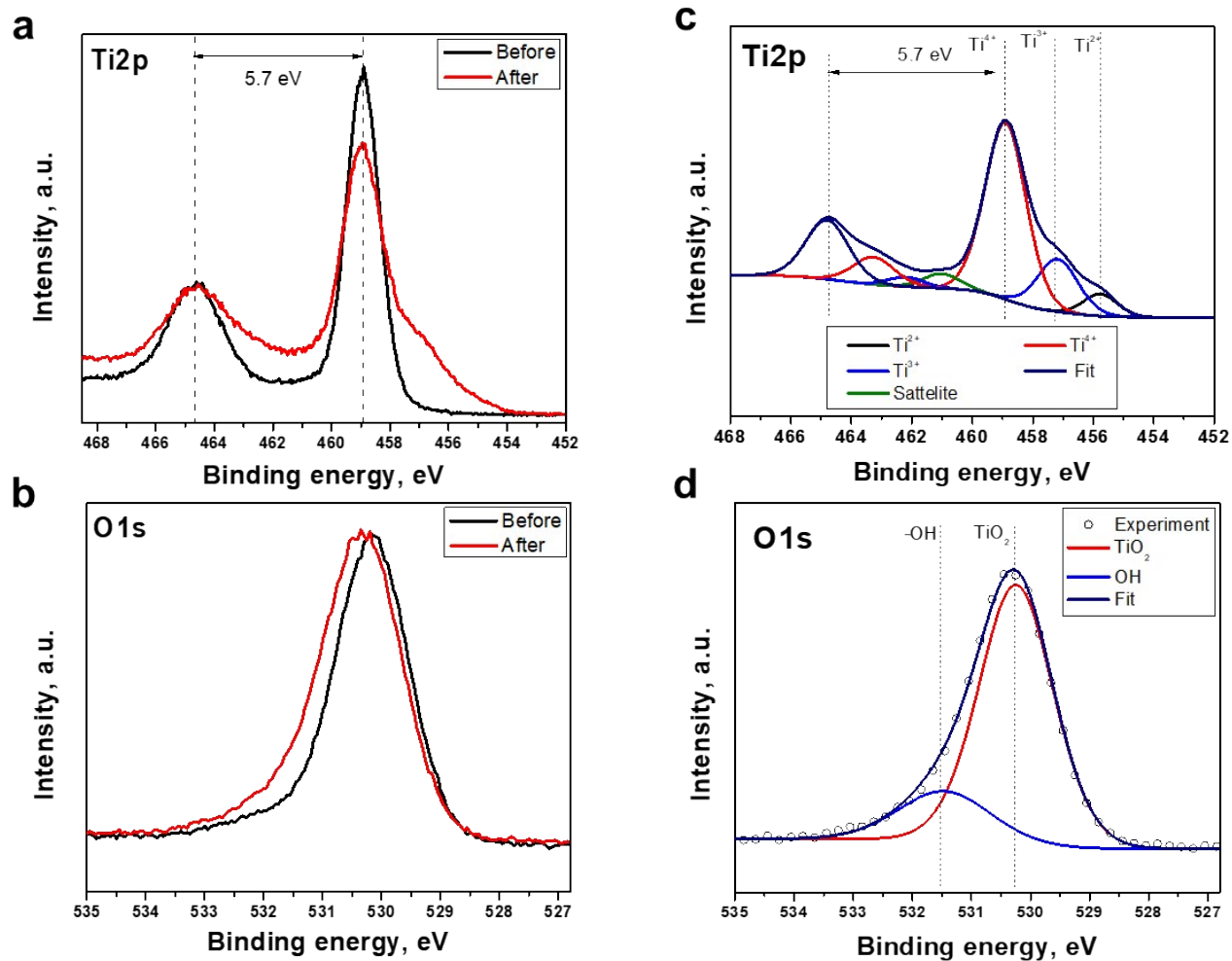


Figure S1. Comparison of the XPS spectra in the vicinity of (a) Ti2p and (b) O1s for the bulk TiO₂ sample before and after Ar ion sputtering, and deconvolution results of (c) Ti2p and (d) the O1s spectra for bulk TiO₂

Table S1. Deconvolution parameters obtained by the fitting analysis of TiO₂ after sputtering in the vicinity of the Ti2p and O1s core-level spectra

Core-level		Binding energy, eV	At%	FWHM, eV
Ti2p	Ti ⁴⁺	458.9	72.0	1.4
	Ti ³⁺	457.2	20.9	1.6
	Ti ²⁺	455.7	7.1	1.6
O1s	Ti ⁴⁺	530.3	83.3	1.6

	-OH	531.5	16.7	1.9
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Optical analysis: the bandgap of the nanostructured TiO₂ anatase

Given that a TiO₂ nanoparticle layer is a highly light-scattering material, E_g of TiO₂ was evaluated by applying the Kubelka–Munk method, which based on the following equation,

$$F(R) = \frac{(1 - R)}{2R},$$

where R is the diffuse reflectance and F(R) is the Kubelka–Munk function, which is proportional to the absorption coefficient (α)⁶.

For an indirect semiconductor such as TiO₂, the expected variation of $hv * F(R)$ with photon energy hv near the absorption edge can be expressed as follows:

$$hv * F(R) = B(hv - E_g)^2, \quad (1)$$

where B is the absorption constant for the indirect transition, h is Plank's constant, ν is the frequency, and E_g is the optical bandgap energy⁷. The plot of $F(R)$ versus hv was fitted using relation (1). The analysis result of the diffusion reflectance spectrum in terms of the indirect optical absorption is shown in Figure S2. A plot of $\sqrt{(hv * F(R))}$ versus the photon energy provides two straight line segments with two intercepts on the energy axis, hv_1 and hv_2 . The E_g values can be estimated as follows, $E_g = \frac{1}{2}(hv_1 + hv_2)$. Thus, the bandgap value of ~ 3.2 eV ($hv_1 = 3.17$ eV; $hv_2 = 3.21$ eV) was derived for nanostructured TiO₂ anatase. The obtained value is in good agreement with our results and with previously reported data^{4,8}.

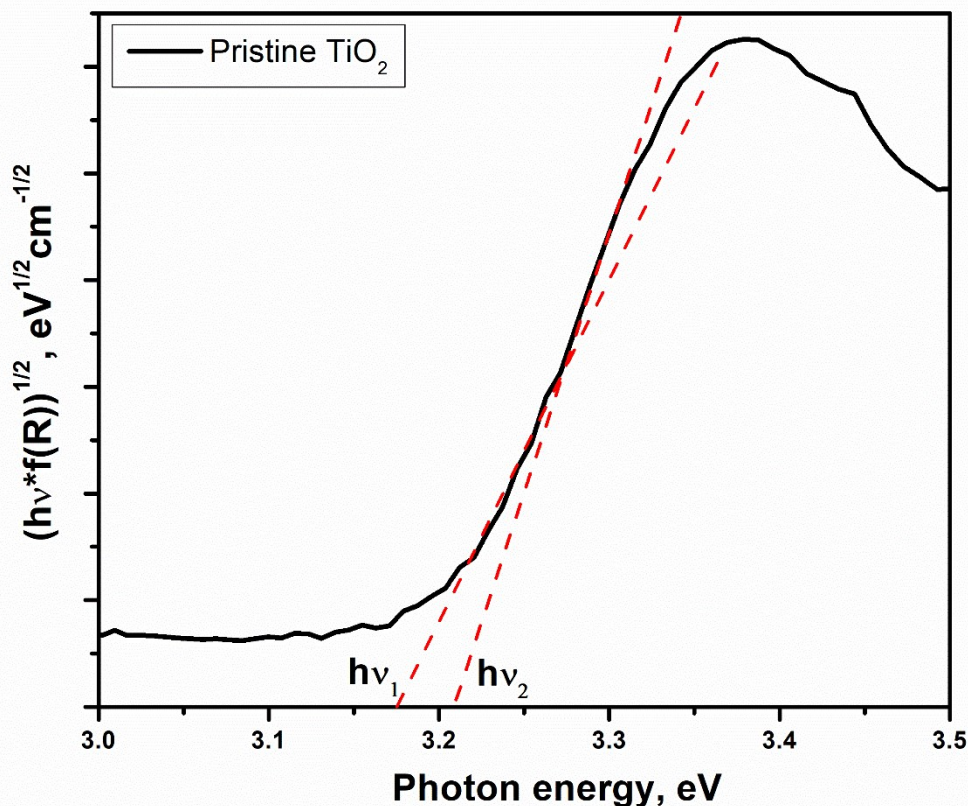


Figure S2. Analysis of the diffuse reflectance spectrum of the TiO₂ nanoparticle layer in terms of indirect optical absorption. A plot of $\sqrt{(hv * F(R))}$ versus the incident photon energy (hv) is depicted by the solid line. The plot of the Kubelka–Munk function versus hv gives two dashed line segments with two intercepts on the energy axis, hv_1 and hv_2 . The E_g value can be estimated as the center between these two intercepts.

References

- 1 O. Omelianovych, L. L. Larina, V. D. Dao and H. S. Choi, *Appl. Surf. Sci.*, 2018, **457**, 381–387.
- 2 R. Steinberger, J. Walter, T. Greunz, J. Duchoslav, M. Arndt, S. Molodtsov, D. C. Meyer and D. Stifter, *Corros. Sci.*, 2015, **99**, 66–75.
- 3 X. Zhou, N. Liu and P. Schmuki, *Electrochem. commun.*, 2014, **49**, 60–64.
- 4 G. Liu, W. Jaegermann, J. He, V. Sundström and L. Sun, *J. Phys. Chem. B*, 2002, **106**, 5814–5819.

- 5 Y. V. Nefedov, V. I. Gati, D. Dzhurinskii, B. F. Sergushin, N. P. Salyn, *Russ. J. Inorg. Chem.*, 1975, **20**, 1279–1283.
- 6 P. Kubelka, *J. Opt. Soc. Am.*, 1948, **38**, 448–457.
- 7 J. I. Pankove, *Optical processes in semiconductors*, Dover Publications, Inc., New York, 1971.
- 8 N. A. Tsvetkov, L. L. Larina, O. Shevaleevskiy, E. A. Al-Ammar and B. T. Ahn, *Prog. Photovoltaics Res. Appl.*, 2012, **20**, 904–911.