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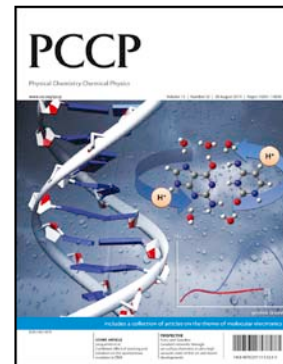
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Tin oxide-surface modified anatase titanium(IV) dioxide with enhanced UV-light photocatalytic activity

Musashi Fujishima,^a Qiliang Jin,^a Hironori Yamamoto,^a Hiroaki Tada^{a*} and Michael Nolan^{b*}

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[Sn(acac)₂]Cl₂ is chemisorbed on the surfaces of anatase TiO₂ via ion-exchange between the complex ions and H⁺ released from the surface Ti-OH groups without liberation of the acetylacetonate ligand (Sn(acac)₂/TiO₂). The post-heating at 873 K in air forms tin oxide species on the TiO₂ surface in a highly dispersion state at a molecular scale ((SnO₂)_m/TiO₂). A low level of this *p* block metal oxide surface modification (~ 0.007 Sn ions nm⁻²) accelerates the UV-light-activities for the liquid- and gas-phase reactions, whereas in contrast to the surface modification with *d* block metal oxides such as FeO_x and NiO, no visible-light response is induced. Electrochemical measurements and first principles density functional theory (DFT) calculations for (SnO₂)_m/TiO₂ model clusters (*m* = 1, 2) indicate that the bulk (TiO₂)-to-surface interfacial electron transfer (BS-IET) enhances charge separation and the following electron transfer to O₂ to increase the photocatalytic activity.

1. Introduction

Recent intensive researches for developing semiconductor photocatalysts have opened up avenues for environmental purification and solar energy conversion into electric or chemical energy.^{1,2} Among many kinds of semiconductor photocatalysts, TiO₂ is one of the most promising because of its high oxidation power, high photostability, relative abundance in nature and nontoxicity.^{3,4} The key to improve its photocatalytic activity lies on increasing the efficiency of charge separation through the suppression of charge recombination. One of the strategies for this is to form the heterojunction between TiO₂ and partner semiconductors⁵⁻⁸ or metals.⁹ Previously, we reported that a patterned bilayer-type heterojunction system composing of the TiO₂ overlayer and the fluorine-doped SnO₂ (F:SnO₂) underlayer has a high photocatalytic activity for the decomposition of acetaldehyde under UV-light irradiation.¹⁰ This effect results from the efficient bulk-to-bulk interfacial electron transfer from the TiO₂ overlayer to the underlying F:SnO₂ film. The photocatalytic activity of the heterojunction system depends on the relative positions of the conduction band (CB) and valence band (VB) edges of TiO₂ and F:SnO₂. In order to construct the heterojunction system with suitable energy band alignments, the surface modification technique named chemisorption-calcination (CC), is very effective.¹¹ In this technique, chemisorption of metal complexes on the TiO₂ surface with successive calcination yields metal oxide species

highly dispersed on the surface at a molecular scale. Recently, we have shown that the surface modification of TiO₂ with iron oxide^{12,13} and nickel oxide¹⁴ using this technique gives rise to a high level of activities under illumination of both visible- and UV-light.

Here we report the UV-light-activity of tin oxide-surface modified TiO₂ ((SnO₂)_m/TiO₂) prepared by the CC technique. The formation mechanism of (SnO₂)_m/TiO₂ and the surface modification effect on the photocatalytic activity for liquid- and gas-phase test reactions are discussed. First principles density functional theory (DFT) simulations of small SnO₂ species adsorbed at the anatase (001) surfaces are presented to provide insights into the experimental findings.

2. Experimental

2.1 Sample preparation

Anatase TiO₂ particles (ST-01 with specific surface area = 309 m² g⁻¹, A-100 with specific surface area = 8.1 m² g⁻¹, Ishihara Sangyo) were used as a standard photocatalyst. By the CC technique utilizing this reaction, (SnO₂)_m/TiO₂ was prepared as follows: After TiO₂ particles (1 g) had been added to 50 mL of a [Sn(acac)₂]Cl₂ ethanol solution, they were allowed to stand for 24 h at 298 K. The [Sn(acac)₂]Cl₂ concentration was changed from 1.6 × 10⁻⁷ mol dm⁻³ to 1.0 ×

10^{-4} mol dm $^{-3}$. The solid samples were separated by centrifugation and washed twice with the solvent for the physisorbed complexes to be removed. Then, they were dried in vacuum at room temperature, followed by heating in air at 873 K for 1 h. For electrochemical measurements, mesoporous TiO $_2$ nanocrystalline film electrodes were used. A paste containing anatase TiO $_2$ particles with a mean size of 20 nm (PST-18NR, Nikki Syokubai Kasei) was coated on F:SnO $_2$ -film coated glass substrates (12 Ω/\square) by a squeegee method, and the sample was heated in air at 773 K to form mesoporous-TiO $_2$ films (mp-TiO $_2$ /FTO).

2.2 Adsorption measurements

The adsorption process of [Sn(acac) $_2$]Cl $_2$ on TiO $_2$ particles (ST-01) was examined by following the change of the electronic absorption spectra with different amount of the TiO $_2$ particles dispersed in 1×10^{-4} mol dm $^{-3}$ [Sn(acac) $_2$]Cl $_2$ ethanol solution (50 mL) at 298 K for 24 h. Adsorption isotherms of Sn $^{4+}$ ions were obtained by exposing TiO $_2$ particles (2 g) to ethanol solutions with different concentrations of Sn(acac) $_2$ Cl $_2$ (50 mL). After the particles were separated from the suspension in both the experiments by centrifugation, the concentrations of [Sn(acac) $_2$]Cl $_2$ was determined from the absorbance at 274.5 nm ($\epsilon_{\max} = 1.54 \times 10^4$ mol $^{-1}$ dm cm $^{-1}$) with a Hitachi U-4000 spectrophotometer. The pH measurement was also performed on the supernatant (5 mL) diluted with 10 mL water after the former experiment.

2.3 Sample characterization

The Sn loading amount was determined by inductively coupled plasma spectroscopy (ICPS-7510, Shimadzu). The sample (0.1 g) was dispersed to hot conc. H $_2$ SO $_4$ (20 mL), and the deposits were thoroughly dissolved into the solution by stirring. The solution was diluted 5 times in volume with water, and then the Sn concentration was measured. UV-vis diffuse reflectance spectrum of (SnO $_2$) $_m$ /TiO $_2$ (A-100) was recorded on a Hitachi U-4000 spectrophotometer. The spectrum was converted to the absorption spectrum by using the Kubelka-Munk function. Diffuse reflectance Fourier transform infrared (DRIFT) spectra of the particles (ST-01) diluted 25 wt % with KBr (spectroscopic grade, > 98 %, Kanto Chemical) were obtained with a JASCO FT/IR-470plus spectrometer equipped with a diffuse reflectance attachment (Spectra Tech, Inc.). In order to determine number of acetylacetonate ligands in the complex-adsorbed ST-01, thermogravimetric analysis (TG)/differential thermal analysis (DTA) was conducted with a thermal analyzer (TG8010D, Rigaku) using dried samples in air by increasing temperature from 293 to 1,273 K at a heating rate of 10 K min $^{-1}$. Transmission electron microscopic (TEM) observation and energy dispersive X-ray (ED) spectroscopic measurements were performed using a JEOL JEM-3000F and Gatan Imaging Filter at an applied voltage of 300kV. X-ray photoelectron spectroscopic (XPS) measurements were performed using a Kratos Axis Nova X-ray photoelectron spectrometer with a monochromated Al K $_{\alpha}$ X-ray source ($h\nu = 1486.6$ eV)

operated at 15 kV and 10 mA. The take-off angle was 90°, and multiplex spectra were obtained for Sn $_{3d}$, O $_{1s}$, and Ti $_{2p}$ photopeaks. All the binding energies (E_B) were referenced with respect to the C $_{1s}$ at 284.6 eV. The electrochemical properties of the (SnO $_2$) $_m$ -surface modified mp-TiO $_2$ /FTO electrodes ((SnO $_2$) $_m$ /mp-TiO $_2$ /FTO) were measured in 0.1 mol dm $^{-3}$ NaClO $_4$ aqueous solution in a regular three-electrode electrochemical cell using a galvanostat/potentiostat (HZ-5000, Hokuto Denko). Glassy carbon and an Ag/AgCl electrode (TOA-DKK) were used as a counter electrode and a reference electrode, respectively.

2.4 Photocatalytic activity evaluation

In both the decomposition of acetaldehyde (CH $_3$ CHO) and 2-naphthol (2-NAP), the reaction cells were irradiated with a Xe lamp (Wacom HX-500) through two pieces of FTO-coated glass transmitting the light of $330 < \lambda < 400$ nm for the UV-light photocatalytic activity evaluation and through a cut off filter (L-42 (Toshiba) transmitting the light of $\lambda > 400$ nm for the visible-light activity evaluation. A 596 ppm standard CH $_3$ CHO gas (CH $_3$ CHO/N $_2$) was introduced into the reaction chamber to be diluted with air such that its initial concentration was kept within the 400 ppm range. After the adsorption equilibrium of CH $_3$ CHO on A-100 or (SnO $_2$) $_m$ /A-100 particles (0.05 g) had been achieved under dark conditions, irradiation was carried out at room temperature. The concentration of CH $_3$ CHO was determined as a function of time by gas chromatography (GC-2014, Shimadzu) with a SHINCARBON A f.i.d. column (1.6 mm ϕ \times 3.1 m): injection and column temperatures were 363 K and 343 K, respectively, and N $_2$ was used as a carrier gas. A-100 or (SnO $_2$) $_m$ /A-100 particles (0.01 g) was placed in 50 mL of 4.0×10^{-5} mol dm $^{-3}$ solution of 2-NAP (solvent, acetonitrile : water = 1 : 99 v/v) in a borosilicate glass container was irradiated. 2 mL of the solution was sampled every 10 min and the electronic absorption spectra of the reaction solutions were measured using a spectrometer (UV-1800, Shimadzu) to determine 2-NAP concentration from the absorption peak at 224 nm.

2.5 SnO $_2$ -TiO $_2$ Calculations

To model the anatase (001) surfaces, we use a three dimensional periodic slab model and a plane wave basis set to describe the valence electronic wave functions within the VASP code.¹⁵ The cut-off for the kinetic energy is 396 eV. For the core-valence interaction we apply Blöchl's projector augmented wave (PAW) method,¹⁶ with Ti described by 4 valence electrons and oxygen by 6 valence electrons; Sn is described with 4 valence electrons. We use the Perdew-Wang91 approximation to the exchange-correlation functional.¹⁷ k -point sampling is performed using the Monkhorst-Pack scheme, with a ($2 \times 2 \times 1$) sampling grid for both surfaces.

For describing the electronic states of Ti in TiO $_2$, we have used the DFT+U approach. DFT+U^{18,19} adds a Hubbard U correction to describe reduced metal cation states, such as Ti $^{3+}$. From the literature, values of U in the range 3 – 5 eV are

reasonable^{20–23} and we apply $U = 4.5$ eV to the Ti 3d states throughout this paper.^{24,25} For Sn, no + U correction is applied, since the electronic states are reasonably well described with DFT. While DFT+ U fixes some of the problems with DFT in describing partially filled d states, it still does not repair the band gap underestimation inherent in approximate DFT and the energy gaps resulting from this work will be underestimated compared with experiment and will show some dependence on the precise DFT+ U setup; our DFT+ U set up uses robust parameters from the author's own work and from the literature^{20–25} and we are primarily interested in qualitative changes in the energy gap as a result of modification of the TiO_2 surface with the metal oxide nanoclusters.

The bulk lattice constants of anatase TiO_2 have been computed by fitting a set of constant volume DFT+ U energies to a Murnaghan equation of state, giving the following bulk lattice constants: $a = b = 4.172$ Å, $c = 9.627$ Å. The anatase (101) surface is the most stable, as measured by surface energy;²⁶ however, the (001) surface can be produced in experiments and has been well studied.^{27,28} The (001) surface is oxygen terminated and shows 5-fold coordinated Ti at the surface. The terminating oxygen are two coordinate, with the next oxygen subsurface layer showing 3 coordinated oxygen. For (001), a (1×4) reconstruction is stable,²⁹ but in this work it is sufficient to consider an unreconstructed surface model. A (4×2) surface supercell is employed for anatase (001); these surface supercell expansions are large enough to allow for adsorption of essentially isolated clusters. The anatase surface slab is 8 O-Ti-O layers thick, with all surfaces having a vacuum gap of 12 Å. The bottom trilayer in each surface is held fixed and all other layers are allowed relax. The convergence in the wavefunction relaxation is 0.0001 eV, while the ionic relaxation is converged when the forces on the atoms are less than 0.02 eV/Å. Fermi level smearing with the Methfessel Paxton scheme is applied, with $\sigma = 0.1$ eV. All calculations are spin polarised.

The bare TiO_2 surface, the metal oxide clusters adsorbed at TiO_2 and the free metal oxide clusters are calculated in the same periodic supercell, with the same plane wave cut off energy, the same k -point sampling grid and the same PAW potentials, ensuring consistency between calculations. To study cluster adsorption, the SnO_x clusters are positioned in a number of configurations at the surface and a full relaxation is performed within a fixed supercell. Some short ab initio molecular dynamics simulations in the NVE ensemble with a 0.1 fs timestep at 600 K have been run for 2 ps, with no change in the adsorption structure. The adsorption energy is computed from

$$E^{\text{ads}} = E((\text{SnO}_x)\text{-TiO}_2) - \{ E(\text{SnO}_x) + E(\text{TiO}_2) \} \quad (1)$$

Where $E((\text{SnO}_x)_m\text{-TiO}_2)$ is the total energy of the SnO_x cluster supported on the TiO_2 surface, and $E(\text{SnO}_x)$ and $E(\text{TiO}_2)$ are the total energies of the free SnO_x cluster (where SnO_x indicates that Sn can be in a +4 or +2 oxidation state) and the bare surface; a negative adsorption energy signifies that cluster adsorption is stable.

In the DOS plots, a smearing of 0.1 eV is used and the

cluster DOS are scaled by a factor of 10 to allow for the fact that the cluster contains a maximum 4 cations and 8 anions, compared to a maximum of 96 surface cations and 192 surface anions in rutile (110) to prevent the surface DOS swamping the cluster DOS if the scaling was not applied.

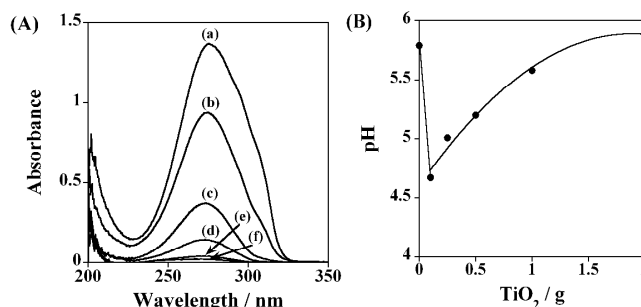


Fig. 1 (A) UV-Vis absorption spectra of a 1×10^{-4} mol dm^{-3} $\text{Sn}(\text{acac})_2\text{Cl}_2$ solution without ST-01 (a), with addition of ST-01 (b) 0.1 g, (c) 0.25 g, (d) 0.5 g, (e) 1 g, (f) 2 g. (B) Plots of the solution pH vs. amount of ST-01 added.

3. Results and discussion

3.1 Experimental results

$[\text{Sn}(\text{acac})_2]\text{Cl}_2$ has an absorption assigned to the $\pi\text{-}\pi^*$ transition in the acetylacetonate (acac)-ligand at 275 nm.³⁰ Fig. 1A shows UV-vis absorption spectra of a 1×10^{-4} mol dm^{-3} $[\text{Sn}(\text{acac})_2]\text{Cl}_2$ solution and the solutions equilibrated with various amounts of ST-01. As the amount of ST-01 increases, the absorption intensity monotonically weakens, while no absorption of acetylacetone (AcacH) at 272 nm appears during the adsorption. Fig. 1B presents the relationship between the amount of ST-01 added and pH of the supernatant. On adding 0.1 g ST-01 to a 1×10^{-4} mol dm^{-3} $[\text{Sn}(\text{acac})_2]\text{Cl}_2$ solution, a steep drop of pH from 5.79 to 4.67 is observed, followed by a gradual increase up to 5.89 with increasing amount of ST-01.

To study the adsorption state of $[\text{Sn}(\text{acac})_2]^{2+}$ on ST-01, diffuse reflectance Fourier transform infrared (DRIFT) spectra

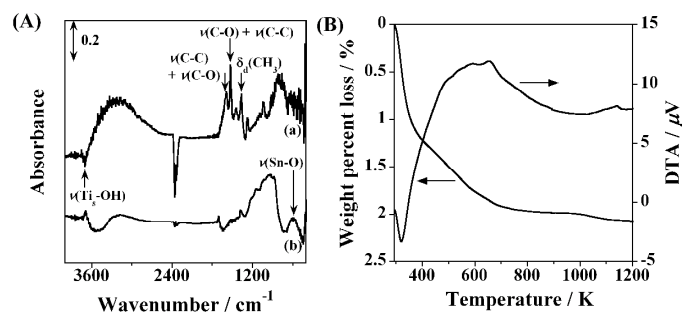


Fig. 2 (A) Difference DRIFT spectra: (a) the complex-adsorbed ST-01 - ST-01; (b) the complex-adsorbed ST-01 after heating at 873 K - ST-01. (B) Thermogravimetric analysis (TG)/differential thermal analysis (DTA) curves of the complex-adsorbed ST-01.

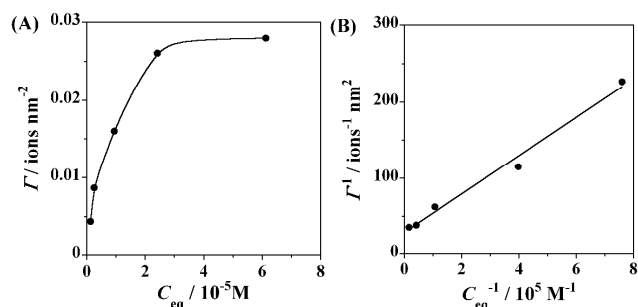


Fig. 3 (A) The adsorption isotherm and (B) the Langmuir plot of $[\text{Sn}(\text{acac})_2]\text{Cl}_2$ on ST-01 at 298 K.

were measured. Fig. 2A-(a) shows the difference DRIFT spectrum for the complex-adsorbed ST-01 minus ST-01. Three sharp positive peaks are observed at 1589, 1532, and 1364 cm^{-1} , which are assignable to the combination of $\nu(\text{C-C})$ + $\nu(\text{C-O})$, the combination of $\nu(\text{C-O})$ + $\nu(\text{C-C})$, and $\delta_s(\text{CH}_3)$, respectively.³¹ Also, a negative peak due to the surface OH group ($\text{Ti}_s\text{-OH}$) appears around 3700 cm^{-1} .^{32,33} Fig. 2A-(b) shows the difference DRIFT spectrum for the complex-adsorbed ST-01 after heating at 873 K minus ST-01. All the signals of the acac-ligands disappear, while new positive signals appear at 600 and ca. 3700 cm^{-1} due to the $\nu(\text{Sn-O})$ and $\nu(\text{SnO-H})$ modes, respectively.^{34,35} To estimate the number of the acac-ligands in one complex molecule adsorbed on ST-01, the thermogravimetric analysis (TG)/differential thermal analysis (DTA) was carried out. Fig. 2B shows TG/DTA curves for the complex-adsorbed ST-01 sample. In the TG curve, a rapid decrease in the sample weight up to ca. 373 K is followed by a gradual weight loss to ca. 873 K. The weight loss with an endothermic DTA signal at $T < 373$ K is derived from desorption of the adsorbed water, while that with an exothermic DTA signal at $373 < T < 873$ K is mainly caused by the acac-ligand oxidation. From the latter value, the number of the acac-ligands in the adsorbed complex was calculated to be ca. 2. Also, weight loss with an exothermic DTA signal due to the phase transition from anatase to rutile is observed above 973 K. Consequently, the heating conditions for obtaining tin oxide-surface modified TiO_2 were

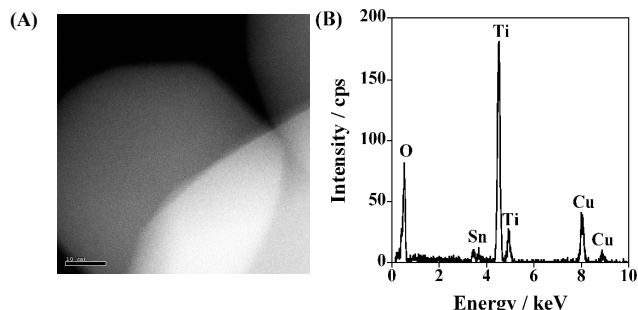


Fig. 4 (A) TEM image (scale bar is 10 nm) and (B) ED spectrum of tin oxide-modified TiO_2 .

set at 873 K in air for 1 h.

Further information about the adsorption mechanism can be gained from the adsorption isotherm. Fig. 3A shows the

adsorption isotherm of $[\text{Sn}(\text{acac})_2]\text{Cl}_2$ on ST-01 at 298 K. The loading amount of Sn is expressed by the number of Sn ions per unit TiO_2 surface area ($\Gamma/\text{ions nm}^{-2}$). The adsorption amount steeply increases with increasing equilibrium concentration (C_{eq}) to be saturated at $C_{\text{eq}} > \sim 1 \times 10^5 \text{ mol}^{-1} \text{ dm}^3$. The Langmuir plot provides a straight line (Fig. 3B), of

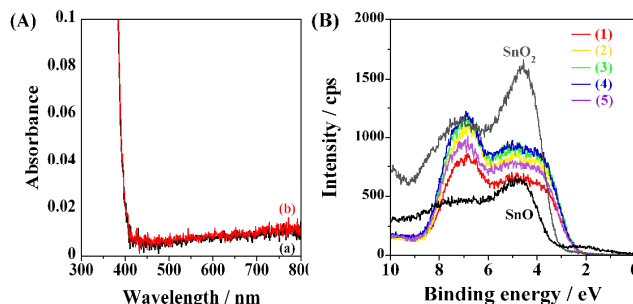


Fig. 5 (A) UV-Vis absorption spectra of (a) A-100 and (b) tin oxide-surface modified A-100 ($\Gamma = 0.024$). (B) Valence band-XPS spectra of tin oxide-surface modified A-100 with varying Γ : (1) 0, (2) 0.037, (3) 0.024, (4) 0.0074 and (5) 0.0061, SnO_2 (gray) and SnO (black).

which slope and intercept yield the saturated adsorption amount and equilibrium constant of 0.034 ions nm^{-2} and $1.2 \times 10^5 \text{ mol}^{-1} \text{ dm}^3$, respectively. Fig. 4 shows the transmission electron microscopic image (A) and energy dispersive X-ray (ED) spectrum (B) of a sample after heating at 873 K ($\Gamma = 0.024 \text{ ions nm}^{-2}$). There exists no observable particle on the TiO_2 surface, while the Sn signals are located at 3.4 and 3.7 keV besides the Ti and O signals in the ED spectrum. The Cu signals arise from the copper grid used for analysis. Evidently, tin oxide species are highly dispersed on anatase TiO_2 as extremely small clusters.

Optical property for the tin oxide-surface modified TiO_2 is of primary importance in connection with its photocatalytic activity. Fig. 5A shows UV-vis absorption spectra of (a) A-100 and (b) tin oxide-surface modified A-100 ($\Gamma = 0.024$). Both the samples have strong absorption at $\lambda < 385 \text{ nm}$ due to the interband electronic transition of TiO_2 , while almost transparent in the visible range. Similar spectra were obtained also for the other samples with varying Γ . In this manner, modifying TiO_2 with tin oxide species does not promote visible-light absorption, in contrast to FeO_x ^{12,13} and NiO ¹⁴-modified TiO_2 . In the subsequent section, we present results from the DFT simulations to understand this difference. Further, in order to characterize the tin oxide species on the TiO_2 surface, X-ray photoelectron spectroscopic (XPS) measurements were performed. Fig. 5B shows valence band (VB)-XPS spectra for A-100 with and without the tin oxide-surface modification, and authentic SnO_2 and SnO for comparison. In the VB-XPS spectra of TiO_2 , the emission from the $\text{O}2p$ -VB extends from 2 to 9 eV, while the VBs of SnO_2 and SnO are located in the range from 3 to ~ 9 eV. Irrespective of Γ , no change in the VB position with the tin oxide modification is appreciated, whereas the VB-tops rise with the surface modification by FeO_x ¹² and NiO .¹⁴ Also, in the VB-XPS spectrum of SnO , there exists a Sn 5s band

around 2 eV. However, in the spectra of the tin oxide-surface modified A-100, the Sn5s band is absent in the same manner as the spectrum of SnO₂. This finding suggests that the oxidation state of Sn in the tin oxide species is 4+, and thus the clusters are denoted as (SnO₂)_m below.

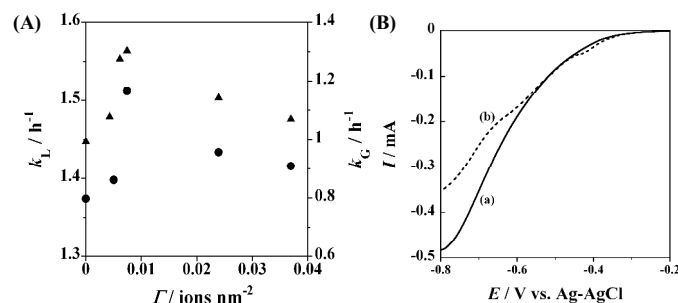
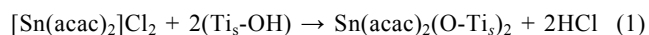
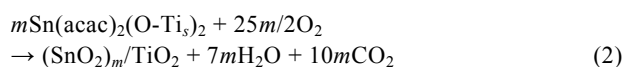


Fig. 6 (A) Plots of the first-order pseudo-constants of the liquid-phase photocatalytic decomposition of 2-NAP (k_L , solid circle) and the gas-phase photocatalytic decomposition of CH₃CHO (k_G , solid triangle) under the illumination of UV-light as a function of Γ . (B) Current-potential curves of (a) (SnO₂)_m/mp-TiO₂/FTO and (b) mp-TiO₂/FTO electrodes in an aerated 0.1 mol dm⁻³ NaClO₄ aqueous solution in the dark.

On the basis of these results, we propose the mechanism on the formation of the SnO₂ clusters on the TiO₂ surface. Firstly, the adsorption of [Sn(acac)₂]²⁺ ions on the TiO₂ surface occurs through the ion-exchange between the complex ions and H⁺ released from the Ti_s-OH groups (eqn 1).



This process does not involve elimination of the acac-ligands, whereas the adsorptions of Mg(acac)₂¹¹ and Fe(acac)₃¹³ on TiO₂, and [VO(acac)₂]³⁶ and [Cr(acac)₃]³⁷ on SiO₂ are accompanied by the acac-ligand exchange. Successively, part of the H⁺ released is adsorbed on the Ti_s-OH groups forming the Ti_s-OH₂⁺ group. The electrostatic repulsion between [Sn(acac)₂]²⁺ ion and the Ti_s-OH₂⁺ group prevents further adsorption to reach adsorption equilibrium. From the ZINDO molecular orbital calculations, the molecular cross-sectional area of the complex ion was estimated to be ca. 0.6 nm² molecule⁻¹. On the other hand, the area occupied by one complex ion on the TiO₂ surface was estimated from the Langmuir plot to be 29.4 nm² ion⁻¹, which is approximately 50 times larger than the molecular cross-sectional area. Secondly, the post-heating process oxidizes the acac-ligands of the adsorbed complex to yield SnO₂ species highly dispersed on the TiO₂ surface (eqn 2).



Probably, this stems from the strong chemical bond between the complex and the surface to inhibit the aggregation of the SnO₂ species.

To evaluate the photocatalytic activity of (SnO₂)_m/TiO₂, the photocatalytic decomposition of 2-NAP and CH₃CHO was

examined under illumination of visible-light ($\lambda > 400$ nm, $I_{420-485\text{ nm}} = 1.0$ mW cm⁻²) and UV-light ($330 < \lambda < 400$ nm, $I_{320-400\text{ nm}} = 1.5$ mW cm⁻² for 2-NAP, $I_{320-400\text{ nm}} = 1.0$ mW cm⁻² for CH₃CHO).³⁸⁻⁴⁰ 2-NAP is the starting material of azo-dyes, while CH₃CHO is a volatile organic compound responsible for sick-house syndrome. These compounds were used as model pollutants in water and air. As predicted from the optical property (Fig. 5A), no decompositions occurred under the visible-light irradiation. On the other hand, UV-light irradiation led to the 2-NAP and CH₃CHO decompositions apparently with the first-order kinetics followed. Fig. 6A shows the first-order pseudo-rate constants for the decompositions of 2-NAP (k_L) and CH₃CHO (k_G) under UV-light irradiation as a function of Γ . The plots of both the k_L and k_G exhibit volcano-shaped dependency on Γ with a maximum at $\Gamma \approx 0.0074$ ions nm⁻². The SnO₂-surface modification hardly affected the adsorptivity for 2-NAP in the dark at $\Gamma < 0.04$. Certainly, the SnO₂-surface modification has an enhancing effect on the UV-light-activity of TiO₂ for both the liquid- and gas-phase reactions, although the effect is smaller than those by FeO_x^{12,13} and NiO¹⁴ surface modification.

In order to obtain the information about the origin of the SnO₂-surface modification effect, current (I)-potential (E) curves were measured for the mp-TiO₂/FTO electrodes in an aerated 0.1 M NaClO₄ aqueous solution in the dark. Fig. 6B shows the I - E curves of (a) (SnO₂)_m/mp-TiO₂/FTO and (b) mp-TiO₂/FTO electrodes. For both the electrodes, the current due to the O₂ reduction is observed at $E < -0.2$ V, whereas the current hardly flew at $-0.8 < E < -0.2$ V without O₂ (data not shown). Importantly, the reduction current at $E < -0.55$ V is enhanced with the SnO₂-surface modification, i.e., the surface SnO₂ species mediate the electron transfer from TiO₂ to O₂.

3.2 Simulation results

To explore the microscopic mechanisms behind the experimental results, we present the results of DFT+U simulations of models of SnO₂-TiO₂, in which small, molecular sized SnO₂ clusters are adsorbed at TiO₂ surfaces. In an earlier paper we showed that Sn of an Sn₂O₄ cluster adsorbed at rutile (110) surface binds with bridging oxygen from the TiO₂ surface, while O from the cluster binds with 5fold coordinated surface Ti.⁴¹ Fig. 7 presents the atomic structures of SnO₂ and Sn₂O₄ species adsorbed at the anatase (001) surface, where we consider only Sn in its +4 oxidation state, as found in the experiments. The bonding mode is quite different from that with the rutile (110) surface, in which there was little displacement of surface oxygen towards the adsorbate⁴¹. For the SnO₂ cluster (Fig. 7(a)), Sn from the cluster interacts with two-fold surface terminating oxygen and pulls two of these oxygen atoms out of the surface layer, with displacements of 0.41 and 1.15 Å, resulting in formation of new Sn-O bonds between the cluster and the surface. Oxygen from the cluster interacts with the outermost surface Ti and leads to breaking of the original surface Ti-O bond, the oxygen from this bond is displaced to make the new Sn-O bonds. For the Sn₂O₄ cluster (Fig. 7(b)), it is clear that the

displaced surface oxygen and oxygen from the cluster take the same bonding environment; the surface oxygen atoms are each displaced by 1.11 Å. The adsorption energies are computed to be -3.32 eV for SnO₂ and -5.29 eV for Sn₂O₄, indicating a strong bonding interaction between the cluster and the surface. Maximising the number of new metal-oxygen bonds plays a key role in assuring stability of the adsorbate

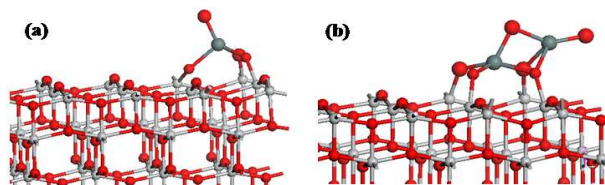


Fig. 7 Atomic structures of SnO₂ species adsorbed at anatase surfaces. (a) SnO₂ anatase (001), (b) Sn₂O₄ anatase (001). In this Fig., surface Ti is the small grey sphere, surface O is the small red ball, Sn from adsorbed SnO₂ is the large dark grey sphere and O from adsorbed SnO₂ is the large red sphere.

structure.

To examine the electronic structure, we plot the projected electronic density of states (PEDOS) for Sn 5s states from the adsorbed SnO₂ species and the Ti 3d states from the anatase (001) surface in Fig. 8. From the PEDOS, we see that, in contrast to other oxides supported on TiO₂,⁴¹ the tin oxide states do not appear inside the TiO₂ energy gap and are in fact found very close to the CB edge of the surface; since the Sn 5s states are unoccupied with an Sn⁴⁺ oxidation state. For other oxides such as TiO₂,⁴² CrO_x and MoO_x,⁴¹ cluster-derived electronic states lie above the VB edge of the surface, pushing the VB edge higher in energy, thus reducing the VB-CB energy gap over the bare surface. In the present system, the SnO₂ and Sn₂O₄-derived states lie well separated from the VB and CB edges of TiO₂ and will not lead to any shift to visible light absorption. These results from the DFT simulations are consistent with the experimental results in Section 3.1, in

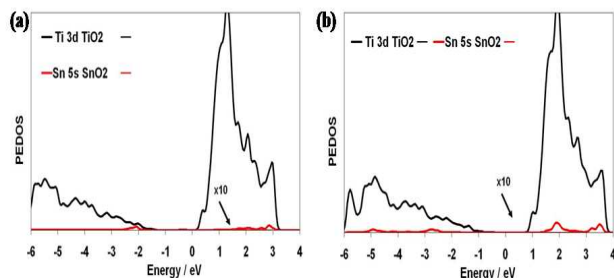
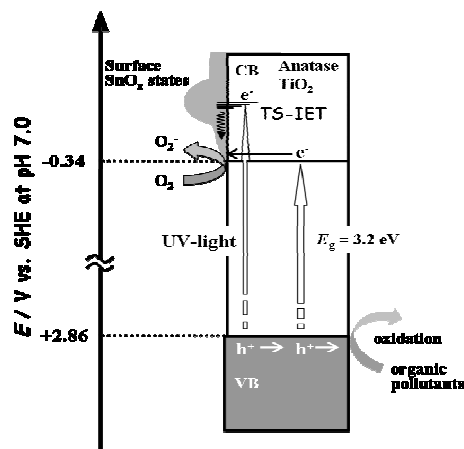


Fig. 8 Electronic DOS projected onto surface Ti 3d states and cluster Sn 5s states for SnO₂ and Sn₂O₄ clusters adsorbed on the anatase (001) surface. (a) anatase (001) SnO₂, (b) anatase (001) Sn₂O₄. The zero of energy is the Fermi level.

which no shift to the visible region was found upon formation of the adsorbed tin oxide species. Another intriguing point is that the Sn5s-derived surface levels are dispersed centred at ~1 eV higher than the CB edge. Upon UV-light excitation, these surface states as well as the CB(TiO₂) can be acceptor levels for the electrons from the VB(TiO₂).



Scheme 1. A Proposed Energy Band Diagram of (SnO_x)_m/TiO₂

3.3 Action mechanism of the surface SnO₂ species

On the basis of the experimental and theoretical calculation results, both the enhanced UV activity and lack of visible light activity of anatase TiO₂ with the SnO₂-surface modification (Scheme 1). In the oxidative decomposition of organic compounds, the key to increasing the TiO₂ photocatalytic activity is the efficient transfer of the excited electrons to O₂.^{43,44} If SnO₂ species are present at the TiO₂ surface, then upon UV excitation, electrons can be promoted to either the TiO₂ CB or the SnO₂ states around the TiO₂ CB. Excitation of an electron to the SnO₂ states results in separation of electrons and holes, with electrons present on the SnO₂ species. This BS-IET is in contrast to the surface-to-bulk (TiO₂) IET (SB-IET) proposed for the (FeO_x)_m/TiO₂^{12,13} and NiO/TiO₂¹⁴ systems. A similar IET mechanism has recently been proposed for Cu(II)-grafted TiO₂ to explain its visible-light-activity for 2-propanol decomposition.⁴⁵ Further, the surface Sn ions with a low coordination number in small clusters (Fig. 7) can act as an adsorption site for O₂ similarly to the reduced SnO₂ surface facilitating its chemisorption⁴⁶ and successive reduction. Consequently, charge recombination is reduced over bare TiO₂, and the holes left in the VB(TiO₂) efficiently oxidize the organic substrates. The excess loading causes the drop of the E_F (TiO₂), decreasing the reducing power of the excited electrons toward O₂.¹² This would explain the presence of the optimum Γ for the photocatalytic activity of (SnO₂)_m/TiO₂. Very interestingly, Boppana and Lobo have recently shown that the SnO_x-surface modification of ZnGa₂O₄ by an impregnation method significantly increases not only the UV-light-activity but also the visible-light-activity.⁴⁷ This finding suggests that the surface modification effect strongly depends on the kind of semiconductors.

4. Conclusions

The CC technique using [Sn(acac)₂]Cl₂ as a precursor enables

to form extremely highly dispersed surface tin oxide species on the TiO₂ surface. There is no shift of the absorption edge to the visible region, in contrast to iron oxide- and nickel oxide modified TiO₂, which is explained by the alignments of the TiO₂ and tin oxide electronic states upon formation of the composite material. However, the surface modification increases the UV-light-activities of TiO₂ for both liquid- and gas-phase reactions. This enhancing effect has been shown to originate from the actions of the surface tin oxide species to accept the excited electrons and promote the electron transfer to O₂.

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