Supporting Information

Design of All-Inorganic Molecular-based Photocatalysts Sensitive to Visible Light: Ti(IV)-O-Ce(III) Bimetallic Assemblies on Mesoporous Silica

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Experimental

Photocatalytic experiments: 10 mg of Ti/Ce-MCM-41 powder was pressed into a self-supporting wafer (13 mm of diameter). The wafer was then mounted in a transmission infrared vacuum cell (volume; 4.6 cm^3) equipped with CaF_2 windows. The IR cell was evacuated by rotary pump (<10 mmTorr) for 1 h at room temperature prior to the photocatalytic reaction. Reaction gas, 10 Torr of 2-propanol and 750 Torr of O_2, was then loaded into the IR cell from the gas handling system. Photocatalysis was conducted at room temperature, using a 1000-W Xe lamp, equipped with monochromator. The monochromic light at 460 nm with the band width of 10 nm was irradiated to the wafers, whose light intensity was adjusted with the neutral density filters. After the photo-irradiation, the IR cell was placed in the sample chamber of an FTIR spectrometer with a deuterated triglycine sulfate (DTGS) detector. Before measurements, the sample chamber was purged with dry N_2 at flow rate of 15 L/min, and the IR cell was kept in the dark for ca. 90 min. The IR intensity (*I*) versus wavelength was obtained by averaging 200 scans at a resolution of 4 cm^{-1}, with a processing time of 3 min for one spectrum. All IR absorption spectra were obtained in the form of absorbance, $\log(I_0/I)$, using an spectrum taken before irradiation as a reference (I_0). Amount of generated acetone was determined by the peak intensity of 1361-cm^{-1} band, δ(HOC), while amount of generated CO_2 was determined by the peak intensity of 2367-cm^{-1} band, ν(C=O). In both cases, linearity of the peak intensity with amount of products was confirmed.

Calculation of apparent quantum efficiency (AQE): The comparison of photocatalytic activities of Ti/Ce-MCM-41 and nitrogen-doped TiO_2 ($TiO_{1.998}N_{0.002}$) was made by calculating the apparent quantum efficiency (AQE) for acetone and CO_2 generation from 2-propanol oxidation under 460-nm irradiation.[3c] Photocatalytic oxidation of 2-propanol was carried out under the same condition as those mentioned above except that the incident light intensity was adjusted in a way that the number of adsorbed photon is equivalent to be 1.70×10^{15} quanta·cm^{-2}·s^{-1} at 460 nm between two samples. The linearity of the rate of

product generation with the incident light intensity was confirmed at this light intensity. The apparent AQE calculations were conducted using the following procedure[3c]. The initial acetone and CO_2 formation rates by IPA decomposition were calculated using the least-squares method. Only one photon participated in the decomposition process of IPA to acetone. Therefore, the QE values for acetone generation were calculated using the following equation: AQE(acetone) = initial acetone generation rate/absorption rate of incident photon. For CO_2 generation, it is not easy to determine the number of photons participating in the reaction because the addition of molecular oxygen to reaction intermediates may cause some radical chain reactions (Hashimoto et al. *J. Phys. Chem. B* **1998,** *102,* 2699-2704). Therefore, we here assumed the following formula, $C_3H_8O + 5H_2O + 18H^+ \rightarrow 3CO_2 + 18H^+$, that is, six photons are required to produce one CO_2 molecule, and calculated the apparent QE values for CO_2 generation using the following equation, QE(CO_2) = 6 × initial CO_2 generation rate / absorption rate of incident photon. The experimental errors for each AQEs, given by the standard error from the least-squares fits for the initial rates of product formation, were less than 14%.

Synthesis of Ce(III)-grafted TiO₂ photocatalysts: The synthesis of Ce(III)-grafted TiO_2 powder was made by following methods. The rutile TiO_2 powder (MT-150A, TAYCA, Ltd.), possessing a BET surface area of 95 $m^2 \cdot g^{-1}$ and a primary particle size of about 15 nm, was dehydrated at 120 °C under vacuum for 4 h. The dehydrated powder was then added to a dry acetonitrile solution of Ce(III)NO$_3$ and stirred at r.t. for 17 h. The intense yellow crystalline were filtered and washed with dry acetonitrile, and finally dried under vacuum.

Synthesis of Ce(III)-grafted TiO₂ electrodes: Film electrodes of Ce(III)-grafted TiO_2 powder for photocurrent measurements were prepared as follows: 1 g of rutile-TiO_2 powder (MT-150A, TAYCA, Ltd.) was suspended into pure water (5 mL) by stirring. The resultant colloidal solution of TiO_2 was then spin-coated at 2000 rpm onto transparent conductive oxide (F-doped SnO_2 or FTO, 20 Ω/square) films, on which an ethanol solution of 50 mM KOH had, in advance, been applied with a spin coater at 1000 rpm to get strong adhesion between TiO_2 and FTO under low-temperature annealing. The TiO_2-coated glass was then dried in air, and heated at 150°C for 15 min with an electric furnace. The above TiO_2 coating was repeated twice, and the TiO_2 film was heated at 150°C for 30 min. The grafting of Ce(III) ions onto TiO_2 film was made by immersing the dehydrated TiO_2 film into a dry acetonitrile solutions of Ce(III)NO$_3$ (2wt.%) at room temperature for 18 h with stirring. Photocurrents for Ce(III)-TiO_2 film electrodes were measured as a function of wavelength, using a 1000-W xenon lamp (Ushio) as the light source together with a monochromator with a bandwidth of 10 nm.

Synthesis and Characterization of nitrogen-doped TiO₂ powder: The nitrogen-doped TiO_2 was synthesized according to our previous work (K. Hashimoto et al. *J. Phys. Chem. B* **2006,** *110,*

13158-13165). The anatase TiO_2 powder (ST-01, Ishihara Sangyo Kaisha, Ltd.), possessing a BET surface area of 300 $m^2\,g^{-1}$ and a primary particle size of about 7 nm, was heated under flowing NH_3 at 550 °C for 3 h. The N 1s and O 1s core levels on the surface were measured by XPS and the x values ($TiO_{2-x}N_x$, nitrogen concentrations) were estimated by comparing the product of the 396 eV peak area multiplied by the nitrogen-sensitive factor to the product of the 531 eV peak area (O 1s, Ti-O bonds) multiplied by the oxygen sensitive factor. The x values were estimated to be 0.002 ($TiO_{1.998}N_{0.002}$). We showed that the nitrogen-doped TiO_2 thus prepared had the highest apparent quantum efficiency among the sample with different amount of nitrogen contents, $x = 0.002, 0.003, 0.007$ (K. Hashimoto et al. *J. Phys. Chem. B* **2006,** *110,* 13158-13165).

XANES measurements: The X-ray absorption near edge structure (XANES) measurements were performed at the undulator beamline (BL39XU) at SPring-8. A diamond (111) double-crystal was employed as the monochromator, and the higher-order harmonics were suppressed using a flat Pt coated mirror. For the standard samples, the XANES spectra were measured using transmission mode, while the fluorescence mode was employed for the measurements of the Ce/Ti samples due to the low Ce density.
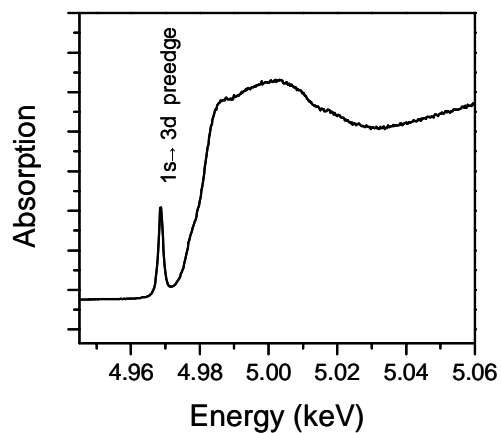
Figure S1: Ti K-edge XANES spectra for dehydrated Ti-MCM-41 (Ti/Si = 0.03). The preedge at 4968 eV is characteristic for 1s→3d transition allowed for tetrahedral Ti(IV) sites (isolated single TiO_4 species).
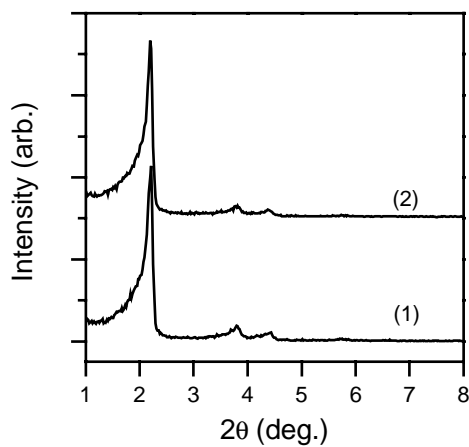

**Figure S2**. Low angle XRD of (1) Ti-MCM-41. (2) Ti/Ce-MCM-41
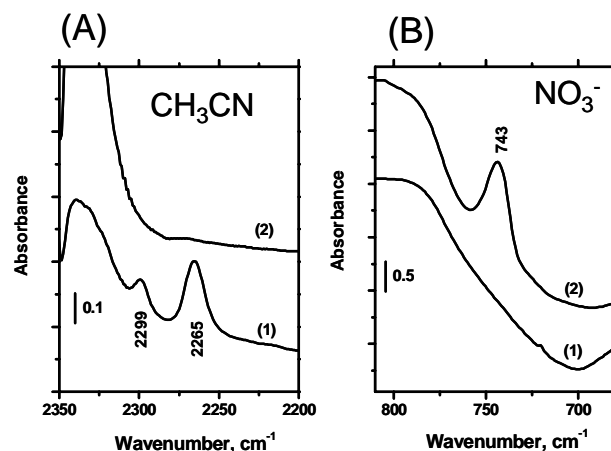
Figure S3. Panel (A): FTIR spectra of as-synthesized Ti/Ce-MCM-41 wafer (1) before and (2) after evacuation at 40 °C. Removal of CH_3CN ligands by evacuation was confirmed by the absence of $\nu(CN)$ absorption bands. Panel (B): (1) FTIR spectra of as-synthesized Ti/Ce-MCM-41. (2) FTIR spectra of $NaNO_3$ mechanically mixed with SiO_2 at 1 wt.% . No band due to the NO_3 was observed for Ti/Ce-MCM-41, confirming the removal of NO_3^- from the samples.
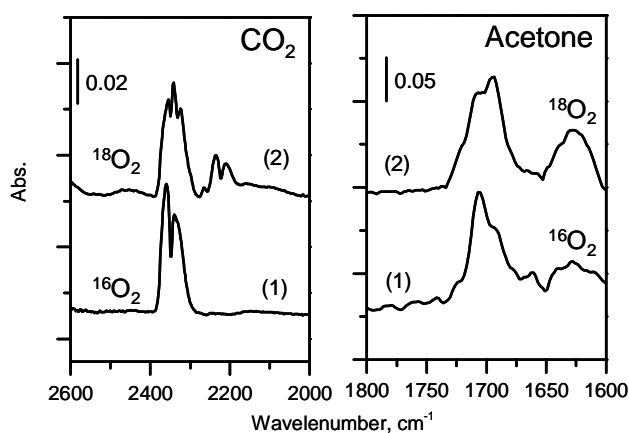
Figure S4. FTIR spectra recorded before and after irradiation (460 nm, 27 mWcm^{-2}) of Ti/Ce-MCM-41 wafer loaded (1) 2-propanol (10 Torr) and $^{16}O_2$ (750 Torr) and (2) 2-propanol (10 Torr) and $^{18}O_2$ (750 Torr). Isotopic shift of $\nu_{as}(CO_2)$ of CO_2 and $\nu(C=O)$ of acetone demonstrates the incorporation of ^{18}O to the products.

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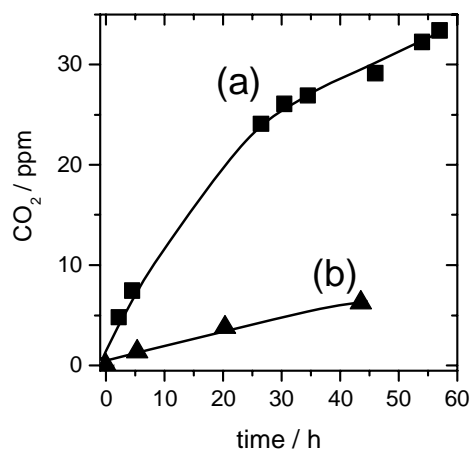
Figure S5. Change in CO_2 concentration with time under visible-light irradiation of (a) Ce(III)-grafted TiO_2 (rutile) and (b) TiO_2(rutile) powder. Photocatalytic experiments were made following conditions. A 300-mg sample powder was spread evenly over the irradiation area in a 500 mL vessel. After sealing the sample in the vessel, the atmosphere in it was replaced by the synthetic air. The 300 ppm of IPA was injected into the vessel and then the samples were stored in the dark. The visible light ranging from 450 to 580 nm was illuminated from 150 W Xe lamp equipped with three optical filters of B-46, Y-47, and C-40C (Asahi Techno glass Ltd.). Light intensity at the surface of catalysts was 1.0 mW/cm^2. Products analysis was made by Gas Chromatography.
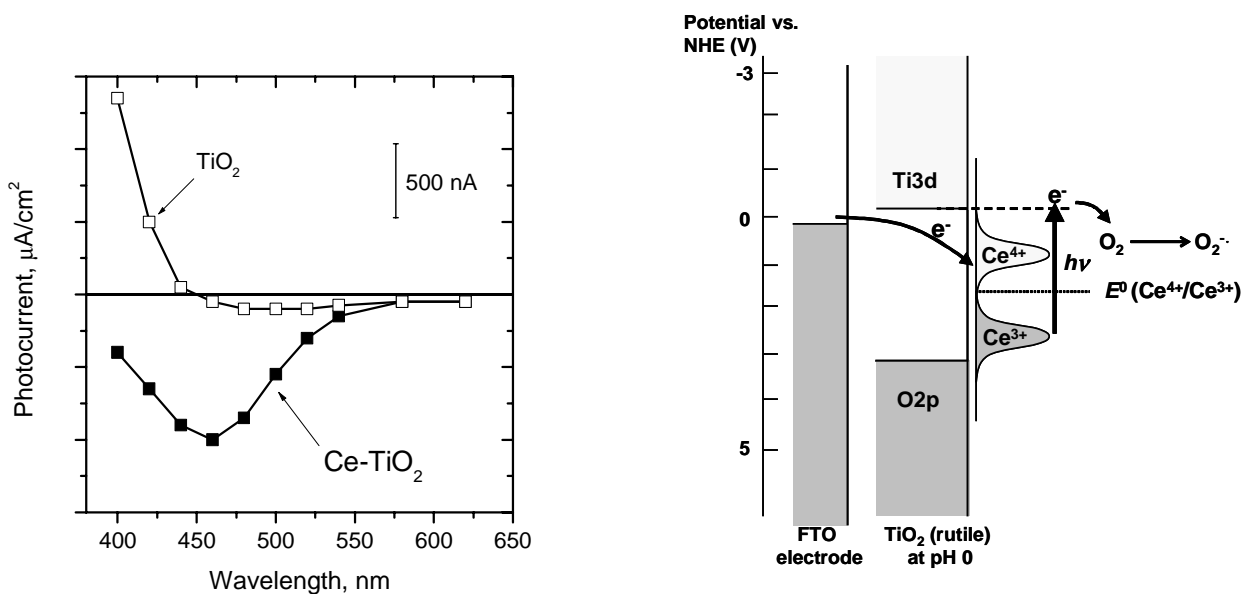
Figure S6. Left; Photocurrent action spectra for Ce(III) grafted particulate TiO_2 thin film and particulate TiO_2 thin film electrodes without Ce(III) ions, recorded in O_2 saturated 0.1 M TBAP in CH_3CN at an applied potential of 0.0 V vs. Ag/Ag^+. Negative photocurrents observed for the Ce-TiO_2 electrode is assigned to the reduction of dissolved O_2. Right; The mechanism of cathodic photocurrent generation for Ce(III)-grafted TiO_2 electrode under visible-light irradiation.