A Novel Visible-light-sensitive Efficient Photocatalyst, Cr^{III}-grafted TiO_2

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TiO_2 powder grafted with Cr^{III} ions was demonstrated to become a novel type of hybrid photocatalyst. It could decompose 2-propanol into CO_2 via acetone under visible-light (450–580 nm) irradiation. The reaction is explained by the photoinduced direct charge transfer from surface Cr^{III} ion to the conduction band of TiO_2, in which injected electron into the conduction band reduces oxygen and the Cr^{IV} oxidizes 2-propanol.

TiO_2 is an efficient photocatalyst, which is activated only by ultraviolet (UV)-light irradiation.[1] Therefore, an important objective of TiO_2 photocatalytic studies is the effective utilization of visible light. For example, studies, in which transition-metal ions (Cr, V, Fe, Mn, Co, Ni, etc.) were substituted for Ti sites, have been performed since the early 1980s.[2] N-Doped TiO_2 was initially reported as an anion-doped visible-light-sensitive photocatalyst in 2001.[3] Since then, various types of TiO_2 doped with anions, including sulfur, carbon, and iodine, have widely studied.[4] Recently, we used Ti^{IV}/Ce^{III} hetero-bimetallic assemblies in meso porous silica to successfully demonstrate that photocatalytic oxidative decomposition can be initiated by a visible-light-induced metal to metal charge transfer (MMCT).[5] The charge transfer proceeds from Ce^{III} to Ti^{IV} ion and results in the formation of Ti^{III}/Ce^{IV}. Then, Ti^{III} and Ce^{IV} can return to their initial states by reducing O_2 and extracting electrons from organics, respectively. Based on this observed MMCT process, we hypothesized that photoirradiation can directly induce a charge transfer from atomic metal ions to the conduction band (C.B.) of TiO_2 when ions are grafted on a TiO_2 surface because the C.B. of TiO_2 mainly consists of Ti3d orbitals.[6] In the present study, we call this charge-transfer process a pseudo-MMCT. Herein, we selected Cr^{III} as the metal ion because it was hypothesized that Cr^{III}-grafted TiO_2 (Cr^{III}/TiO_2) may absorb visible light and show photocatalytic activities due to Cr^{IV}/Cr^{III} redox couples, $E^0 = 2.1$ V,[7a] and the energy level of the C.B. in rutile TiO_2, -0.4 V (pH 7).[7b]

TiO_2 powders in rutile form (MT-150A, TAYCA Corp.) were modified with 0.1 wt % of $CrCl_3{\cdot}6H_2O$ (Aldrich) by the impregnated method (See Supporting Information (S.I.) 1).[12] As a reference, ZrO_2 powders (Aldrich) were also modified with Cr^{III} ion by the same method. UV–vis absorption spectra using the diffuse reflection method were obtained by a spectrometer (UV-2550, Shimadzu Ltd.). The photocatalytic oxidation activity was evaluated by the decomposition of gaseous 2-propanol under visible light (450–580 nm, S.I. 1).[12]

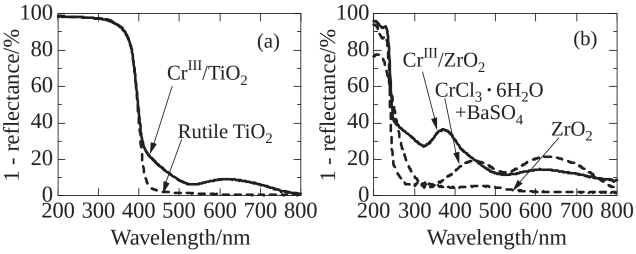

Figure 1. UV–vis diffuse reflectance spectra for (a) rutile TiO_2 and Cr^{III}/TiO_2, and (b) ZrO_2, Cr^{III}/ZrO_2 and the mixture of $CrCl_3{\cdot}6H_2O$ and $BaSO_4$ insulating powders.

Figure 1a shows the UV–vis spectra for bare rutile TiO_2 and Cr^{III}/TiO_2. Figure 1b shows the spectra for ZrO_2, Cr^{III}-grafted ZrO_2 (Cr^{III}/ZrO_2), and a mixture of $CrCl_3{\cdot}6H_2O$ and $BaSO_4$ insulating powders. The potential of the bottom of the C.B. in ZrO_2, which consists of mainly Zr4d, is approximately 1 V more negative than that of rutile TiO_2.[8] As shown in Figure 1b, the absorption of ZrO_2 initially increases at ca. 250 nm, indicating a band gap of ca. 5.0 eV, which is consistent with previously reported values, 4–5 eV[8a] and 4.5–6.1 eV.[8b] The spectrum of the mixture of $CrCl_3{\cdot}6H_2O$ and $BaSO_4$ shows an absorption centered at ca. 450 and 620 nm, which corresponds to Cr^{III} d–d transitions.[9] The spectrum of Cr^{III}/ZrO_2 possesses absorptions centered at ca. 365 and 620 nm as well as an interband absorption shorter than ca. 250 nm. The absorption at ca. 620 nm is assigned to the Cr^{III} d–d transition. The peak position of this absorption does not change when Cr^{III} is grafted on ZrO_2. Hence, it is likely that the one at ca. 450 nm, which is derived from another d–d transition, also remains unchanged. In fact, the absorption at ca. 450 nm appears as a shoulder of the peak at ca. 365 nm in the spectrum of Cr^{III}/ZrO_2. In contrast, the absorption peak at ca. 365 nm appears only when the ZrO_2 surface is grafted with Cr^{III} ions. Figure 2A schematically illustrates the band structure of ZrO_2 and the redox potential of Cr^{IV}/Cr^{III} with occupied and unoccupied states. Based on this figure we can expect that the absorption at ca. 365 nm of Cr^{III}/ZrO_2 is due to the direct charge transfer from Cr^{III} to the C.B. of ZrO_2, a pseudo-MMCT.[10] This charge-transfer process is shown by the arrow in Figure 2A. As for Cr^{III}/TiO_2 in Figure 1a, the spectrum possesses an absorption peak near 620 nm and a relatively strong absorption shoulder in the region from ca. 410 to 550 nm. Similar to Cr^{III}/ZrO_2, the onset at ca. 410 nm corresponds to the interband transition of rutile TiO_2, and the absorption at ca. 620 nm is assigned to the Cr^{III} d–d transition. Moreover, another d–d transition of Cr^{III}, which forms the shoulder, should exist around 450 nm. In addition to these d–d transitions, the pseudo-MMCT from Cr^{III} to the C.B. of TiO_2 may also contribute to the absorption spectrum. Comparing the energy diagrams of Cr^{III}/ZrO_2 and Cr^{III}/TiO_2 in Figure 2, the pseudo-MMCT of Cr^{III} to the C.B. of TiO_2 may appear in a longer wavelength region by ca. 1 eV (140 nm) than that of Cr^{III} to the C.B. of ZrO_2. Hence, we conclude that the broad absorption in the region of 410–550 nm consists of both Cr^{III} d–d transition and a pseudo-MMCT

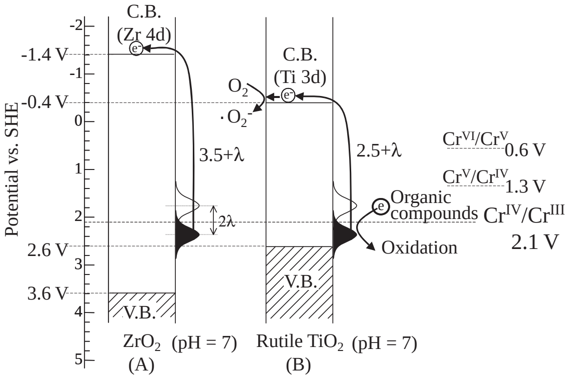

Figure 2. Energy diagrams of ZrO$_2$, TiO$_2$, and redox potential of Cr^{IV}/Cr^{III} with occupied and unoccupied states. λ represents the reorganization energy. Light absorption induces charge transfer from the occupied state to the conduction bands of (A) ZrO$_2$ and (B) TiO$_2$. Redox potentials of Cr^{V}/Cr^{IV} and Cr^{VI}/Cr^{V} are also shown as references.

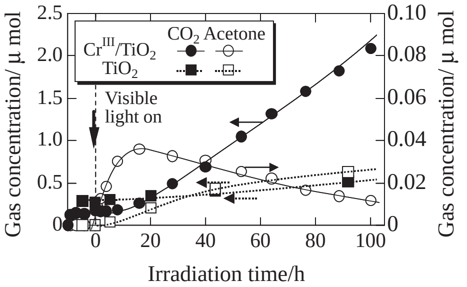

Figure 3. Changes in acetone and CO$_2$ concentrations as functions of time in the presence of Cr^{III}/TiO$_2$ and TiO$_2$ photocatalysts under visible-light irradiation.

from Cr^{III} to the C.B. of TiO$_2$ (See S.I. 2).[12]

Figure 3 represents the changes in concentration of acetone and CO$_2$ evolved as functions of time in the presence of Cr^{III}/TiO$_2$ and bare TiO$_2$ photocatalysts under visible-light irradiation. In the presence of Cr^{III}/TiO$_2$, soon after irradiating, acetone was produced. The acetone concentration initially increased and then began to decrease. This decrease was accompanied by the production of CO$_2$. This phenomenon is plausible considering that 2-propanol decomposes into the final product CO$_2$ via an intermediate product, acetone.[11] Moreover, it is feasible that this photocatalyst under visible-light irradiation can completely decompose 2-propanol into the final product CO$_2$. Note that acetone is the intermediate product, and thus the apparently detected acetone and CO$_2$ amounts were not stoichiometrically balanced. Using a previously reported method,[4a] we calculated the quantum efficiency (*QE*) for CO$_2$ generation to be 1.7% (See S.I. 3).[12] Even with bare TiO$_2$, both acetone and small amount of CO$_2$ were detected. This is because the optical filters did not cut off the shorter wavelength of light (<413 nm) completely that activates rutile TiO$_2$. It is clear that the production of CO$_2$ as the final product was much larger in the presence of Cr^{III}/TiO$_2$ than those of bare TiO$_2$. Thus, it could be considered that the visible light sensitivity generated only after Cr^{III} was grafted onto TiO$_2$ (See S.I. 3).[12]

Figure 2B explains the possible photosensitization mechanism of Cr^{III}/TiO$_2$. Visible light initiates the pseudo-MMCT, i.e., the electron in Cr^{III} is directly injected into the C.B. of TiO$_2$ (Ti^{IV}), which forms Cr^{IV}. The injected electrons in the C.B. reduce the adsorbed oxygen molecules and, thus, are consumed.[7b] The produced Cr^{IV} may oxidize 2-propanol and return back to Cr^{III} (See S.I. 4, 5).[12] We confirmed that the turnover number of the reaction exceeded four, indicating that this system functioned catalytically (See S.I. 3).[12]

Not shown here, but Cr^{III}/ZrO$_2$ could also decompose 2-propanol producing both acetone and CO$_2$, when the pseudo-MMCT band was excited (340–410 nm light, See S.I. 1, 3).[12] The photosensitization of Cr^{III}/ZrO$_2$ can be explained by the same mechanism as Cr^{III}/TiO$_2$.

In summary, we demonstrated that TiO$_2$ grafted with Cr^{III} ions became a novel type of stable photocatalyst, which can efficiently decompose 2-propanol into CO$_2$ via acetone under visible-light irradiation. We expect that a more dispersed grafting on a TiO$_2$ surface with Cr^{III} will greatly enhance the efficiency. In addition, there are candidate materials for this system. For example, Ce^{III} (Ce^{IV}/Ce^{III}, $E^0 = 1.7\,\mathrm{V}$) may be a good candidate as the metal ion. Hence, we believe that the present results will open a new research direction for visible-light-sensitive photocatalysis.

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12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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