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Enhancement of the Photocatalytic Activity Under Visible-Light Irradiation over N-doped TiO_2 Modified by Platinum Chloride

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Abstract N-doped TiO_2 adsorbed platinum chloride ($PtCl_x$/N-TiO_2, x being an unidentified number) was found to show much higher photocatalytic activity than either N-TiO_2 or $PtCl_x/TiO_2$ for the decomposition of acetic acid into CO_2 and H_2O under Visible-light irradiation, while neither $PtCl_x/SiO_2$, $PtCl_x/Al_2O_3$ nor an aqueous solution of H_2PtCl_6 was active. An enhancement of the photo-activity on $PtCl_x$/N-TiO_2 has been proposed as a Z-scheme mechanism.

Keywords Visible light · Photocatalyst · N-doped TiO_2 · Platinum chloride

1 Introduction

In a few decades, TiO_2 photocatalysts have been extensively studied for environmental applications to reduce toxic agents in the polluted atmosphere or water [1–7]. However, TiO_2 (anatase) works as a photocatalyst only under UV-light (3.2–3.4 eV) irradiation. Several attempts have been made to realize photocatalysts that work under Visible-light irradiation. Anpo et al. have succeeded in the band gap narrowing of TiO_2 by the doping of such transition metal ions as V, Cr, Cu ions by an ion-implantation technique. These samples exhibited the photocatalytic decomposition of 2NO into N_2 and O_2 under Visible-light irradiation [8, 9]. Asahi et al. have reported that the doping of N atoms into TiO_2 causes a shoulder band in the visible region and these samples exhibited the photodegradation of methylene blue or gaseous acetaldehyde, and hydrophilicity properties of the film surface [10]. In another application, Kisch et al. have reported that the incorporation of a few weight percentages of transition-metal chlorides ($PtCl_4$, $RhCl_3$, $AuCl_3$, $PdCl_3$, etc.) in the bulk of amorphous titanium dioxide led to visible light-induced reactions such as the photomineralization of 4-chlorophenol [11–15]. Also, Morikawa et al. reported that photocatalytic decomposition of acetaldehyde in the gas phase was enhanced on N-TiO_2 by loading with copper ions under Visible-light irradiation [16].

Here, we report on a drastic enhancement of the photocatalytic activity of N-doped TiO_2 modified by platinum chloride ($PtCl_x$/N-TiO_2) for the decomposition of acetic acid in a liquid phase under both visible-light and UV-light irradiation, and have proposed a possible mechanism for this photocatalytic reaction.

2 Experimental Details

2.1 Materials

The N-doped TiO_2 materials were prepared by the hydrolysis of 35 mL of tetra-isopropyl titanate (TiPOT) with 100 mL of an ammonium aqueous solution (28–30 wt% as NH_3) at room temperature under vigorous stirring. In fact, the temperature of solution is 10–15 °C since the reaction is endothermic under hydrolysis. The products were washed several times with distilled water, recovered by

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filtration, dried at 343 K for 12 h, calcined at 673 K for 3 h in air and then labeled N-TiO_2. Commercial TiO_2 (Degussa P-25) was used for comparison. N-TiO_2 and TiO_2 were modified by adsorption of platinum chloride complex from an aqueous solution of 0.01 M H_2PtCl_6 at room temperature in dark. The solid products were washed several times with distilled water, recovered by filtration, dried at 343 K for 12 h, then the Pt-loaded N-TiO_2 and TiO_2 were labeled $PtCl_x$/N-TiO_2 and $PtCl_x/TiO_2$, respectively. Here, x and y are an unidentified number. In the same manner, N-TiO_2 was modified from an aqueous solution of $PtCl_4$ and labeled $PtCl_y$/N-TiO_2. The amount of Pt loadings for the sample was determined by atomic absorption spectroscopy. The flatband potentials of the samples were measured by the Motto-Schottky plots in an aqueous solution of 0.5 M acetic acid using a potentiostat (HZ3000, Hokuto Denko). Working electrodes were prepared by casting a suspension of samples in water onto the ITO-glass (10 Ω cm^{-2}) and drying at 343 K for 1 h.

2.2 Sample Characterizations

The morphology of the samples was observed by SEM (JEOL JSM-840A). The powder X-ray diffraction (XRD) patterns were obtained with a RIGAKU RINT2000 using Cu K_α radiation ($\lambda = (1.5417$ Å) in a scan range of 20–60° and scan speed of 2 min^{-1}. The UV–Vis spectroscopic measurements on diffuse reflectance mode were carried out using a spectrophotometer, UV-2200A. The collected data were transformed into Kubelka-Munk function. The atomic composition of samples was analyzed with XPS (KRATOS, AXIS Ultra) with and without sputtering by Ar for 60 s before analysis. Radical species involved in samples were detected by ESR (JES-RE1X).

2.3 Photocatalytic Reactions

Photocatalytic tests of samples were carried out in the pyrex tube (20 mL) involving an aqueous solution of 0.5 M acetic acid (10 mL) purged by O_2 in the gas phase at room temperature. Photo-irradiation was carried out using a 500 W xenon lamp (Ushio Inc.) through different low cut-off filters (Asahi Technoglass Co. Ltd.). The products were analyzed by a gas chromatograph equipped with a thermal conductivity detector (TCD) for analysis of CO_2. In the blank test, photo-irradiation of the samples in distilled water led to the formation of small amounts of CO_2, probably due to the residual carbon source in the samples. It was confirmed that no decomposition of acetic acid proceeded under UV irradiation without any catalysts in the system. These results were evaluated after subtraction of the CO_2 yields of a blank test from those by the photo-induced decomposition of acetic acid.

3 Results and Discussion

XRD analysis showed that the prepared N-TiO_2 and $PtCl_x$/N-TiO_2 consist of anatase structures and no other phase was observed. SEM micrograph showed them to have a porous morphology. XPS analysis of N-TiO_2 and $PtCl_x$/N-TiO_2 showed an N-1s peak at 397–400 eV, which is assignable to adsorbed nitrogen compounds such as NO_x [17] or NH_x [18]. The quantity of N atoms on N-TiO_2 and $PtCl_x$/N-TiO_2 were roughly estimated to be 0.34 and 0.29 at%, respectively. Thus, N-TiO_2 prepared by hydrolysis involves low quantity of N after calcinations at 673 K$\sim$, as reported by Sato et al. [19]. Alternatively, ESR analysis showed that a signal due to NO_2^{2-} species was observed both on N-TiO_2 and on $PtCl_x$/N-TiO_2. It was confirmed that they involve nitrogen, partially in the form of NO_2^{2-}. Also, it was observed that $PtCl_x$/N-TiO_2 involves platinum (+IV) ions mainly, and chloride anions by XPS.

N-TiO_2 (pale yellow) prepared by thermal treatment at 673 K for 3 h exhibits a band gap at around 3.1 eV together with a shoulder band gap at 2.3 $\sim$ 2.4 eV, as shown in Fig. 1. This shoulder band in Visible-light regions cannot be observed in pure TiO_2 and is similar to previous findings [10]. Ihara et al. have previously suggested that N-doped TiO_2 powder involves not only nitrogen atoms but also oxygen vacancies, with energy levels slightly below the conduction band edge of TiO_2, which may be responsible for the visible-light responses [20]. Furthermore, $PtCl_x$/N-TiO_2 exhibits an absorption band at around 2.3 $\sim$ 2.4 eV, which can be superimposed on the absorption bands of N-TiO_2 and aqueous solutions of H_2PtCl_6 and $PtCl_4$ (Inset

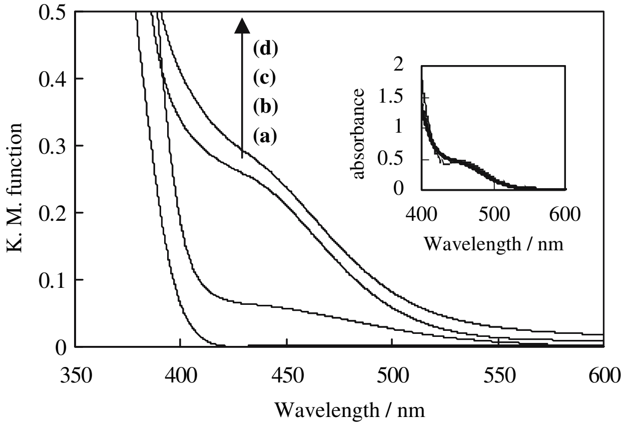

Fig. 1 Diffuse reflectance spectra of (a) TiO_2, (b) $PtCl_x/TiO_2$ (0.7 wt% as Pt), (c) N-TiO_2 and (d) $PtCl_x$/N-TiO_2 (0.8 wt% as Pt). Inset shows the absorbance of aqueous solutions of 0.01 M H_2PtCl_6 and $PtCl_4$

of Fig. 1). The HOMO-LUMO gap was estimated to be $E_g = 2.3 \sim 2.4$ eV for the aqueous solutions of H_2PtCl_6 or $PtCl_4$. It is known that an aqueous solution of H_2PtCl_6 forms $H_2[PtCl_4(OH)_2]\ 3H_2O$, however, the structure of the platinum chloride adsorbed on N-TiO_2 is still under investigation.

The yields of CO_2 for the photo-induced decomposition of acetic acid in the presence of O_2 on various samples are shown in Fig. 2. The N-TiO_2, $PtCl_x$/N-TiO_2 and $PtCl_y$/N-TiO_2 show photo-activity under Visible-light irradiation ($\lambda > 420$ nm) and, among these, $PtCl_x$/N-TiO_2 shows the highest photocatalytic activity. Under air, $PtCl_x$/N-TiO_2 retained its pale yellow color for 24 h under photo-irradiation in an acetic acid solution, while in the absence of O_2, small amount of CO_2 for photo-degradation was observed on $PtCl_x$/N-TiO_2, its color turning from yellow to gray, indicating that an electron transfer took place from the N-TiO_2 to $PtCl_x$, probably to form Pt metal particles. On the other hand, platinum chloride supported on SiO_2 or Al_2O_3 ($PtCl_x/SiO_2$, $PtCl_x/Al_2O_3$) or aqueous solutions of H_2PtCl_6 or $PtCl_4$ by themselves were inactive for photo-reactions (not shown) under both UV and Visible-light irradiation. These results indicate that the photo-induced electrons and holes themselves on $PtCl_x$ do not directly participate in the photocatalytic reaction and that the surface of N-TiO_2 plays a major role in charge separations.

N-TiO_2 shows photocatalytic activity for the decomposition of acetic acid to form CO_2 with a linearity against the photo-irradiation time under Visible-light irradiation ($\lambda > 420$ nm), while no products were observed in the dark, as shown in Fig. 3. Furthermore, $PtCl_x$/N-TiO_2 showed 7 times higher photocatalytic activity than N-TiO_2. The turnover numbers (TONs), defined as the number of acetic acid molecules consumed per number of platinum ions, were estimated to be about 4 on $PtCl_x$/N-TiO_2 (0.8 wt% as Pt) within 6 h under Visible-light irradiation ($\lambda > 420$ nm).

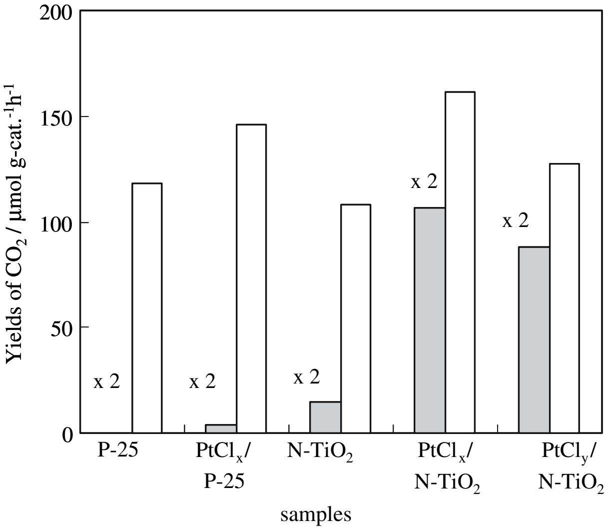

Fig. 2 Yields of CO_2 for the photo-induced decomposition of acetic acid under $\lambda > 420$ nm (gray bar: magnified 2 times) and under $\lambda > 320$ nm (white bar) on various samples

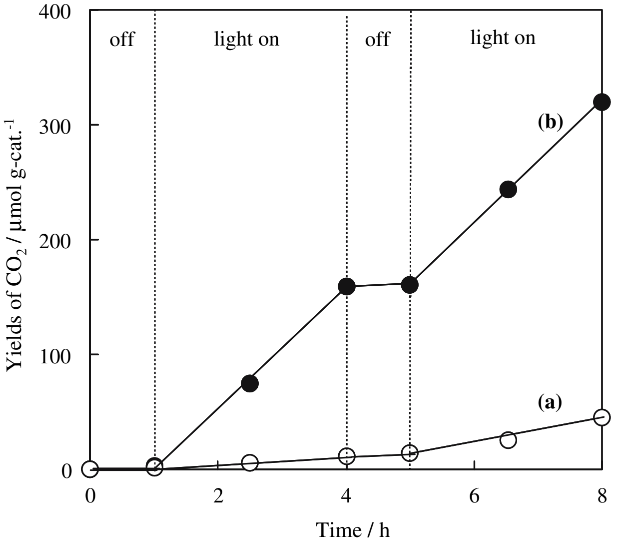

Fig. 3 Reaction time profiles for the photocatalytic decomposition of acetic acid on (a) N-TiO_2 and (b) $PtCl_x$/N-TiO_2 (0.8 wt% as Pt) photocatalysts under $\lambda > 420$ nm

The dependence of CO_2 yields on the photo-irradiation using cut-off filters are shown in Fig. 4. It was observed that the photo-response of N-TiO_2 and $PtCl_x$/N-TiO_2 is extended towards $2.3 \sim 2.4$ eV, and $PtCl_x$/N-TiO_2 exhibits higher reactivity than N-TiO_2 under both visible-light and UV-light irradiation.

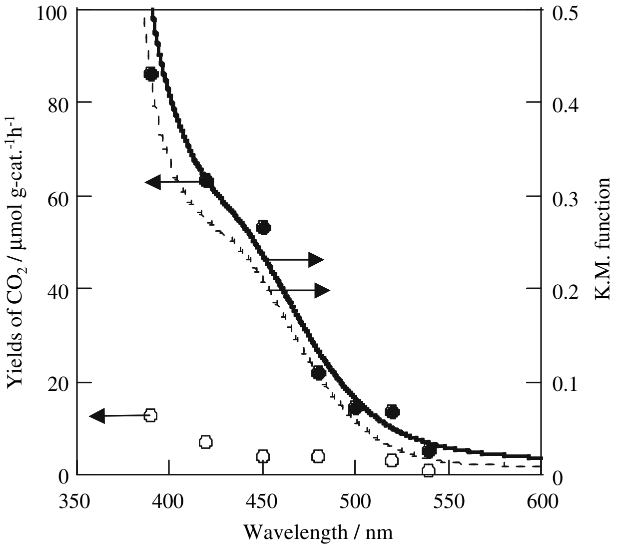

Fig. 4 Dependence of CO_2 yields on the photo-irradiation through different low cut-off filters, and the diffuse reflectance spectra for N-TiO_2 (○, dotted line) and $PtCl_x$/N-TiO_2 (●, solid line: 0.8 wt% as Pt). Each yield of CO_2 was plotted at the wavelength which can transmit by ca. 50% through low cut-off filters

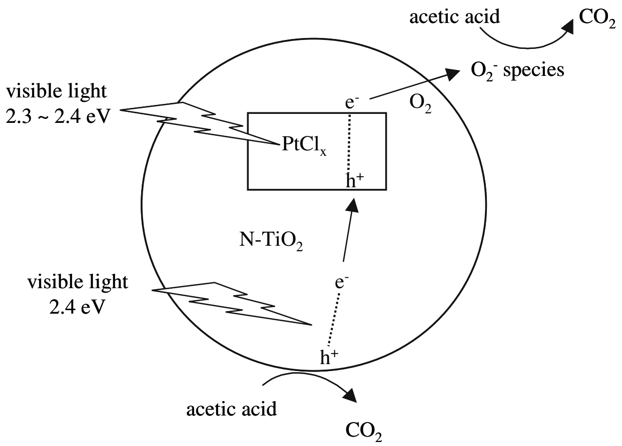

Fig. 5 Tentative reaction mechanism for the photocatalytic decomposition of acetic acid on $PtCl_x/N\text{-}TiO_2$ under Visible-light irradiation

Kisch et al. have proposed a reaction mechanism for the degradation of 4-chlorophenol, i.e., a photo-induced electron transfer takes place from Cl^- to Pt^{4+} on $PtCl_4/TiO_2$ under Visible-light irradiation so that the photo-formed chlorine atoms oxidize the substrate, while the photo-formed electrons trapped in the TiO_2 matrix induces the reduction of oxygen to form super oxide anion radicals, O_2^- species, followed by the oxidation of the substrate [11]. In our system, a schematic diagram of the photo-induced charge separation on $PtCl_x/N\text{-}TiO_2$ has been proposed in Fig. 5. Charge separation of the photo-induced holes and electrons ($h^+ \cdots e^-$) was seen to take place on $PtCl_x/N\text{-}TiO_2$ by double excitation of both $N\text{-}TiO_2$ and $PtCl_x$ under Visible-light irradiation. The photo-induced holes on $N\text{-}TiO_2$ can oxidize the acetic acid and electrons were scavenged by the holes on $PtCl_x$ as an electron acceptor. Judging from the flatband potential of $PtCl_x/N\text{-}TiO_2$ at -0.18 V vs. NHE and the redox potential of O_2/O_2^- couple at -0.16 V vs. NHE [21], the photo-induced electrons on the surface of $PtCl_x/N\text{-}TiO_2$ transfer to form O_2^- species, leading to the multi-step reactions. Thus, the mechanism for the photocatalytic decomposition of acetic acid on $PtCl_x/N\text{-}TiO_2$ under Visible-light irradiation could be proposed as a Z-scheme reaction.

4 Conclusions

It was found that a simply prepared $N\text{-}TiO_2$ works as an efficient photocatalyst under visible-light irradiation. Moreover, an enhancement of the photocatalytic activity was achieved when $N\text{-}TiO_2$ was modified by the adsorption of platinum chloride ($PtCl_x/N\text{-}TiO_2$). These materials show promise for applications in various photocatalytic systems.

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