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Structural defects cause TiO_2-based photocatalysts to be active in visible light

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Oxidation of TiO or Ti_2O_3 led to the formation of TiO_2 with activity in visible light much higher than when TiN was used as a precursor, pointing out the importance of oxygen defects/vacancies for extension of activity of TiO_2 into the visible region.

One of the most promising ways to destroy toxic organic compounds is their photocatalytic oxidation over TiO_2.[1,2] Though this process can occur in air at room temperature, the necessity of ultraviolet light presents a serious limitation. Recently a number of approaches have been undertaken to extend activity of TiO_2 into the visible range. In a series of publications[3] Anpo and co-workers have demonstrated that vacuum implantation of certain metal ions lowers the TiO_2 bandgap and renders the samples photoactive in the visible range. There is a growing number of publications reporting beneficial influence of substitution of oxygen in TiO_2 by nonmetals such as nitrogen,[4–7] carbon,[8,9] sulfur,[10] and boron[11] on bringing activity of the photocatalysts into the visible range. Perhaps the simplest method of preparation of a nonmetal-doped TiO_2 is a partial oxidative annealing of the corresponding precursor successfully exploited earlier for TiC[12,13] and TiS_2.[14] In the current work, for the development of this approach, four different titanium compounds namely, TiC, TiN, Ti_2O_3, and TiO were used as starting materials for the preparation of TiO_2. A widely known material, TiO_2 P25 from Degussa was treated in the similar way and considered as a reference.

Oxidative annealing of all materials except TiO_2 P25 created powders of light yellow color with slightly different tints. TiO_2 rutile was the only crystalline phase observed by XRD for the final materials (see Table 1). Surprisingly, diffuse-reflectance spectra of the powders (Fig. 1) prepared from TiC, TiN, Ti_2O_3, and TiO were qualitatively similar showing unstructured tails extending up to ca. 650 nm. Practically no absorption in the visible range was created when TiO_2 P25 was used as a starting material.

The bandgap of TiO_2 made from TiO_2 P25 was *ca.* 3.04 eV, close to the values reported earlier. However, oxidative annealing of other precursors resulted in TiO_2 with lower bandgaps (Table 1). Variation of the unit cell parameters noticed earlier for boron-doped TiO_2[11] is an interesting feature that we find to be precursor dependent (Table 1).

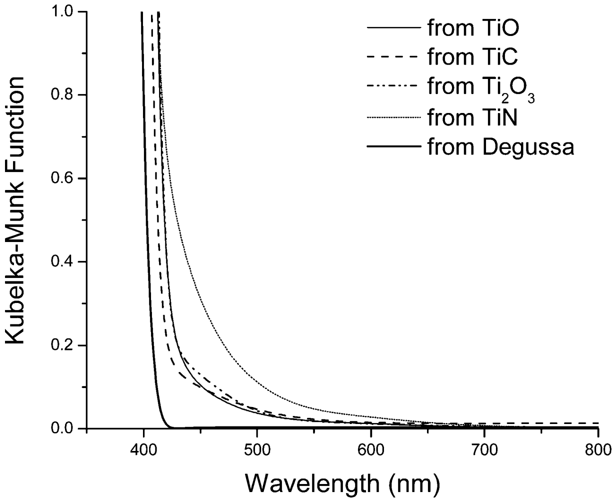

Fig. 1 Visible part of optical spectra of the titanium dioxides prepared from different precursors.

A typical indoor air pollutant, acetaldehyde, was chosen as a probe molecule for testing photoactivity of the samples in visible light. Powdered samples (about 200 mg) of the catalysts were placed in an air filled static reactor. The temperatures for all the experiments were carried out at 25 °C. The reactor was closed after the introduction of gaseous acetaldehyde (2 mM). The samples were illuminated with a 1000 W high pressure Hg lamp. Appropriate cut off filters were used to produce a monochromatic light of wavelength 546 nm. Gaseous samples (10 μl) were extracted and analyzed by GC-MS (Gas Chromatograph equipped with a mass selective detector GCMS-QP5000 from Shimadzu) to follow the concentration of the reactant and the products. Samples of TiO_2 made from TiC and TiN demonstrated predictable activity (Fig. 2). Production of CO_2 over TiO_2 prepared from TiO_2 P25 was small but real, while no activity at all was observed in visible light ($\lambda > 420$ nm) for original TiO_2 Degussa P25. Intriguingly, the TiO_2 made from Ti_2O_3 was also active, whereas TiO_2 made from TiO was more than four times as active as TiO_2 from TiN.

What makes TiO_2 prepared from Ti_2O_3 and from TiO active in visible light? Treatment of stoichiometric TiO_2 with a hydrogen plasma was described earlier as an efficient way to extend TiO_2 activity into the visible region.[15] Since, additionally, the treatment of modified materials in air at a temperature as low as 400 °C rendered them inactive, the surface or subsurface centers were likely involved. Formation of $[O^{-}\cdot O_2]$[16] and photoadsorption of hydrogen and methane[17] upon subbandgap illumination were

Table 1

Starting compound	Treatment (temperature/time/atmosphere)	Material after oxidative annealing[a]	Crystalline form[a]	Surface area/$m^2\ g^{-1}$[b]	Bandgap/eV[c]	Unit cell volume/Å^3[d]
TiC (Aldrich)	800 °C/2 h/air	TiO_2	Rutile	3.8	2.95	62.406(1)
TiN (Aldrich)	800 °C/2 h/air	TiO_2	Rutile	2.5	2.94	62.359(2)
Ti_2O_3 (Aldrich)	800 °C/2 h/air	TiO_2	Rutile	1.4	2.9	62.312(3)
TiO (Aldrich)	800 °C/2 h/air	TiO_2	Rutile	1.7	2.9	62.436(2)
TiO_2 P25 (Degussa)	800 °C/2 h/air	TiO_2	Rutile	11.6	3.04	62.355(2)

[a] XRD data. [b] Obtained from nitrogen adsorption isotherms with BET method. [c] Determined from UV-Vis spectra as in ref. 17. [d] XRD data, margin error is given in parentheses.

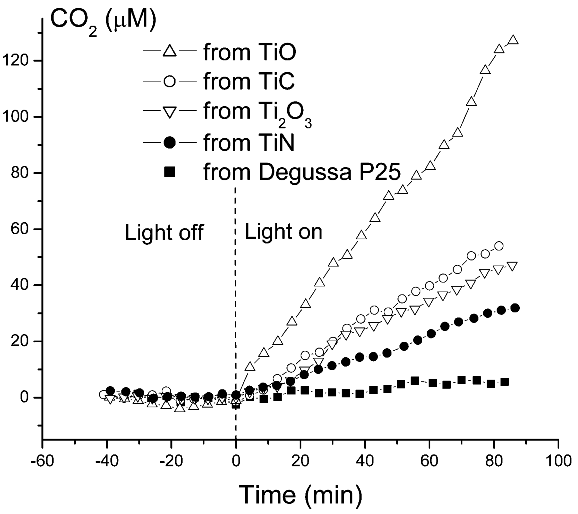

Fig. 2 Influence of the precursors on photoactivity of TiO_2 in the reaction of acetaldehyde oxidation in air under visible light ($\lambda = 546$ nm, green to the eye; 7.4×10^{16} photon s^{-1} cm^{-2}) at 25 °C. Initial gas phase acetaldehyde concentration is *ca.* 2 mM, initial concentration of carbon dioxide fitted to zero. Corresponding consumption of acetaldehyde and production of acetic acid are not shown for the sake of clarity.

studied earlier and attributed to the photoresponse of TiO_2 surface centers as well.

In our case, bulk rather than surface oxygen vacancies can be expected to form. Indeed, it seems natural to assume that high temperature treatment of Ti_2O_3 and TiO precursors in air results in their oxidation. However, due to large crystallite sizes, the oxidation process does not go to completion (does not reach equilibrium), thus leaving oxygen vacancies deep inside titanium dioxide. It is likely then that so formed bulk oxygen defects can successfully serve as color centers creating absorption and more importantly making TiO_2 active in visible light.

Observation of visible light activity of the TiO_2 from Ti_2O_3 and TiO raises the possibility that residual carbon or nitrogen in TiO_2 (prepared by oxidation of TiC or TiN), is simply eliminated to yield oxygen vacancies, and it is these vacancies that led to visible light photoactivity. As for now, no conclusive evidence can be provided; our observation would be consistent with the recent results by Yates and co-workers who found that success in extending activity of TiO_2 into the visible range depends on the source of nitrogen employed for doping. In particular, they found that treatment of TiO_2 by easily oxidized NH_3 extends activity into the visible range[18] as reported earlier, whereas incorporation N^- in TiO_2 has just the opposite effect, increasing the bandgap of the photocatalyst.[19]

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