Photocatalysis

Efficient Photocatalytic Decomposition of Organic Contaminants over $CaBi_2O_4$ under Visible-Light Irradiation**

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Photocatalysis is a "green" technology for the treatment of all kinds of contaminants, especially for the removal of organic contaminants with solar energy,[1] which mainly includes oxidative decomposition of the volatile organic compounds (VOC) and purification of waste water.[2–10] Photocatalysis has many advantages over other treatment methods, for instance, the use of the environmentally friendly oxidant O_2, the reaction is performed at room temperature, and oxidation of the organics compounds, even at low concentrations.[3,5] To date, TiO_2 has undoubtedly proven to be the most excellent photocatalyst for the oxidative decomposition of many organic compounds under UV irradiation.[4–6,8] However, the relatively wide band gap of 3.2 eV limits further application of the material in the visible-light region ($\lambda > 400$ nm).[7] In view of the efficient utilization of visible light, the largest proportion of the solar spectrum and artificial light sources, the development of a photocatalyst with high activity under a wide range of visible-light irradiation is indispensable.

There are two ways to exploit the photocatalysts responsive to visible-light irradiation: The first involves the modification of TiO_2, the second is the development of a new material. The former has been largely investigated by doping or ion-implanting methods to effect photocatalysis under visible-light irradiation.[2,5,6,9–11] Recent work by Asahi et al. and Kisch et al. is representative of a few successful examples.[2,9] On the other hand, there have only been a few reports on the development of new materials.

We have reported the synthesis of several visible-light-sensitized photocatalytic materials to effect the efficient utilization of solar energy.[12] Herein, we report a novel photocatalyst, $CaBi_2O_4$, which is active in the photocatalytic oxidative decomposition of organic contaminants under visible-light irradiation. Acetaldehyde is known as a key indoor air pollutant and is also largely formed as an intermediate during photocatalytic oxidation of other organic compounds, ranging from alkanes to alcohols. Methylene blue (MB) is a representative of organic dyes in textile effluents. These two organic compounds are often considered as model contaminants in the photocatalytic decomposition of VOC and in the purification of dye waste water, respectively.[2–6,8,10] In the work described herein, they were also selected as model contaminants. The photocatalytic activities of $CaBi_2O_4$ for the decomposition of acetaldehyde and MB were investigated in turn under visible-light irradiation for the same sample. In detail, the $CaBi_2O_4$ photocatalyst was firstly used to decompose acetaldehyde under gaseous phase conditions; the used oxide was then collected and employed again to degrade MB under liquid-phase conditions.

Figure 1 represents the photocatalytic decomposition (versus time) of acetaldehyde over $CaBi_2O_4$ under visible-light irradiation ($\lambda \geq 440$ nm). CO_2 is the final product in the photocatalytic oxidation of organic contaminants.[5] The yield of CO_2, the formed CO_2 divided by the theoretical value of CO_2 for which 100% of the organic compounds would be converted, was used to evaluate the activity of the photocatalyst in the work described herein. It is amazing that 65% of acetaldehyde was photocatalytically oxidized to CO_2 after irradiation for 20 min with visible light over $CaBi_2O_4$. With increasing irradiation time, the conversion of acetaldehyde into CO_2 increased. After irradiation for 2 h, the detected CO_2 yield reached a stable value, 80%. The concentration of acetaldehyde in the reaction system also decreased from the initial 837 ppm to 0 ppm. There seemed to be a discrepancy (~20%) between the acetaldehyde conversion and CO_2 yield. Similar phenomena were also reported in the catalytic decomposition of acetaldehyde over a TiO_2-based photocatalysts under UV irradiation.[6] Possible reasons include: 1) adsorption of intermediates such as formic acid, etc. and

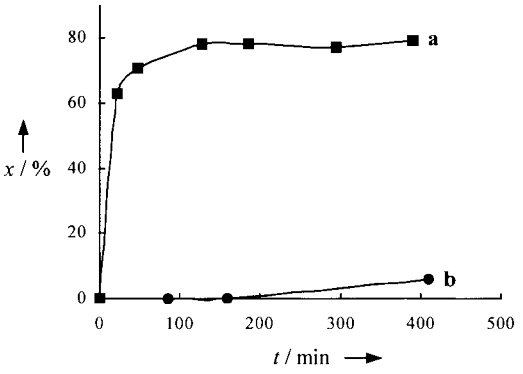

Figure 1. Conversion of acetaldehyde into CO_2 (x) as a function of irradiation time (t) under visible light ($\lambda \geq 440$ nm). a) $CaBi_2O_4$ photocatalyst; b) TiO_2 photocatalyst.

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deposition of coke-like substances,[4d,6] 2) balance adsorption of formed CO_2 in a closed-cycle system. We checked the products of the photocatalytic reaction and did not find the coke-like substances formed on the surface of $CaBi_2O_4$ after the reaction. Therefore, some intermediates (such as acetic acid, etc.) were possibly formed. These intermediates and some CO_2 were absorbed onto the surface of the photocatalyst and the reaction system. We also confirmed a little amount of CO_2 evolution when heating the photocatalyst in the presence of O_2 after the photocatalytic reaction.

By comparison, acetaldehyde decomposition over TiO_2 was also carried out under the same conditions (Figure 1). The results indicated that TiO_2 was inactive, as reported by Asahi et al.[2] The following experiments were also performed: 1) a dark experiment (without irradiation), 2) blank experiment (in the absence of the photocatalyst), 3) in the absence of oxidant O_2. In any case, CO_2 was hardly detected. Thus it is noteworthy that light irradiation, $CaBi_2O_4$ photocatalyst, and molecular O_2 are all indispensable for the catalytic degradation of acetaldehyde.

The wavelength dependence of the photocatalytic reaction is used to prove if the reaction is really driven by light irradiation.[2,12b,13] The wavelength dependence of acetaldehyde decomposition was investigated with cut-off filters of different wavelengths, and the results are shown in Figure 2.

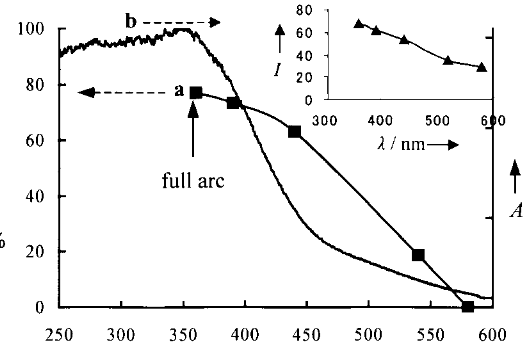

Figure 2. a) Wavelength (λ) dependence of yield of CO_2 (x) from the decomposition of acetaldehyde over $CaBi_2O_4$ upon irradiation with visible light (20 min); b) Relative absorbance (A) of $CaBi_2O_4$ photocatalyst. Insert: wavelength dependence of light intensity (I/mWcm^{-2}) with different cutoff filters.

The intensity variation of the irradiated light when using different cutoff filters is also included in the figure for reference. From Figure 2, clear activity with visible light of a wide range (up to 550 nm) was observed. The light-responsive range is wider than that reported by Asahi et al. for the $TiO_{2-x}N_x$ photocatalyst (500 nm).[2] It can be seen that the yield of CO_2 decreased with increasing wavelength of light, especially in the visible-light region, in good agreement with the optical properties of the photocatalyst as shown in Figure 2. The photocatalyst finally lost its activity when a cutoff of 580 nm (near the absorption edge) was used, although the intensity of the irradiated light at this wavelength was still as strong as 28 mWcm^{-2}. This indicates that the present catalytic reaction is driven by light and that the absorption property of the photocatalyst governs the reaction rate. In other words, the decomposition reaction of acetaldehyde into CO_2 over $CaBi_2O_4$ is a photocatalytic reaction.

Subsequently, the photocatalytic activity of $CaBi_2O_4$ was measured in a liquid medium. Figure 3 represents the variation of MB concentration with irradiation time over $CaBi_2O_4$. As a comparison, MB degradations over TiO_2 and MB photolysis were also performed under the same conditions and are shown in Figure 3. Wu, Zhao, and co-workers reported that many dyes could be degraded over TiO_2 based on the self-photosensitized process of dyes under visible-light irradiation.[7] However, a similar phenomenon was not observed in the degradation of MB over TiO_2 under visible-light irradiation (Figure 3), consistent with the results reported by Li and co-workers[4c] In contrast, the $CaBi_2O_4$ catalyst exhibited a high activity for MB degradation under visible light ($\lambda \geq 420$ nm), although the sample had been employed in the abovementioned photocatalytic acetaldehyde decomposition. The high activity of $CaBi_2O_4$ can also be confirmed from Figure 4, for which the colors of the solutions of MB before and after the photocatalytic reaction over $CaBi_2O_4$ are compared with that over TiO_2.

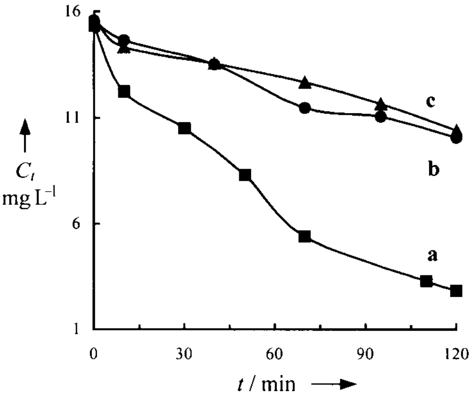

Figure 3. Concentration (C_t) of MB dye as a function of irradiation time (t) under visible light ($\lambda \geq 420$ nm). a) $CaBi_2O_4$ photocatalyst; b) TiO_2 photocatalyst; c) MB photolysis.

The photocatalytic oxidation of organic compounds in the presence of oxygen is mainly considered to be controlled by the following processes: 1) the photoelectron transition from the valence band (VB) to the conduction band (CB) of the semiconductor catalyst, 2) the oxidation of the organic compounds by the photohole in the VB or formed $OH^{\bullet}$ radical, 3) the reduction of oxygen by the photoelectron in the CB. Thus the photocatalytic activity of the semiconductor is closely related to its band structure. For the p-block metal-oxide semiconductor with a d^{10} configuration, the VB and CB are the 2p orbital of the oxygen atom and the lowest unoccupied molecular orbital (LUMO) of p-block metal

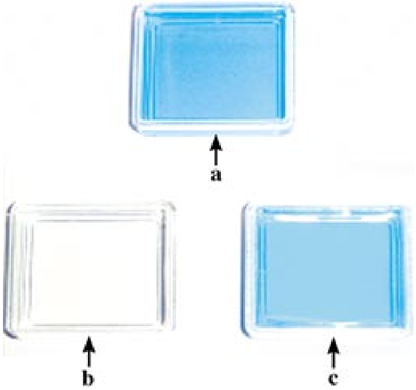

Figure 4. Pictures of solutions of MB: a) before photocatalytic degradation; b) after photocatalytic reaction (120 min) over $CaBi_2O_4$; c) after photocatalytic reaction (120 min) over TiO_2.

center, respectively.[14] For bismuth(III)-based semiconductors, it was also found that the Bi 6s and O 2p levels can form a preferable hybridized VB.[15] In terms of the above depiction, we assumed that the VB of $CaBi_2O_4$ is composed of hybridized Bi 6s and O 2p orbitals, whereas the CB is composed of Bi 6p orbitals, and these bands meet the potential requirements of organic oxidation. An active photocatalyst for the decomposition of the organic compounds must have a VB with strong oxidizing ability and photogenerated holes with high mobility. The hybridized VB of $CaBi_2O_4$ has shown strong oxidative ability in the work described herein. Meanwhile, the hybridization of the Bi 6s and O 2p levels makes the VB largely dispersed, which favors the mobility of photoholes in the VB[16] and is beneficial to the oxidation reaction.

The stability of a photocatalyst is important to its application; doped TiO_2 photocatalysts sometimes suffer from this problem.[2] After each photocatalytic degradation reaction of organic contaminants, the crystal structure of the $CaBi_2O_4$ photocatalyst was checked by X-ray diffraction (XRD) analysis. The analysis showed that $CaBi_2O_4$ belongs to a monoclinic crystal structure (space group: $I2/a$, $a = 1.4002$, $b = 1.1596$, $c = 1.2198$ nm, $\beta = 101.541°$).[17] XRD analysis of the sample also showed that the crystal structure of the photocatalyst was not changed after the photocatalytic reaction. The stability of the photocatalyst will be investigated further in more detail by other characterization methods. The BET (Brunauer–Emmett–Teller) measurement showed that the surface area of the $CaBi_2O_4$ photocatalyst was only $0.6\ m^2g^{-1}$, nearly 1% of the surface area of TiO_2. It is well known that the surface area of a catalyst greatly affects its catalytic activity.[18] The present method for the preparation of the material greatly limits the activity of the photocatalyst. Nano-sized photocatalysts are under investigation and are expected to increase significantly the surface area of the catalyst and therefore the photocatalytic activity.

In summary, the $CaBi_2O_4$ semiconductor was found to be a novel visible-light-driven photocatalyst for the degradation of various organic contaminants. The catalyst exhibits a high photocatalytic activity, not only in the decomposition of acetaldehyde, but also in the degradation of MB dye under wide-ranging visible light irradiation. Furthermore, its activity and crystal structure did not change after a series of continuous investigations under different experimental conditions. Furthermore, this work provides some insight into the design of new green heterogeneous photocatalysts for the degradation of organic contaminants.

Experimental Section

The $CaBi_2O_4$ photocatalyst was prepared by a simple soft chemical method. Stoichiometric amounts of $Ca(NO_3)_2{\cdot}4H_2O$ and $Bi(NO_3)_3{\cdot}5H_2O$ were dissolved in water. The composite was formed by adding a solution of ethylenediaminetetraacetic acid in ammonia and citric acid to the above aqueous solution. A xerogel was then prepared by ageing and drying the composite. The xerogel was calcined at 623 K for 10 h, and crystallized at 1073 K for 12 h in air. The crystal structure of the sample was determined by X-ray diffraction methods (JEOL JDX-3500 Tokyo, Japan). The UV/Vis diffuse reflectance spectrum of $CaBi_2O_4$ was measured on a UV/Vis spectrometer (UV-2500, Shimadzu). The surface area of the material was measured by BET measurements of nitrogen adsorption at 77 K (Micromeritics Automatic Surface Area Analyzer Gemini 2360, Shimadzu). TiO_2 (surface area $50\ m^2g^{-1}$) is commercially available and was used as a reference photocatalyst. The photocatalytic decompositions of acetaldehyde was performed with 1.0 g of the powdered photocatalyst placed at the bottom of a Pyrex glass cell at room temperature in a gas-closed system; the reaction gas mixture (0.5 atm) consisted of 837 ppm CH_3CHO, 21% O_2, and Ar balance gas. The photocatalytic degradation of MB was carried out with 0.3 g of the powdered photocatalyst suspended in a solution of MB ($15.3\ mg L^{-1}$, 100 mL), which was prepared by dissolving the MB powder in distilled water in a Pyrex glass cell at room temperature under air. The optical system for the catalytic reaction included a 300 W Xe arc lamp (focused through a shutter window), a cutoff filter (providing visible light of different wavelengths), and a water filter (to prevent IR irradiation). CO_2 and acetaldehyde were detected by GC (CO_2, GC-8A with TCD detector, Shimadzu; acetaldehyde and other organic substances, GC-14B with FID detector, Shimadzu). MB degradation was determined by UV/Vis spectroscopy (UV-2500, Shimadzu).

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