New Visible Light Active Photocatalyst, Carbon-coated $W_{18}O_{49}$

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Visible light active photocatalyst, carbon-coated $W_{18}O_{49}$, was prepared by the heat treatment of the powder mixtures of ammonium paratungstate with poly(vinyl alcohol) at a temperature of 800 °C for 1 h in Ar gas flow. From the measurements of the decomposition of methylene blue and phenol in water, carbon-coated $W_{18}O_{49}$ was shown to be active only under visible light.

Photocatalysts have been attracted attentions as one of promising advanced oxidation techniques of environment pollutants.[1] Anatase type titanium dioxide (TiO_2) has been exclusively studied on its preparation, modification and applications to get high performance,[2] even though it is active under ultraviolet (UV) irradiation. Since UV rays are contained only about 4% in solar light, many efforts have been devoted to develop photocatalysts activated under visible light. Doping of light elements, such as C, S, and N, and of different metal ions, such as Cr, Ni, etc., into TiO_2 was reported to give visible light activity.[3–8] Also, several semiconductive compounds, such as $BiNO_4$, $In_{1-x}Ni_xTaO_4$, and TaON, were found to be visible light active.[9–11] We developed successfully a new photocatalyst, carbon-coated $W_{18}O_{49}$, which is active under visible light.

Ammonium paratungstate $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$ (PAT) and poly(vinyl alcohol) (PVA) were mixed in equal mass ratio in aqueous solution at 60 °C and then dried to a powder mixture. This powder mixture was heat-treated at a temperature of 800 and 900 °C for 1 h in a flow of Ar. On the course of heating up to a high temperature, WO_3 formed by the pyrolysis of PAT was reduced to WO_2 through $W_{18}O_{49}$, as its XRD patterns shown in Figure 1. From reagent grade WO_3 powder, the reduced phase $W_{18}O_{49}$ without carbon coating was also prepared by heating in a flow of N_2 gas containing 3 vol % H_2. Heating rate up to programmed temperature was 5 °C/min and a flow rate of gases during heat treatment was 60 mL/min.

After 800 °C treatment, the substrate WO_3 was reduced by the reaction with coated carbon to form $W_{18}O_{49}$ and WO_2 (Figure 1a). The relative amount of WO_2 to $W_{18}O_{49}$ was increased by heating to 900 °C, reduction of tungsten oxides being proceeded (Figure 1b). The carbon formed in this process was supposed to be amorphous, this being the reason why no carbon detected in XRD patterns. A single phase of $W_{18}O_{49}$ was obtained by heating of WO_3 to 900 °C in H_2-containing N_2 gas, as shown in Figure 1c.

Decomposition of methylene blue ($C_{16}H_{18}N_3S$, MB) in the aqueous solution (initial concentration c_0 of 100 ppm) including the photocatalyst was followed by measuring the MB concentration c remained against the irradiation time of either visible light or UV rays at room temperature. The concentration c was evaluated from the absorbance at a wavelength of 664 nm in a UV–vis spectrum. The results under irradiation of either UV or visible light, together with that in the dark, are shown on the sample prepared at 800 °C (0.3 g in 300 mL MB solution) in Figure 2, where relative concentration of MB in the solution c/c_0 is plotted in logarithmic scale against time t. MB concentration decreases with increasing time in the dark, which is supposed to be due to adsorption of MB into carbon coated on the $W_{18}O_{49}$ surface. The carbon coated on ceramic particles through the same procedure as the present was shown to be porous.[12] Under UV irradiation with the strength of 900 μW/cm^2 (in the wave length range of 220–300 nm) at the surface of the solution, the concentration change was the same as that in the dark, suggesting that the sample is not UV active. Under visible light with the strength of 18 W/cm^2 (in the wave length range of 400–700 nm) from fluorescent lamp, where UV rays are cut off by using a filter, however, the change in MB concentration was much accelerated. The comparison among three curves, under visible light

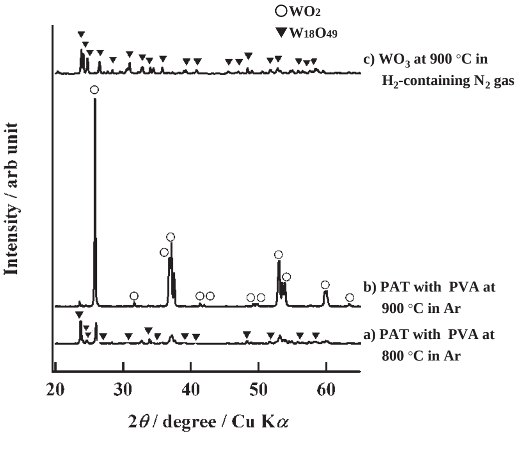

Figure 1. XRD patterns of the samples prepared.

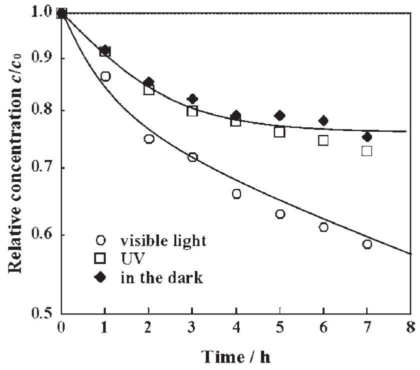

Figure 2. Changes in relative concentration of c/c_0 with time for carbon-coated $W_{18}O_{49}$ prepared at 800 °C under UV irradiation, under visible light irradiation and in the dark.

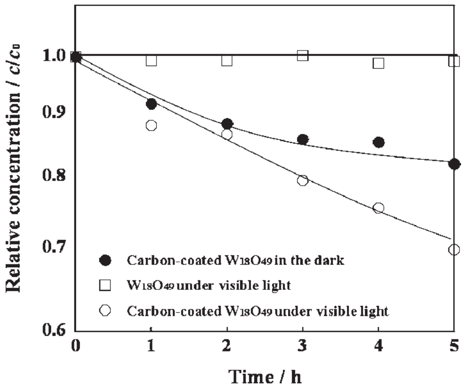

Figure 3. Changes in relative concentration of c/c_0 with time for $W_{18}O_{49}$ with carbon coating prepared at 800 °C and $W_{18}O_{49}$ without carbon coating under visible light irradiation and in the dark.

irradiation, UV rays irradiation and in the dark, demonstrates that the present carbon-coated $W_{18}O_{49}$ is visible light active, not active under UV rays.

On the same carbon-coated $W_{18}O_{49}$ and $W_{18}O_{49}$ without carbon coating, decomposition of phenol C_6H_6O in its aqueous solution (initial concentration c_0 of 10 ppm) was followed at room temperature under visible light from fluorescent lamp with cutting of UV part and also in the dark. The concentration c of phenol was determined by high performance liquid chromatography (HPLC) on an ODS-silica column with 30% MeOH/70% water of mobile phase. The results are shown in Figure 3 by plotting relative concentration c/c_0 in logarithmic scale against time t. Carbon-coated $W_{18}O_{49}$ shows relatively fast decrease in the concentration of phenol both under the irradiation of visible light and in the dark, but the former was much faster. In the solution irradiated by visible light for 7 h in the dispersion of carbon-coated $W_{18}O_{49}$ powder, some of oxidation products of phenol, hydroquinone, and catechol, were clearly detected. On the other hand, $W_{18}O_{49}$ without carbon coating does not show any change in concentration with time under the irradiation of visible light, revealing no adsorption and no photocatalytic activity.

Carbon-coated sample prepared at 900 °C, which consisted of large amount of WO_2 and a small amount of $W_{18}O_{49}$, was experimentally confirmed to be visible light active, much faster concentration decrease under visible light irradiation than in the dark, and not UV active. However, the activity for visible light was much smaller for the sample prepared at 900 °C than that at 800 °C, suggesting that $W_{18}O_{49}$ is responsible for the activity. This result suggests that the importance for $W_{18}O_{49}$ substrate to be coated by porous carbon in order to show noticeable activity under visible light. The increase in the concentration of pollutant around $W_{18}O_{49}$ particles through the adsorption by porous coated carbon seems to be essential. Carbon coated on photocatalysts may retard the process of electron–hole recombination, which may accelerate photodecomposition of pollutants.

WO_3 was reported to be visible light active,[13] but it was not applied practically, because of its relatively high solubility for water. We tentatively confirmed that no detectable dissolution of $W_{18}O_{49}$ from its carbon-coated particles into water was observed.

Previously, we reported that carbon-coated reduced phases of TiO_2, Ti_nO_{2n-1} ($3 \leq n \leq 9$), were prepared through the same procedure, i.e., heat treatment of rutile type TiO_2 with PVA in inert atmosphere at high temperatures and they have visible light activity.[14,15] These reduced phases of Ti_nO_{2n-1} previously reported and the present $W_{18}O_{49}$ have oxygen vacancies in ordered arrangement in the matrix. In the cases of visible light active TiO_2 reported before,[3–8] the dopants, as C, Cr, etc., are reasonably supposed to be associated with some lattice defects, probably oxygen vacancies, in disordered manor. The present results, therefore, may suggest that activity of these semiconductive oxides under visible light of some oxides is closely related to the presence of oxygen vacancies in the matrix lattice either in ordered or disordered arrangement.

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