Photocatalytic activity for methylene blue decomposition of $NaInO_2$ with a layered structure

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There is wide interest in the development of novel oxide semiconductor photocatalysts that are applicable to environmental purification and water splitting to generate clean energy hydrogen by light energy conversion [1–6]. Recently, $NaInX_2$ (X = O or S) compounds crystallizing in the α-$NaFeO_2$ layered-type structure have been reported as promising candidates for photocatalytic water splitting by Kudo *et al.* [7], Sato *et al.* [8] and Wang *et al.* [9]. Their special α-$NaFeO_2$ layered-type structures are considered to contribute to the efficient separation of the photoinduced electron-hole pairs. Further, these reports also imply that the $NaInX_2$ compounds are possibly effective photocatalysts for the degradation and mineralization of organic matters. In this letter, the photocatalytic activity for the methylene blue (MB, $C_{16}H_{18}N_3S$) decomposition of the $NaInO_2$ compound is evaluated in order to explore the possibility of the $NaInO_2$ compound acting as a photocatalyst, which can be applied for environmental purification.

Four kinds of $NaInO_2$ powders were used as photocatalysts in the present study. Firstly, the original $NaInO_2$ powders were synthesized through the solid-state reaction, from the stoichiometric amounts of In_2O_3 (99.9%, WAKO Chem., Japan) and Na_2CO_3 (99.5%, JUNSEI Chem., Japan) in an oxygen atmosphere [10]. A conventional RINT-2000 diffractometer with Cu K_α radiation ($\lambda = 1.54178$ Å) was used at room temperature for examining the crystal phase of the obtained $NaInO_2$ powders. The results, as shown in Fig. 1, revealed that the powders are pure and have an α-$NaFeO_2$ layered-type structure [11]. Secondly, surface modifications of the original $NaInO_2$ powders were conducted separately by loading three kinds of co-catalysts: NiO, RuO_2, and Pt [12, 13]. The 0.5 wt%-NiO and 0.5 wt%-RuO_2 co-catalysts were loaded from standard solutions of $Ni(NO_3)_2$ and $RuCl_3$, respectively, using the impregnation method. The 0.5 wt%-Pt co-catalyst was loaded using the photoplatinization method from a standard solution of H_2PtCl_6. Finally, the residues were dried at 38 °C, and subsequently heated at 500 °C for 2 hr in air.

The photocatalytic activities of the four kinds of $NaInO_2$ powders were evaluated by the decomposition of the MB aqueous solution [14] in a quartz cell, under the irradiation of a 27 W black light (SANKYO DENKI, FPL27BLB) with an intensity of about 13.63 mW cm^{-2}. The sample powders (0.075 g) were suspended in the MB aqueous solution (2.67×10^{-5} mmol dm^{-3}, 75 cm^3) using a magnetic stirrer. After the pipetted solution (6 cm^3) was subjected to centrifugation, the optical absorption spectrum of the supernatant (3 cm^3) was measured by a UV-Vis spectrophotometer (UV-2450, SHIMADZU). The MB decomposition was judged by the decrease in the absorbance of MB aqueous solution, at a wavelength of about 664 nm. Before the photocatalytic reactions were initiated, the adsorption capability of each of these four kinds of $NaInO_2$ powders was observed in the dark, over a period of 30 min. After the photocatalytic reactions were initiated, samplings were performed after the following irradiation times: 10, 20, 30, and 60 min.

Fig. 2 shows the absorbance variation in the UV-Vis absorption spectrum of the MB aqueous solution under dark and light irradiation, when the four samples of the original $NaInO_2$ (A), 0.5 wt%-NiO/$NaInO_2$ (B), 0.5 wt%-RuO_2/$NaInO_2$ (C), and 0.5 wt%-Pt/$NaInO_2$ (D) were individually used as photocatalysts. All the spectra were recorded from a wavelength range of 500 to 800 nm. The absorbance of the MB aqueous

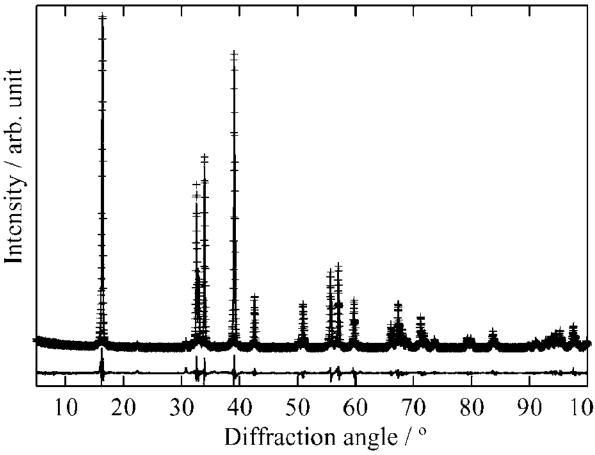

Figure 1 Powder X-ray diffraction patterns of the $NaInO_2$ compound synthesized in the present study (plus sign: observed; solid line: calculated; lower profile: difference between calculated and observed intensities). The result revealed that the sample is pure and crystallizes in the α-$NaFeO_2$ layered-type structure.

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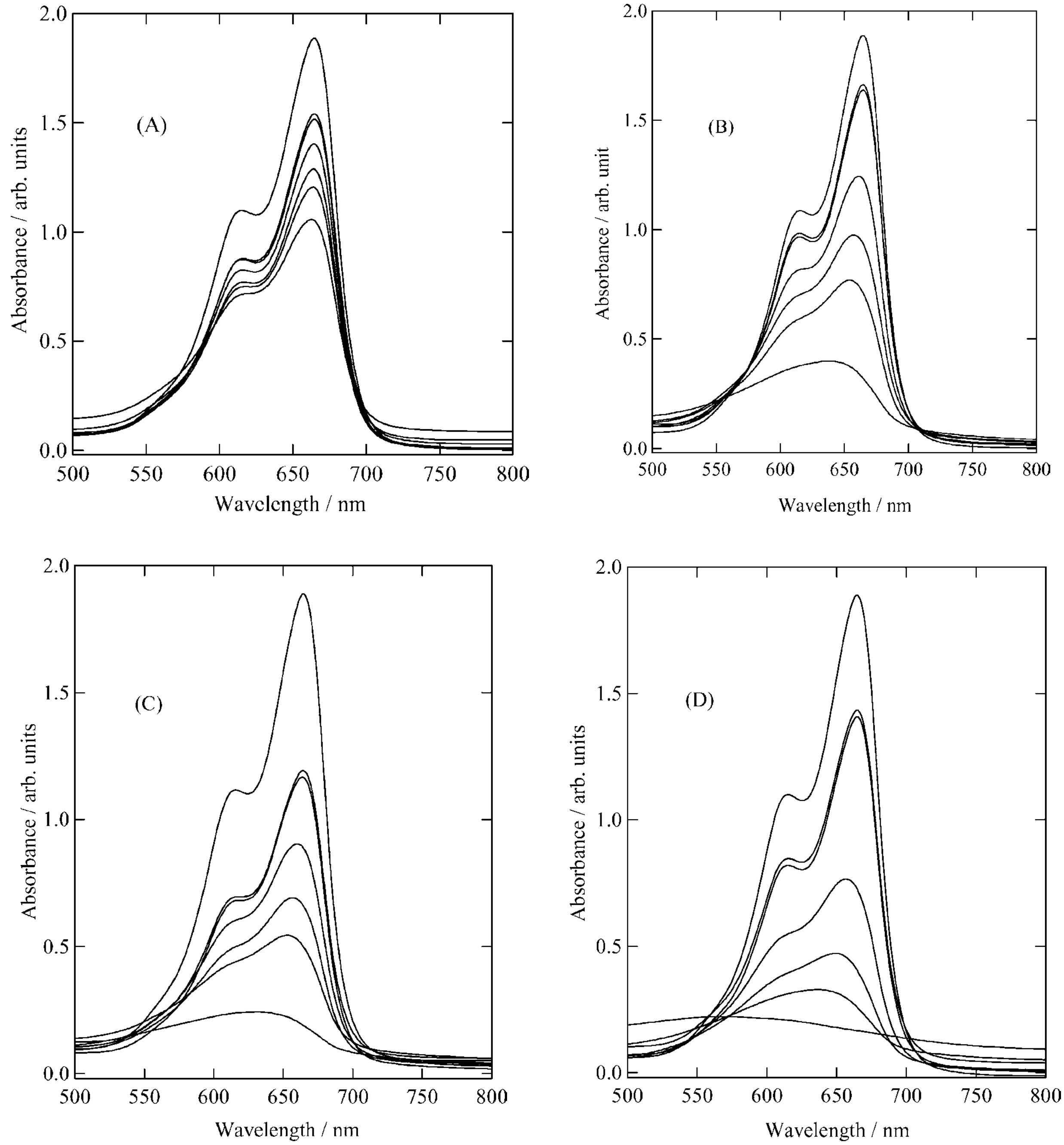

Figure 2 The absorbance variation in the UV-Vis absorption spectrum of MB aqueous solution (2.67×10^{-5} mmol dm^{-3}) under dark and light irradiation when the four kinds of powders of the original $NaInO_2$ (A), 0.5 wt%-NiO/$NaInO_2$ (B), 0.5 wt%-RuO_2/$NaInO_2$ (C), and 0.5 wt%-Pt/$NaInO_2$ (D) were used separately as photocatalysts (MB: 75 cm^3; photocatalyst: 0.1 g dm^{-3}; 27 W black light lamp; quartz cell). The absorption spectra were measured separately after the following times (from top to bottom): MB aqueous solution (2.67×10^{-5} mmol dm^{-3}, no photocatalyst); after 5 min of adding the photocatalyst; put in a darkroom after 30 min; light irradiation after 10, 20, 30, and 60 min.

solution in a wavelength of about 664 nm clearly decreased after the addition of photocatalyst powders. This indicates that all the photocatalyst powders have strong adsorption abilities in MB aqueous solution. It is observed that the adsorption ability of the RuO_2-loaded $NaInO_2$ powders is the strongest by comparing the difference between the absorbance of a blank solution (only MB, no photocatalyst) and the photocatalyst suspension. Furthermore, the adsorption of the photocatalyst powders in MB could be saturated within several minutes because no absorbance variation (a wavelength of about 664 nm) is observed in the UV-Vis absorption spectra, before and after the dark test (see Fig. 2A–D).

When the photocatalyst suspension was under light irradiation, the color gradually became light, and the absorbance at a wavelength of about 664 nm became weak, uninterrupted by four kinds of $NaInO_2$ photocatalysts. This indicated that the MB molecules in the photocatalyst suspension decomposed gradually under light irradiation. The photocatalytic activity for the MB decomposition of the $NaInO_2$ powders enhanced noticeably when each of the NiO, RuO_2, and Pt cocatalysts were loaded on its surface. Among these, the 0.5 wt%-Pt/$NaInO_2$ powders showed the maximum photocatalytic activity, and could decolorize the MB aqueous solution completely within 1 hr, under the above mentioned experimental conditions.

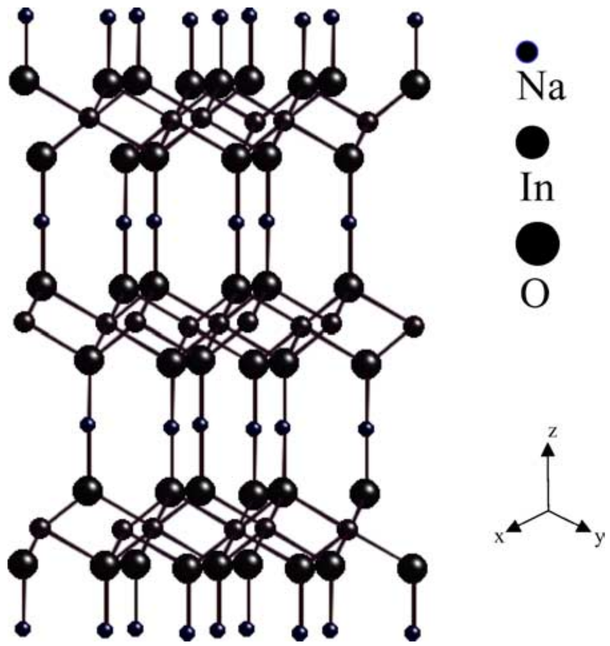

Figure 3 Scheme of the structural framework of the NaInO$_2$ compound with a special α-NaFeO$_2$ layered-type structure.

Matsushima and Kohiki [15] have reported that the conduction and valence bands of the NaInO$_2$ compound are primarily constructed from In-5s and O-2p orbits, respectively. At the same time, the O-2p orbits in the valence band strongly hybridize with the In-5s orbits. As mentioned earlier, the NaInO$_2$ compound has an α-NaFeO$_2$ layered-type structure. This crystal structure can be described as the alternate stacking of edge-shared $[\text{InO}_2]_\infty$ octahedral layers and Na layers perpendicular to the z-axis, as shown in Fig. 3 [16]. Each Na atom is coordinated linearly by two oxygen atoms. The special α-NaFeO$_2$ layered-type structure can be considered to efficiently prevent the photoinduced electron-hole pairs from recombining and contribute in moving them to the surface of NaInO$_2$ photocatalyst particles, as reported earlier for the photocatalytic water splitting over the NaInO$_2$ compound [7–9].

A plausible mechanism of the NaInO$_2$ photocatalysis can be illustrated by comparing it with a well-known semiconductor oxide TiO$_2$ photocatalyst [17]. The electron-hole pairs can be induced when the NaInO$_2$ particles are irradiated by light. The holes produced in the valence band can move to the surface of the NaInO$_2$ particles and react with hydroxyl ions (OH$^-$) or H$_2$O to yield ·OH radicals and protons. On the other hand, oxygen molecules dissolved in the MB aqueous solution can react with the electrons produced in the conduction band to yield superoxide radical anions ($O_2^{\cdot-}$), which can generate the hydroperoxy, ·OOH, radicals. The ·OH (or ·OOH) radicals have strong photooxidation abilities and decompose the MB molecules under light irradiation.

It is clear that the concentration of the ·OH (or ·OOH) radicals will affect the efficiency of MB decomposition by the semiconductor oxide NaInO$_2$-driven photocatalysis. In order to increase the concentration of the ·OH (or ·OOH) radicals, the recombination rate of the photoinduced electrons and holes needs to be reduced. The NiO$^-$, RuO$_2^-$, and Pt$^-$ loaded NaInO$_2$ powders have higher photocatalytic activity for the MB decomposition in comparison with that of the unloaded NaInO$_2$ powders. This is reasonable because the separation of the photoinduced electrons and holes became more efficient and then the recombination rate was reduced when the three kinds of co-catalysts were loaded on the surface of the NaInO$_2$ powders. In this situation, it can be considered that most of the photoinduced electrons generated by the band gap transition of the NaInO$_2$ compound, move to the co-catalysts NiO or RuO$_2$, similar to that in TiO$_2$-SnO$_2$ composite films, reported by Tada *et al.* [18], and the co-catalyst Pt cluster similar to that in Au/TiO$_2$ composite particles, reported by Wang *et al.* [19], where those electrons were reduced. The concentration of the holes left in the valence band of the NaInO$_2$ compound can be considered to increase, and subsequently, more holes can move to the surface of the NaInO$_2$ particles. The holes that produced larger amounts of ·OH radicals by the photooxidation of hydroxyl ions (OH$^-$) and/or chemisorbed H$_2$O exist on the NaInO$_2$ surface and, therefore, contribute to improving the efficiency of the photocatalytic MB decomposition over the NaInO$_2$ powders.

In conclusion, the MB aqueous solution can be decomposed photocatalytically over the NaInO$_2$ powders, under black light irradiation. The photocatalytic activity for MB decomposition of the NaInO$_2$ powders can be remarkably enhanced by depositing the noble metal Pt particles on its surface, and by coupling the other semiconductor oxides, NiO and RuO$_2$, with the NaInO$_2$ powders. The 0.5 wt%-Pt/NaInO$_2$ powders have the highest photocatalytic activity under the present experimental conditions, and can completely decolorize the MB aqueous solution (2.67×10^{-5} mmol dm^{-3}) within 1 hr. At the same time, the present study proved that the NaInO$_2$ compound, with a special α-NaFeO$_2$ layered-type structure, is also a promising photocatalyst for the purpose of environmental purification, such as decomposition of toxic organic matters, etc.

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