Green Phosphorescence-Assisted Decomposition of Rhodamine B Dye by Ag_3PO_4

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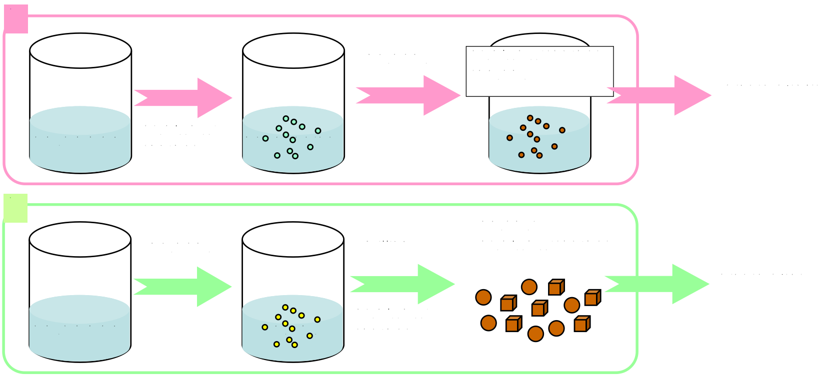
Supplementary information

1. Synthesis of phosphorescence assisted Ag_3PO_4

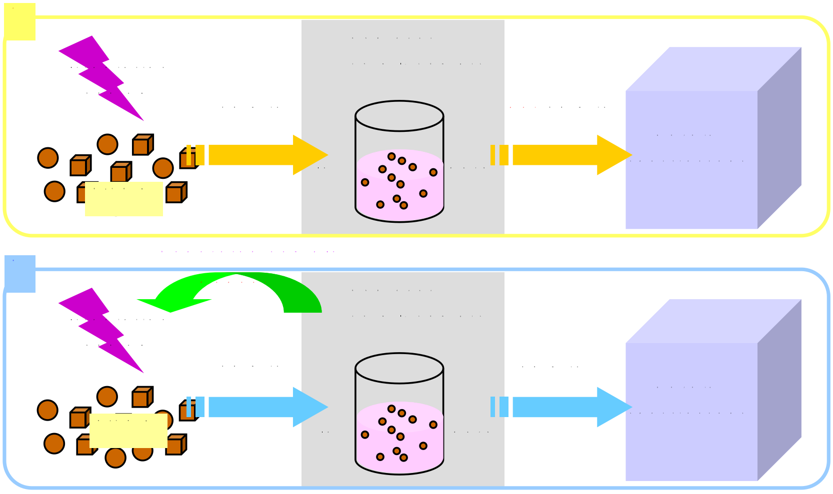


Scheme S1. Schematic illustration of the synthesis process of the Ag_3PO_4 based photocatalysts with different routes.

The $Sr_4Al_{14}O_{25}$:(Eu,Dy)/Ag_3PO_4 composite photocatalysts were prepared by two different methods with the same starting materials as shown in Scheme S1. In a typical synthesis, after dispersing a desired amount of purchased $Sr_4Al_{14}O_{25}$:(Eu,Dy) powders in CH_3COOAg aqueous solution (0.004 M, 300 ml) (shown in Scheme S1A), Na_2HPO_4 aqueous solution (0.15 M) was added drop by drop to form dark yellow precipitations, where the solution pH was slightly changed from 6.1 to 6.4. After that, the obtained samples were collected by centrifugation, followed by repeated washing with water to remove the CH_3COO^-, and dried in air. The $Sr_4Al_{14}O_{25}$:(Eu,Dy)/Ag_3PO_4 composites were also prepared by mixing synthesized Ag_3PO_4 with $Sr_4Al_{14}O_{25}$:(Eu,Dy) powders using an agate mortar (shown in Scheme S1B).

2. Photocatalytic reactions

2.1. RhB dyes decomposition



Scheme S2. Schematic illustration of the photocatalytic process of RhB dye decomposition via phosphorescence assisted Ag_3PO_4 composite photocatalyst with different ways.

Photocatalytic activity measurements were carried out in a solution of rhodemine B (RhB) dyes (20 ml, 10 mg/L) with 0.1 g of a sample. The efficiencies of the RhB dye decomposition were evaluated by the two methods. Method I (Once irradiation): After keeping the sample under black lamp (8 W) irradiation for 30 min, the sample was put into the RhB aqueous solution in the dark without light irradiation (shown in Scheme S2A). The RhB concentration was measured by UV/Vis spectroscopy every 30 min. Method II (repeated irradiation): After keeping the sample under black lamp (8 W) irradiation for 30 min, the sample was put into RhB solution in the dark without light irradiation (shown in Scheme S2B). After 30 min, the degradation of RhB dye was monitored by UV/Vis spectroscopy. Then, the sample was removed from the RhB solution and irradiated again for 30 min, followed by returning to the reaction solution for another 30 min. This procedure was repeated, and the RhB concentration was determined by UV/Vis spectroscopy very time. Before the spectroscopy measurement, all the samples were removed from the reaction solution by centrifugation. In order to study the effect of the Ag_3PO_4 content in $Sr_4Al_{14}O_{25}$:(Eu,Dy)/Ag_3PO_4 composite on the degradation of RhB dyes in the darkroom, the degradation evaluation of RhB dyes on the composite photocatalysts consisted of different mass ratios were proceeding under the same condition. Furthermore, the influence of irradiation intensity on the performance of pure Ag_3PO_4 was also investigated by RhB decomposition under irradiation of a solar simulator (HAL-302, Asahi Spectra Co. Ltd., Japan).

2.2. Photocatalytic degradation of NO

The characterization system of degradation of NO (deNO$_x$) used in the present research was similar to that of the Japanese Industrial Standard which was established at the beginning of 2004 [S1]. In this JIS standard, it is recommended that the photocatalytic activity of photocatalyst should be characterized by measuring the decrease in the concentration of NO at the outlet of a continuous reactor. One ppm of NO gas at a flow rate of 3.0 dm^3/min is introduced into a reactor then irradiated by a lamp with different light wavelength.

The photocatalytic mechanism involved in the NO degradation over catalyst has been reported by Anpo [S2]. During the deNO$_x$ photocatalytic reaction, The NO gas reacts with these reactive oxygen radicals, molecular oxygen, and very small amount of water in air to produce HNO_2 or HNO_3 [S2]. It was confirmed that about 20 % of nitrogen monoxide was decomposed to nitrogen and oxygen directly.

Photocatalytic activity during the oxidative destruction of NO was determined by measuring the concentration of NO gas at the outlet of the reactor (373 cm^3) during photoirradiation under a constant flow of 1 ppm NO-50 vol.% air (balanced N_2) mixed gas (200 cm^3 min^{-1}) [S3, S4]. Approximately 0.04 g of powder catalyst was placed into a 20×15×0.5 mm glass holder, which was kept in the bottom center of the reactor. A 450-W high-pressure mercury lamp was used as the light source, in which the wavelength was controlled by various filters, i.e., Pyrex glass for cutting off the light of wavelength < 290 nm, Kenko L41 Super Pro (W) filter < 400 nm and Fuji triacetyl cellulose filter < 510 nm. The concentration of NO was determined using a NO$_x$ analyzer (Yanaco, ECL-88A).

3. Characterization techniques

The X-ray diffraction (XRD) patterns of the catalysts were measured from 10 to 80 degrees 2θ using a Bruker D2 PHASER X-ray diffractometer and graphite-monochromic CuKα radiation. The catalyst morphology was observed by using a Hitachi S-4800 field-emission scanning electron microscope (SEM). The accelerating voltage for SEM was 15.0 KV. The diffuse reflectance spectra (DRS) were determined by diffuse reflectance measurements of powder samples (Shimadzu UV-2450). The specific surface areas were determined by the amount of nitrogen adsorptions at 77 K (Quantachrome NOVA 4200e) using the Brunauer-Emmett-Teller (BET) method. The photoluminescence spectra and intensity were measured by a spectrofluorophotometer (Jasco FP-8500).

References

[S1] Japanese Industrial Standard (JIS) R 1701-1:2004(J), Japanese Standards Association.

[S2] M. Anpo in *Recent Development on Visible Light Response Type Photocatalyst*, ISBN4-86043-009-03, NTS, Tokyo, 2002, pp.9.

[S3] S. Yin, B. Liu, P. Zhang, T. Morikawa, K. Yamanaka, T. Sato, J. Phys. Chem. C 112 (2008) 12425.

[S4] I. -C. Kang, Q. Zhang, S. Yin, T. Sato, F. Saito, Environ. Sci. Technol. 42 (2008) 3622.

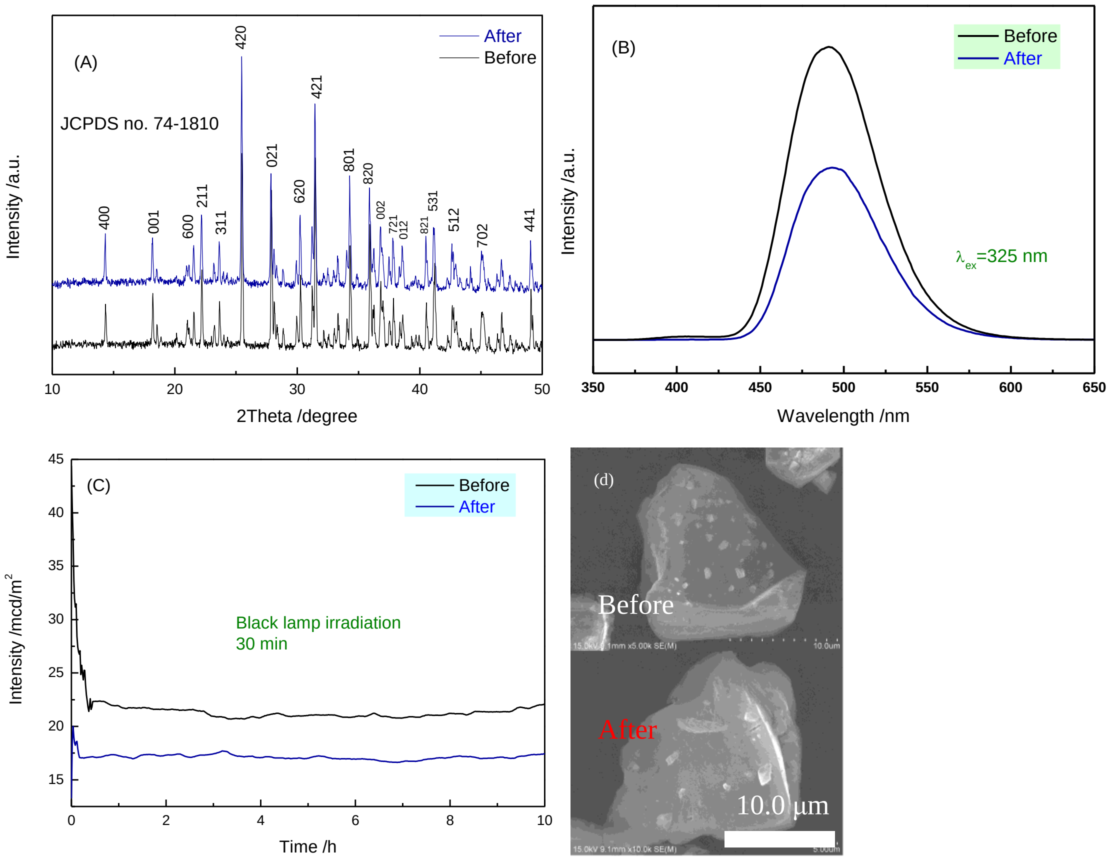


Figure S1. (A) XRD patterns of $Sr_4Al_{14}O_{25}$:(Eu, Dy) before and after dispersed in H_2O (1g/L) for 10 h. (B) Emission spectra. (C) Decay profiles of emission intensity. (D) SEM images.

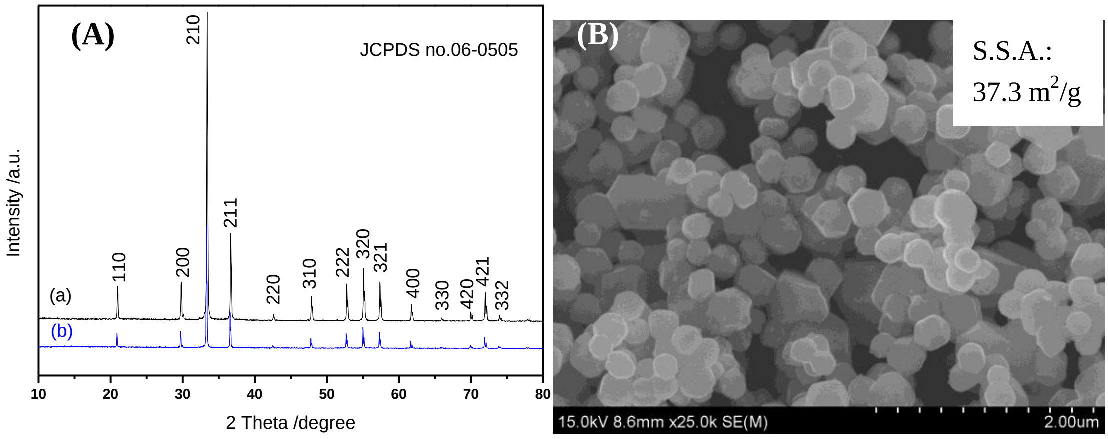


Figure S2. (A) XRD patterns of Ag_3PO_4 (a) before and (b) after irradiation by a black lamp for 30 min. (B) SEM image and specific surface area of Ag_3PO_4.

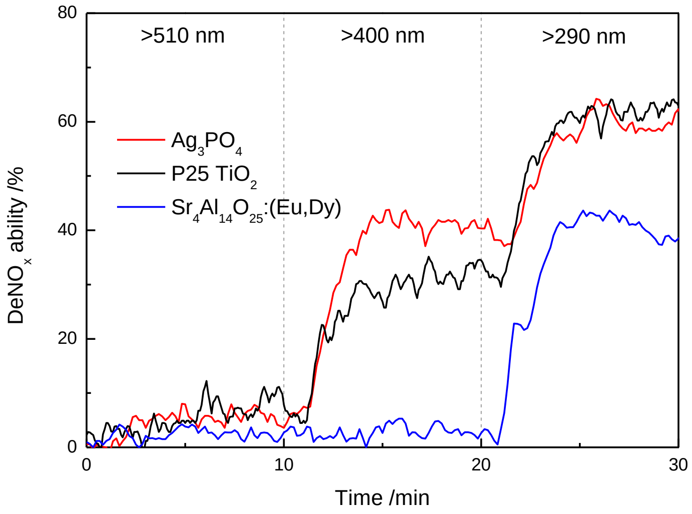


Figure S3. $DeNO_x$ ability of Ag_3PO_4, P25 TiO_2 and $Sr_4Al_{14}O_{25}$:(Eu, Dy) under irradiation with different wavelengths.

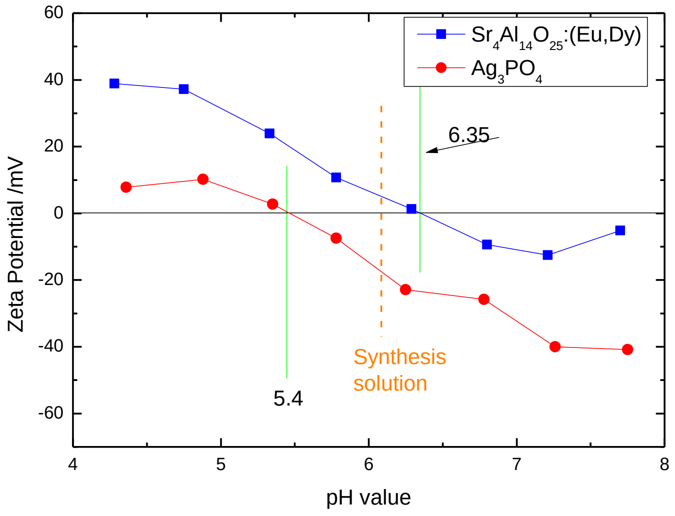


Figure S4. Zeta potential versus pH for $Sr_4Al_{14}O_{25}$:(Eu,Dy) and Ag_3PO_4.

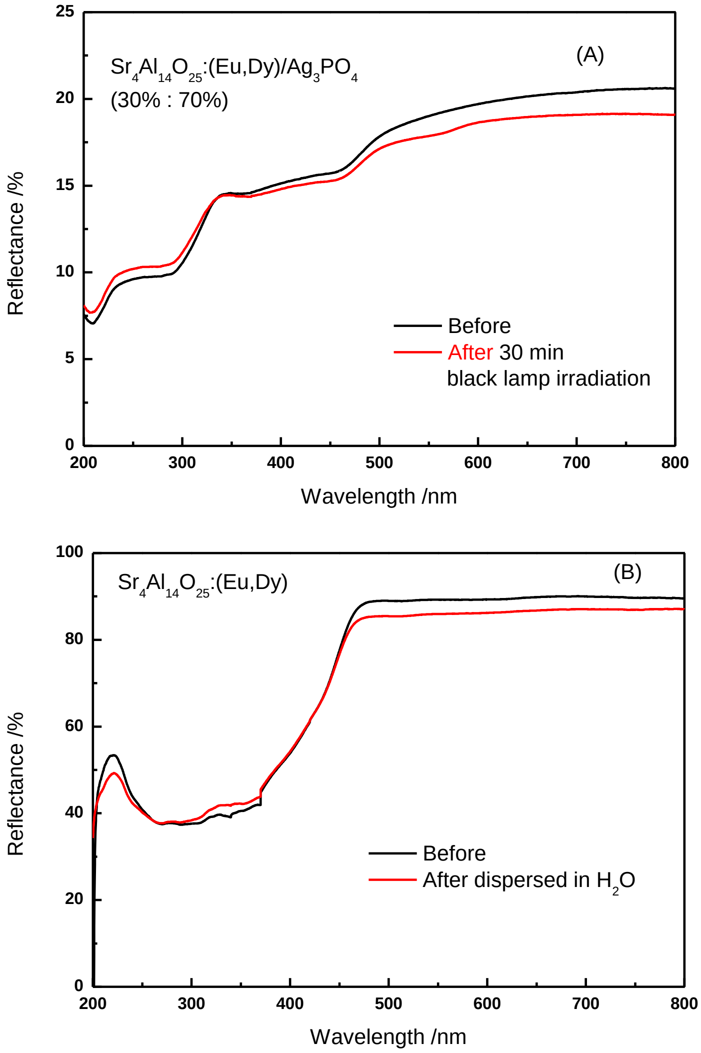


Figure S5. DRS spectra of (A) $Sr_4Al_{14}O_{25}$:(Eu,Dy)/Ag_3PO_4 composite and (B) pure $Sr_4Al_{14}O_{25}$:(Eu,Dy).

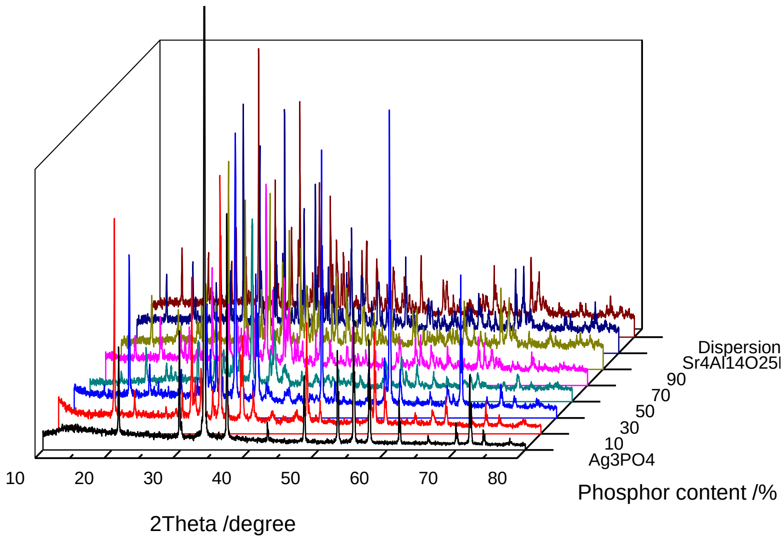


Figure S6. Mass ratio dependent XRD patterns of Ag_3PO_4 based composite samples.

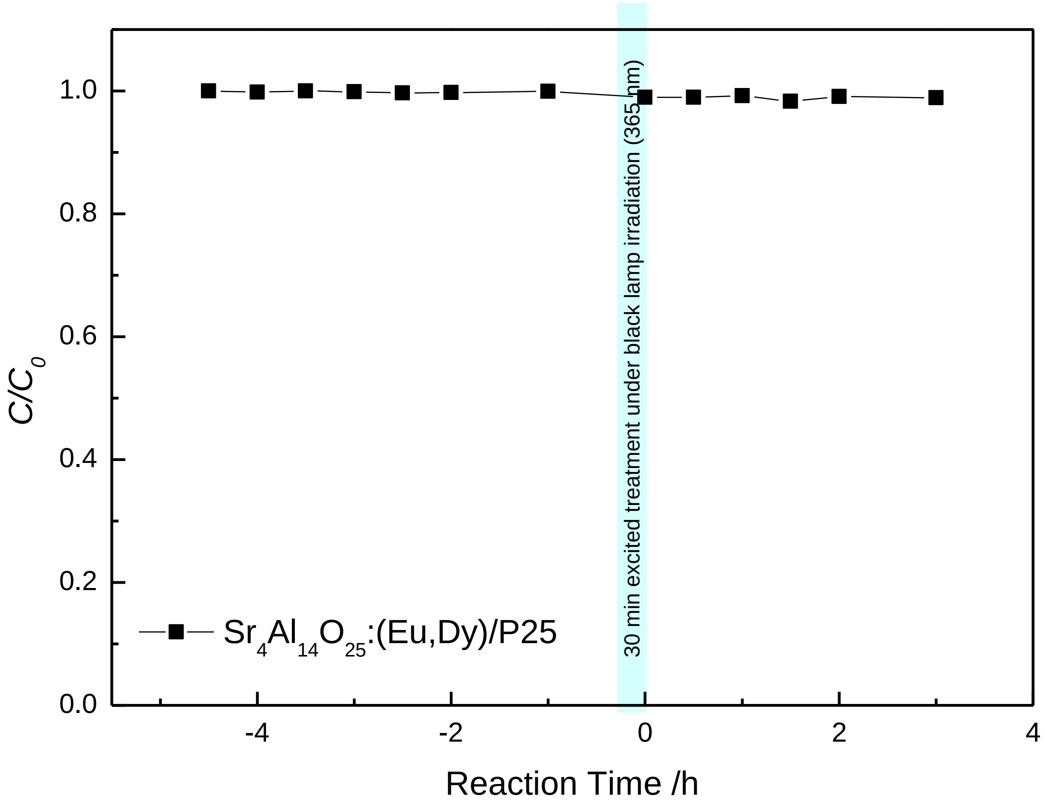


Figure S7. Photocatalytic activities of $Sr_4Al_{14}O_{25}$:(Eu,Dy)/TiO_2 P25 for RhB degradation by irradiation 30 min for powder sample only once (method I).