Preparation of Ag-TiO$_2$/Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ Photocatalyst on Phosphor Beads and Its Photoreaction Characteristics

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Abstract: Long-lasting Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor beads were prepared with inorganic sodium silicate binders and coated to support Ag-doped TiO$_2$ catalyst by the sol–gel coating method. Energy dispersive spectroscopy and X-ray photoelectron spectroscopy confirmed that Ag and TiO$_2$ were loaded on the bead surface. Photocatalytic degradation of toluene volatile organic compound was evaluated under ultraviolet and visible light through 410 nm filters. The photocatalyst/phosphor beads of Ag-TiO$_2$/Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ decorated with 0.035 M Ag in N$_2$ and N$_2$-H$_2$ atmospheres exhibited higher photocatalytic efficiencies compared with beads heat treated in air. A low amount of Ag impregnation and the reducing atmosphere of N$_2$/N$_2$-H$_2$ were beneficial for enhancing photocatalytic efficiency because Ag-doping in TiO$_2$ imparted low energy levels for visible light sensitization. The synthesized powder-free beads possess compressive strength for possible applications, and easy recovery of the photocatalysts is beneficial for preventing any secondary pollution of nano-powders.

Keywords: Ag-TiO$_2$ photocatalyst; Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$; phosphor beads; toluene VOC

1. Introduction

Titanium dioxide (TiO$_2$) nanoparticles (NPs) are photoactive to combat air and water pollutants under ultraviolet (UV) activation. To date, several studies have been conducted to enable the sensitization of visible light by TiO$_2$ NP [1]. The prevalent approaches for extending TiO$_2$ absorption edge are doping with metals/non-metals [2,3] and coupling with metal oxides [4] or noble metals [5,6]. The effect of coupling 3-composites was also studied and reported to show that TiO$_2$ forms heterojunctions in the presence of coupling TiO$_2$/g-C$_3$N$_4$/rGO compounds [7]. One of the cost-effective practical techniques of doping and coupling TiO$_2$ is the wet process method. The disadvantage of coupling two or more NP composites is uncontrollable agglomeration in wet processes. This results in the incorporated phases being dominant and even deterioration of photocatalytic efficiencies.

In metal doping of TiO$_2$, Ag is among the most studied materials owing to its antibacterial property and 3d energy level, which induces low energy states in the TiO$_2$ conduction band. Doping TiO$_2$ with Ag NP to improve TiO$_2$ sensitivity to visible light has been reported to be effective in enhancing photocatalytic properties [8]. However, several studies were conducted in the slurry type of reactor, where detachment of Ag NP and leaching problems limited the reusability of the TiO$_2$-Ag NP in the slurry reactor [9]. Much research focuses on doping Ag on the TiO$_2$ NP surface [10].

Nowadays, many researchers in this field are working towards the commercialization of TiO$_2$ nanoparticles (NPs) in water and air purification systems [11–13]. However, owing a to high specific surface-to-volume ratio, TiO$_2$ NPs require immobilization on substrates for practical application [14,15]. There are studies where TiO$_2$ NPs are practically immobilized on stainless steel mesh [16], glass slides [17], glass mesh [18], quartz substrate [19], concrete [20], coconut fibers [21], and Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor beads [22]. One merit for immobilizing TiO$_2$ is reusability and a less tedious recovery for the catalysts, even in slurry reactors. Furthermore, TiO$_2$ on the substrate is applicable for continuous airflow
type of reactors facilitating air cleaning performances [23]. Coating TiO$_2$ on substrates eliminates several processes to reduce particle agglomeration, which is cost-effective for the catalyst. Most importantly, crystalline phases are confined on the support surface and this improves the formation of inter-particle heterojunction. However, in hydraulic systems, catalysts suffer from hydro-abrasion during photoreaction mixing [24]. Meanwhile, sampling the photocatalysts in air environments minimizes the antifouling of the catalyst [25]. There has been little research on evaluating the photocatalytic performance of TiO$_2$ supported on a substrate decorated with Ag NP.

The reusability of a catalyst depends on physical and chemical stability after the photocatalytic reaction. Crystalline substrates such as long-lasting Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor beads have been reported to show stable support and photocatalytic activity in benzene [22]. Long-lasting phosphors are reported to enhance light harvesting and improve photocatalytic efficiencies through heterojunctions with TiO$_2$ NP. There is a need to determine the optimum coating conditions on long-lasting phosphors owing to the afterglow characteristic, which is affected by the presence of other elements on the surface [26,27]. The afterglow property may aid the recovery of catalyst supports from photocatalytic reaction mixtures in large-scale applications. Up to now, there have been no reports of the photocatalytic performance of a TiO$_2$ NP support on long-lasting phosphor beads doped with varying amounts of Ag.

In this study, long-lasting phosphor beads were synthesized from inorganic binder Na$_2$SiO$_3$ and decorated with Ag/TiO$_2$. The photocatalytic performance was evaluated at various Ag-molar concentrations and the effect of reducing atmospheres. The mechanical strength of phosphor bead substrates was evaluated to confirm whether the beads are mechanically stable for reusability.

2. Results

X-ray diffraction spectra (XRD) of 0.035 M Ag-TiO$_2$/phosphor is shown in Figure 1 as compared to Joint Committee on Powder Diffraction Standards (JCPDS) cards for (a) Sr$_4$Al$_{14}$O$_{25}$(Al$_{10}$O$_{23}$), (b) AgO, and (c) TiO$_2$. The Ag-doped TiO$_2$/phosphor exhibited high crystallinity as indicated by intense XRD spectra. All the major peaks were matched and indexed in reference to Sr$_4$Al$_{14}$O$_{25}$(Al$_{10}$O$_{23}$). However, only the peak at 27.0$^\circ$ is referenced to TiO$_2$ rutile JCPDS 75-1753. While the AgO and TiO$_2$ peaks coincided with the Sr$_4$Al$_{14}$O$_{25}$(Al$_{10}$O$_{23}$) peaks (Figure 1b,c).

Scanning electron microscopy (SEM) images of (a) Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$, (b) TiO$_2$/Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$, (c) Ag-TiO$_2$/Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$, and (d) AgO on TiO$_2$/Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ photocatalyst/phosphor beads are shown in Figure 2. Phosphor bead morphology after drying at 100 $^\circ$C consists of angular submicron particles of irregular sizes ranging from 1 to 10 µm with pore space. The TiO$_2$-coated beads exhibit a spherical shape owing to the TiO$_2$ coating. With Ag-doping, silver oxide appears as white spots decorated on the TiO$_2$/Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ beads. After a two-step coating of Ag and TiO$_2$, the bead surface inter-particle porosity is covered over. However, thermal cracks and confined micro-pores result from heat treatments at 450 $^\circ$C after the Ag and TiO$_2$ coating processes. Figure 2d shows a high-resolution SEM image of AgO nanoparticles on phosphor and the respective supplementary images for energy dispersion spectroscopy (EDS) are shown in Figure S1a,b. The AgO nanoparticles were the brightest particles in Figure 2d (as indicated by arrows) after scanning EDS map with the highest Ag in back-scattering mode.
Figure 1. XRD spectra for 0.035 M Ag-TiO$_2$/phosphor compared to JCPDS for (a) Sr$_4$Al$_4$O$_{25}$(Al$_{10}$O$_{23}$), (b) AgO, and (c) TiO$_2$.

Figure 2. SEM images of phosphor beads (a) Sr$_4$Al$_4$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$, (b) TiO$_2$/Sr$_4$Al$_4$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$, (c) Ag-TiO$_2$/Sr$_4$Al$_4$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$, and (d) AgO on TiO$_2$/Sr$_4$Al$_4$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$. 

![Figure 1](image1.png)

![Figure 2](image2.png)
Mapping analysis for the distribution of the elements on the bead surface and energy
dispersion spectroscopy (EDS) spectra is shown in Figure S1c,d, respectively. Details of the
elemental composition of the Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor bead and the atomic percent
confirming the presence of O, Na, Al, Si, and Sr are shown in Table 1. The silicon content of
14.81 atom percent originated from the Na$_2$SiO$_3$ inorganic binder. However, Eu and Dy
were undetected because they are embedded in the core matrix and their atomic percent is
also small when compared with the bulky bead surface.

| Table 1. Elemental analysis for Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor beads. |
|-----------------------------------------|---------|------|
| Element      | Mass % | Atom % |
| O            | 43.21  | 59.62 |
| Na           | 7.19   | 6.90  |
| Al           | 19.29  | 15.78 |
| Si           | 18.84  | 14.81 |
| Sr           | 11.47  | 2.89  |
| Totals       | 100    | -     |

Elemental compositions for TiO$_2$/Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ photocatalyst/phosphor beads
are shown in Table 2. The composition of 2.71 atom percent Ti merely confirms that the
coating process impregnates the phosphor surfaces with TiO$_2$ particles. The remaining
atomic composition is for the bead surface, namely O, Na, Al, Si, and Sr. Eu and Dy
were below the detection limit, as also observed in Table 1, because of the bulky struc-
ture of the bead. The elemental mapping and EDS spectra for this sample are shown in
Figure S1e,f, respectively.

| Table 2. Elemental analysis for TiO$_2$/Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ photocatalyst/phosphor beads. |
|-----------------------------------------|--------|------|
| Element      | Mass % | Atom % |
| O            | 45.68  | 60.96 |
| Na           | 14.81  | 13.75 |
| Al           | 10.30  | 8.15  |
| Si           | 17.02  | 12.94 |
| Ti           | 6.09   | 2.71  |
| Sr           | 6.10   | 1.49  |
| Totals       | 100    | -     |

Elemental compositions of Ag-TiO$_2$/Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ photocatalyst/phosphor beads are shown in Table 3. The amount of Ag-doped and Ti on phosphor was 1.30 and 2.21 atom percent, respectively. As mentioned in Tables 1 and 2, the rare earth ions Eu and Dy were below the detection limit. The EDS mapping for Ag-doped TiO$_2$/Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$, Dy$^{3+}$ beads and the corresponding spectra are shown in Figure S1g,h, respectively.

| Table 3. Elemental analysis for Ag-TiO$_2$/Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ photocatalyst/phosphor beads. |
|-----------------------------------------|--------|------|
| Element      | Mass % | Atom % |
| O            | 47.75  | 64.31 |
| Na           | 11.51  | 10.79 |
| Al           | 7.09   | 5.67  |
| Si           | 19.46  | 14.93 |
| Ti           | 4.91   | 2.21  |
| Ag           | 5.29   | 1.30  |
| Sr           | 3.98   | 0.80  |
| Totals       | 100    | -     |

Compressive stress averages for the Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor photocatalyst/
beads are shown in Table 4. The phosphor beads show the highest average compressive
strength of 15.36 kgf compared with the TiO2-coated and Ag/TiO2-beads with 8.71 and 5.80 kgf, respectively. This is a result of the thermal cracks observed in the SEM images in Figure 2 that were caused by heat treatment procedures conducted after the coating processes. Despite the stress strain curves shown in Figure S2a–c, the beads withstood compressive strength above 5 kgf. Therefore, the beads are reusable because mechanically they are able to endure fragmentation during the handling and packaging process.

Table 4. Compressive strength averages for Sr4Al14O25:Eu²⁺,Dy³⁺ phosphor beads.

| Bead Samples          | Speed (mm/min) | Compressive Load (kgf) | Average (kgf) |
|-----------------------|----------------|------------------------|---------------|
| Phosphor              | 0.5            | 16.33                  | 15.36         |
| TiO2/Phosphor         | 0.5            | 14.39                  | 8.71          |
| Ag-TiO2/Phosphor      | 0.5            | 9.96                   | 8.71          |

X-ray photoelectron spectroscopy (XPS) spectra of (a) TiO2/SrAl14O25:Eu²⁺,Dy³⁺ and (b) Ag-TiO2/SrAl14O25:Eu²⁺,Dy³⁺ photocatalyst/phosphor beads are shown in Figure 3. The depth profile of TiO2/SrAl14O25:Eu²⁺,Dy³⁺ photocatalyst/phosphor beads exhibits the elements of O and Ti as the highest on the surface, while Al and Sr increase with etching time (Figure 3a,b). This shows that the TiO2 NPs are loaded at the surface while Sr and Al are in the core of the bead. The composition of Ag varied from 0.76 at the surface to 0.48 atomic percent after 3000 s etching (supplementary Tables S1 and S2).

Figure 3. XPS depth profile spectra of (a) TiO2/SrAl14O25:Eu²⁺,Dy³⁺ and (b) Ag-TiO2/SrAl14O25:Eu²⁺,Dy³⁺ photocatalyst/phosphor beads.

XPS spectra of the photocatalyst/phosphor bead surface of 0.035 M Ag decorated TiO2/SrAl14O25:Eu²⁺,Dy³⁺ are shown in Figure 4 as (a) survey, (b) Ti 2p, (c) Ag 3d, and (d) O 1s. The spectra show peaks of Na 1s, O 1s, Ti 2p, Ag 3d5, C 1s, and Si 2p (Figure 4a). Except for C impurity from the instruments and the environment, all the elements are part of the SrAl14O25:Eu²⁺,Dy³⁺ bead/TiO2/Ag composite. The atomic compositions of the respective elements are provided in supplementary Tables S3 and S4. Ti 2p spectra for the Ag-TiO2/SrAl14O25:Eu²⁺,Dy³⁺ bead are shown in Figure 4b. The binding energy of 464 and 458 eV confirms the bonding of Ti to O. Atomic percent for TiO2 is 2.7% (supplementary Table S2). The spectrum has two peaks at 369.5 and 375.7 eV, which correspond to the core level of Ag 3d₅/₂ and Ag 3d₇/₂ (Figure 4c). These peaks are referenced to Ag₂O compounds.
owing to Ag and O bonds, where at Ag$^0$ and Ag$^+$ exist in the deconvoluted peak of 360 to 370 eV [28]. The spectra for O 1s with a maximum binding energy peak at 532 eV are shown in Figure 4d.

**Figure 4.** XPS spectra on the surface of Ag-TiO$_2$/Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ beads (a) survey, (b) Ti 2p, (c) Ag 3d, and (d) O 1s.

Photoluminescence (PL) spectra of the TiO$_2$/Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ beads containing varying amounts of Ag-doping in Figure 5 show that the maximum emission from the phosphor beads peaks at 490 nm. TiO$_2$ without Ag on Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor beads exhibits about a 5% decrease in luminescence intensity compared to Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor beads. The phosphor beads with and without TiO$_2$ coating were inserted as control samples. The emission peak intensity decreased as the doping amount of Ag increased from 0.017 M to 0.14 M. Phosphor emission centers are localized at the surface, such that only transparent materials effectively emit light. However, TiO$_2$ and AgO seem to partially absorb and simultaneously hinder the propagation of emitted light from phosphor photons.

The PL spectra of the Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor beads coated with/without Ag and TiO$_2$ calcined in (air, N$_2$ or N$_2$-H$_2$) unique atmospheres are shown in Figure 6. In comparison with other beads, Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor maintains the most extraordinary intensities, followed by the TiO$_2$-coated phosphor beads. Evidently, Ag-doped beads coated in an N$_2$ environment show a higher luminescence than ones treated in N$_2$-H$_2$ and air atmospheres. As can be observed in SEM images, the coating of phosphor with Ag-sol showed AgO nanoparticle clusters along the phosphor surface. On this account, AgO clusters cause light obstruction from the emitted phosphor photons. Ag calcined in air shows the least peak intensity, undoubtedly owing to possible significant amounts of AgO on the bead surface.
The variation of toluene photodegradation over the Ag-doped TiO$_2$/phosphor beads under a UV light source is shown in Figure 7. These beads were calcined in the N$_2$ atmosphere. The photocatalysts exhibit photocatalytic activity reaching over 80% efficiency in 1 h. Although the 0.035 M doped samples displayed an outstanding photocatalytic performance, the 0.14 M doped TiO$_2$ phosphor beads exhibited less efficiency as an indication of the undesirable AgO barrier between the TiO$_2$/Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ interface (enlarged Figure 7b, extracted from Figure 7a). The variation of toluene degradation in the presence of commercial TiO$_2$ (for 1-h cycle) was also inserted in Figure 7b. Clearly, commercial TiO$_2$ exhibits 70% efficiency as compared to phosphor/TiO$_2$ composites with above 80% efficiency in a 1-h cycle. The reason being the Ag-doping and phosphor bead support improves light sensitization.
Figure 7. Photocatalytic degradation of toluene over Ag-TiO$_2$/Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ photocatalyst/phosphor beads under UV light activation.

The photodegradation of toluene with the Ag-doped TiO$_2$/phosphor beads under a visible light source is shown in Figure 8. The photoreactions exhibited a degradation of toluene in a 240-min cycle, where the 0.035 M Ag doped sample shows the highest photocatalytic efficiency and the 0.14 M sample is the lowest. In detail, the 0.035 M degrades over 70% while the 0.14 M reaches only 40% efficiency in 120 min (enlarged Figure 8b, extracted from Figure 8a). Photodegradation of toluene in TiO$_2$ commercial powder (Figure 8b) shows that TiO$_2$ on its own is not activated by visible light owing to the large band gap of 3.2 eV. However, by coupling with phosphor and with additional Ag-doping, the composites exhibit significant photocatalytic activity. The reason for the fastest photolysis rate in 0.035 M Ag-TiO$_2$/Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ photocatalyst/phosphor beads is enhanced sensitization by Ag ions causing the overall electron–hole generation and separation that occurs unexpectedly with visible light.

Figure 8. Photocatalytic degradation of toluene over Ag-TiO$_2$/Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ photocatalyst/phosphor beads under visible light irradiation.

Photodegradation of toluene with the 0.035 M Ag-doped TiO$_2$/phosphor beads heat treated in air, N$_2$ and N$_2$-H$_2$ as activated by visible light is shown in Figure 9. The photocatalytic performance in commercial TiO$_2$ powder was inserted for comparisons. As discussed in Figure 8b, TiO$_2$ is not activated by visible light. Thus, only adsorption of the
toluene volatile organic compound (VOC) occurs on the commercial TiO$_2$ nano powders. At the 30-min sampling intervals, samples calcined in N$_2$ and N$_2$-H$_2$ gas exhibited about 90% efficiency while heat treated in air samples maintained about 70% efficiency. The samples heat treated in air exhibited 20% points less efficiency than those in the reducing atmosphere. Consequently, the reducing atmosphere shows improved photocatalytic efficiencies while the oxidizing condition increases AgO oxides, which become barriers to photocatalytic enhancement.

![Photocatalytic degradation of toluene over visible light irradiation.](image)

**Figure 9.** Photocatalytic degradation of toluene with the 0.035M Ag-doped TiO$_2$/phosphor beads over visible light irradiation.

3. Discussion

Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor beads synthesized from sodium silicate binders revealed thermal cracks as an effect of heat treatment. This is prevalent with sodium silicate additive because the glass phases transform and cause inter-particle encapsulation. However, owing to different thermal expansions, cracks and voids form within sintered specimens. As observed, the detrimental effects of the cracks and pores were low compressive strength because the cracks and pores act as centers of weakness as fracture points. One advantage of porosity and micro-cracks is the possible active sites formed during incipient wetness impregnation. As observed in depth profiling for 3000 s, the Ag:Ti ratio was observed from 12:0.76 at the surface to 3.16:0.48. Therefore, the cracks and micro-pores were loaded with Ag/TiO$_2$, which resulted in enhanced photocatalytic efficiencies.

The amount of Ag$_x$Ti$_{2-x}$O$_2$ on the phosphor surface and heat treatment in air, N$_2$, and N$_2$-H$_2$ affect photoluminescence emission. This is a common phenomenon on long-lasting phosphors coated with non-luminescence materials. Nanoparticles on the surface of phosphor block the emitted photons. The photocatalytic efficiencies were enhanced in 0.035 M as optimum Ag concentration, while the efficiencies were lower on 0.14 M. This is a possible indication of excess Ag-O on the phosphor surface, which acts as a barrier to luminescent light. Additionally, the inter-phosphor-TiO$_2$ junction is increased, which merely renders phosphor inefficient to TiO$_2$ performance [23].

The effect of heat treatment condition on photocatalytic efficiencies of 0.035 M Ag (Figure 9) is elaborated on as the best activity in N$_2$ and N$_2$-H$_2$ over-oxidizing atmospheres. The reducing atmospheres enhance oxygen deficient Ag, which easily migrates into Ti at interstitial sites. While in an oxidizing atmosphere, Ag crystallizes as oxygen-rich oxides that limit the chances of TiO$_2$ doping. Thus, sensitization of UV/visible light is enhanced because of lower Fermi levels imparted by Ag-doping. Therefore, separation of electron-hole pairs is improved with Ag-doping for more superior photocatalytic efficiencies [10].
TiO$_2$ commercial powder showed no photocatalytic variation in visible light owing to its large band gap. While under UV light activation, significant photocatalytic decomposition of toluene in TiO$_2$ commercial powder was observed since irradiated photons activated the catalyst. Overall, the Ag-doped–TiO$_2$/phosphor showed better photocatalytic performances than commercial TiO$_2$ because of an improved light sensitization by phosphor support and the Ag-doping. The results in our research also confirm enhancement of photocatalytic efficiencies after Ag-doping compared to only TiO$_2$ coating. A similar trend was reported in Ag-doped calcium aluminate phosphor/TiO$_2$ beads [23]. The test conditions in the reference were a 75-W mercury lamp UV light and 200-W visible light incandescent lamp over a 410 nm filter. However, the photocatalytic activity of Ag-doped/TiO$_2$-Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor beads has been reported for the first time with fast photoactivity completing in 60 to 240 min under UV and visible light, respectively. Therefore, Ag-doped/TiO$_2$-Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor beads are possible candidates for alleviating volatile organic compounds.

4. Materials and Methods
4.1. Experimental

Phosphor beads were prepared using the long-lasting phosphorescent Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ (Luminova BG-300M, Nemoto & Co., Ibaraki-ken, Japan) and sodium alginate (C$_5$H$_{10}$O$_4$·(COOH)$_n$) solution. The alginate process for phosphor beads is described in detail elsewhere [22]. Ag-doping sol was prepared from silver nitrate (AgNO$_3$ 99.8%, Junsei Chemical Co., Tokyo, Japan). Four batches of 0.017 M, 0.035 M, 0.07 M, and 0.14 M concentration Ag-doping sol were coated batch-wise on Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor beads. Each AgNO$_3$ batch was dissolved in a beaker of 38 mL distilled H$_2$O, 2 mL ethyl alcohol (C$_2$H$_5$OH 99.9%, Duksan Pure Chemicals Co., Korea) and 2 mL NH$_4$OH (extra pure grade, Duksan Pure Chemicals Co., Korea) and stirred at 30 $^\circ$C for 2 h. Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor beads weighing 40 g were dip-coated in 40 mL of Ag-doping sol and filtered through a funnel. After drying in an oven at 100 $^\circ$C for 6 h, the beads were placed in a closed crucible for heat treatment. Heat treatment was performed on the 40 g batches in a tube furnace (AJ-MBT6, AHJEON Industrial Co., Korea) at 450 $^\circ$C for 2 h. TiO$_2$-sol stock solution was prepared from 40 mL titanium tetraisopropoxide (97%, Sigma Aldrich, MO, USA), 200 mL ethyl alcohol (C$_2$H$_5$OH 70%, Daegung Chemicals, Korea), 4 mL nitric acid (HNO$_3$ 70%, Daegung Chemicals, Korea), and 40 mL distilled H$_2$O. Afterwards, 40 g of Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor beads were dip-coated in 40 mL of TiO$_2$ solution, filtered and dried at 100 $^\circ$C for 6 h. Ag-doped Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor beads were also coated with TiO$_2$ using a similar process. TiO$_2$-coated beads were calcined at 450 $^\circ$C for 2 h in a box furnace (DSF-7GFS, Daegung Science Co., Korea). Images of (a) Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor beads, (b) TiO$_2$/Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor beads, and (c) Ag-TiO$_2$/Sr$_4$Al$_{14}$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor beads are shown in Figure 10. The 4–6 mm diameter phosphor beads in Figure 10a are off-whitish while TiO$_2$ and Ag-doped/TiO$_2$ samples in (b) and (c) are colored greyish and yellowish-olive, respectively. Thus, Ag coating shows that it imparts a deep olive color which may reduce the light-scattering phenomenon common in whitish TiO$_2$ surfaces.
4.2. Characterizations

The crystallinity of the 0.035 M Fe-TiO₂/phosphor bead was analyzed by XRD with Cu Ka irradiation (Bruker AXS8 Advanced, D8 Discover, GmbH, Karlsruhe, Germany). Surface morphology and element composition were evaluated by SEM (Hitachi S4300, Tokyo, Japan), EDS (JEOL, JSM-6010PLUS, Peabody, MA, USA) and XPS (ThermoFisher Scientific, Nexsa, Waltham, MA, USA). A fluorescence spectrometer (Hitachi F4500, Tokyo, Japan) was used to measure the luminescence characteristics of the synthesized composite materials. The photodecomposition of toluene (C₇H₈ 10.7 µmol/mol), one of the hazardous volatile organic compounds (VOCs) was analyzed by gas chromatography (GC, 7890A, Agilent Technologies Inc., Santa Clara, CA, USA).

The compressive strength of the phosphor beads was measured using a compression testing machine (Intron 3344, Intron Co., Norwood, MA, USA). The maximum compressive strength for each bead was measured using a tip of 7 cm in diameter at a constant crosshead speed of 0.5 mm/min. Two samples of Sr₄Al₁₄O₂₅:Eu²⁺,Dy³⁺, TiO₂/Sr₄Al₁₄O₂₅:Eu²⁺,Dy³⁺, and Ag-TiO₂/Sr₄Al₁₄O₂₅:Eu²⁺,Dy³⁺ beads were evaluated for compressive strength measurements.

The toluene photodegradation experiment was performed in 1-L Teflon bags containing 40 g of TiO₂/Sr₄Al₁₄O₂₅:Eu²⁺,Dy³⁺ photocatalyst/phosphor beads and 10 ppm toluene under UV and visible light conditions. The 40 g phosphor beads were a mixture consisting of 4 mm and 6 mm diameter at 1:1 ratio, respectively. At intervals of UV (6 W, 2 fluorescent lamps, G6T5 Sankyo Denki, Sankyo Denki Co., Kanagawa, Japan) or 100 W visible light (ST55 L Ilkwang Lamp Co., Daegu, Korea) irradiation with 410 nm filters, 1 mL of toluene was sampled and injected into the GC analyzers. The lights were placed at 15 cm height illuminating the samples throughout the experiments. The light flux was measured by a Digital Lux Meter (Smart Sensor AR823). For the two photocatalytic conditions, one 100 W bulb (visible light) and two fluorescent lamps (UV light) of 6 W each emitted an average

![Figure 10. Images of phosphor beads (a) Sr₄Al₁₄O₂₅:Eu²⁺,Dy³⁺, (b) TiO₂/Sr₄Al₁₄O₂₅:Eu²⁺,Dy³⁺, and (c) Ag-TiO₂/Sr₄Al₁₄O₂₅:Eu²⁺,Dy³⁺.](image-url)
of 1200 and 30 lux at 15 cm height, respectively. For comparisons, 1 g of commercial TiO$_2$ powder (Aeroxide TiO$_2$ P25, Evonik, Essen, Germany) was spread on a 9.4 cm diameter quartz petri dish and tested for toluene photodegradation using similar conditions. The photocatalytic tests were conducted without any pH modifiers.

5. Conclusions

Ag-TiO$_2$/Sr$_4$Al$_4$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ photocatalyst/phosphor beads were synthesized and decorated with Ag NP prior to TiO$_2$ coating. Depth profile etching confirmed that the Ag/Ti elements were on the surface and in the inner bead structure. Despite microcracks/pores, the beads showed a high compressive strength which is beneficial for reuse as photocatalyst supports. Photocatalytic performances on phosphor beads with 0.035 M Ag showed the highest photodegradation of toluene VOC in both UV and visible light activation. Compared with air and N$_2$-H$_2$, the reducing atmosphere of N$_2$ preserved PL emission, which is beneficial for aesthetic afterglow and recovery of the catalyst.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/2073-4344/11/2/261/s1, Figure S1: (a) EDS mapping for AgO on TiO$_2$/Sr$_4$Al$_4$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor bead, (b) EDS spectra and map elemental composition analysis for AgO on TiO$_2$/Sr$_4$Al$_4$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor bead, (c) EDS mapping for Sr$_4$Al$_4$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor bead, (d) EDS spectra for Sr$_4$Al$_4$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ phosphor beads, (e) EDS mapping for Ag-TiO$_2$/Sr$_4$Al$_4$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ photocatalyst/phosphor beads, (f) EDS spectra for Ag-TiO$_2$/Sr$_4$Al$_4$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ photocatalyst/phosphor beads, (g) EDS mapping for Ag-TiO$_2$/Sr$_4$Al$_4$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ photocatalyst/phosphor beads, (h) EDS spectra for Ag-TiO$_2$/Sr$_4$Al$_4$O$_{25}$:Eu$^{2+}$,Dy$^{3+}$ photocatalyst/phosphor beads.

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