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ORIGINAL ARTICLE

# The Study on Titanium Dioxide-Silica Binary Mixture Coated $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$ Phosphor as a Photoluminescence Pigment in a Waterborne Paint

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**Abstract**
After proper stimulation, long afterglow phosphors formulated as pigment in waterborne paints can emit light after the removal of the excitation light source. The encapsulation of $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$ phosphor by TiO2 and SiO2 individually, and in combination by a precipitation method was studied. The water resistance and photoluminescence behavior of the coated phosphors as a pigment for potential use in waterborne photoluminescence paints were evaluated. It revealed that the TiO2- SiO2 content coating layer was precipitated on the studied phosphor successfully. The higher trend of the TiO2 for coating on the phosphor when compared with the SiO2 was observed from EDS spectra. The SEM micrographs showed a continuous and uniform SiO2-TiO2 layer on the coated phosphor. Based on XRD results, the existence of the TiO2 in the coating layer had beneficial effect on the average crystallite size values. The pH solution versus time showed that the availability of the TiO2 in coated layer improved water resistance of the coated phosphor, although, in comparison with SiO2, it was less effective. The coated phosphor with TiO2 had the minimum afterglow brightness decay and consequently, it was recommended as a suitable pigment for waterborne photoluminescence paints.

**Keywords** Waterborne paint · Pigment · Phosphor · TiO2 · SiO2 · Coating

## Introduction

The long-lasting luminescence phenomena have been observed in metal ion-doped aluminates, silicates, phosphates, and oxy sulfides since 1996 [1]. After proper stimulation, long afterglow (long-lasting) luminescent materials (phosphors or phosphorescent particles) can emit light in the range of visible to near-infrared region after the removal of the excitation light source. So far, a massive number of luminescent materials have been developed for different applications, highlighting fluorescent proteins [2], organic pigments [3], metal complex [4, 5], semiconductors [6] and inorganic phosphors [7, 8]. The phosphors also can be used in the composition of waterborne or environment friend coating and paints for marking the road surfaces. The resulted persistent luminescence can be observable by eyes at the night for a period of time ranging from several minutes to few days. Based on emission color, the persistent phosphors were divided into five groups, i.e., red, green, blue, white, and near-infrared [1]. The $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$ as a strontium mono-aluminate europium dysprosium based phosphor widely used in paints and coating because it has high fluorescence intensity and brightness, non-radioactivity and long afterglow time (> 16 h) [9]. It emits blue-green light in the dark after sunlight excitation. According to the experimentally collected emission spectra, it could be excited by the light at wavelengths ranging from 200 to 450 nm and be able to produce a broad green emission located at 520 nm [10]. The resulted broadband emission indicated that the underlying optical transition occurred within Eu2+ ions originates from the electrical dipole allowed *5d*-*4f* transition. This persistent luminescence material consists of an inorganic matrix act as a trap known, host ($SrAl_2O_4$) and two earth elements as activated doping ions known activators (Eu2+ and Dy3+). The host stores the excitation energy and the activators give radiation after the excitation [3]. However, the $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$

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phosphor has some disadvantages including weak water resistance resulting in breaking bond of O-Sr-O. Hence, this phosphor tends to hydrolyze and deteriorate [11]. For this reason, some encapsulation techniques have been carried out by means of inorganic, i.e., SiO2 [9, 12–14], fluoride [15], boric acid [16], pyrophosphoric acid (PPA) [17], alumina [18], phosphoric acid [19] and or organic (Maleic anhydrate) [20], amino [21], ammonium difluoride [22], polymer matrix [23, 24] and methylmethacrylate (MMA) [25], layers. However, in most cases, these layers have not had the result expected to prevent hydrolysis of the strontium aluminate. Moreover, the water resistance improved at the expense of a loss on luminescence intensity. In paints, titanium dioxide ($TiO_2$) is mainly used as a white pigment. Moreover, it acts as a UV filter protecting the paints' binder material. It degrades organic materials via generation of radicals which aids the paint for self-cleaning surfaces. In this study the effect of encapsulation of $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$ phosphor by titanium dioxide and silica individually, and in combination on the water resistance and luminescence behavior of the coated phosphor as a potential use in waterborne paints was studied and the results were discussed. A heterogeneous precipitation method was used for surface modification of the phosphor.

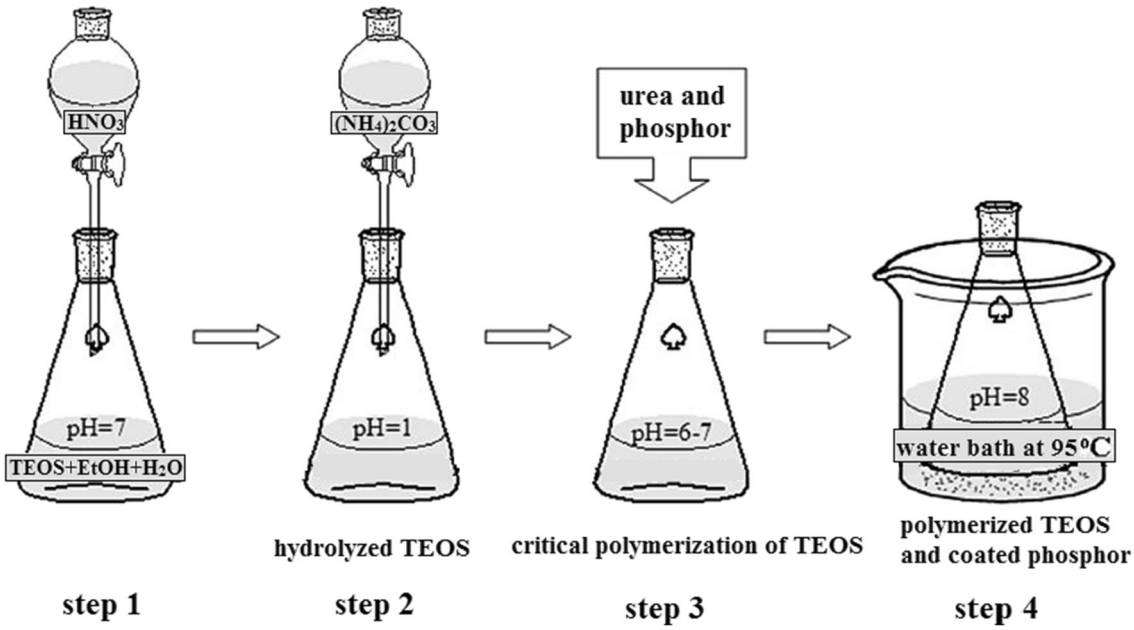
## Experimental

### Materials

Commercial titanium dioxide, TiO2 content>94% (chemical agent and pigment, rutile, PR900, Parshwanath Colour Chem,India), Commercial $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$ phosphor with particle size of $50\mu m - 75\ \mu m$ and melting point of $1200^{\circ}C$ (emitting agent, Hangzhou Yeming Science & Technology Co. Ltd., China), Urea (agent, Khorasan petrochemical complex, Bojnord), Ammonium bicarbonate, nitric acid and ethanol (chemical agents, Merck, Germany), Tetraethyl orthosilicate (TEOS) (analytical reagent, TITRACHEM, Tehran).

### Identification and Behavior Study Techniques

Attenuated total reflection (ATR) is a sampling technique used in conjunction with infrared spectroscopy which enables samples to be examined directly in the solid or liquid state without further preparation [26]. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, AVATAR 370FT-IR, Termo Nicolet, USA) analysis was used to study the structure of the unmodified and modified used phosphor. The wavelength ranged between 400 and 4000 $cm^{-1}$. X-ray diffraction is a non-destructive technique used for determining the qualitative and quantitative analysis of a crystalline material, in which the crystalline cause a beam of incident X-rays to diffract into many specific directions [27]. The angles and intensities of diffracted beams to used phosphor was measured by a X-ray diffraction crystallography (XRD) instrument (GNR, Italy), under beam incident of 10 to 80 degree, $\lambda = 0.154\ nm$ with Cu K$\alpha$ radiation at 40KV tube voltage and 30 mA tube current. The detector type was Scintillator. Morphology of phosphors was assessed by a SEM LEO 1450VP (Germany) field emission gun scanning electron microscope (SEM) with a resolution of 2.5 nm at 20kv. An Energy-dispersive X-ray spectroscopy (EDS) instrument (7353, Oxford, UK) with 133ev resolution was used for




**Scheme 1** The coating sequential process diagram [9]

**Table 1** The SiO2-TiO2 weight ratios in binary mixtures

| | | |
|---|---|---|
| A100 | SiO2- TiO2 | 100–00 |
| A90 | SiO2- TiO2 | 90–10 |
| A70 | SiO2- TiO2 | 70–30 |
| A50 | SiO2- TiO2 | 50–50 |
| A30 | SiO2- TiO2 | 30–70 |
| A00 | SiO2- TiO2 | 00–100 |

elemental analysis of the samples. The samples also were examined and photographed in the SEM and the shapes and their morphology were subsequently studied from SEM micrographs. For assessing the water resistance of un-modified and modified phosphors, a pH meter (pH 211-HANNA instruments, Italy) was used to monitor solution pH variation versus time. For this purpose, 0.5 g coated or uncoated phosphors were dispersed in 10 ml distilled water and the pH value changes of the solutions were recorded against the time. Afterglow decay curves and photoluminescence spectra were measured by a fluorescence spectrophotometer (Cary Eclipse,VARIAN, USA) after the phosphors were excited by a Xe lamp at 390 nm for 15 min at PMT voltage of 700v and Ex Slit of 10 nm.

## Sample Preparation

In this study, a heterogeneous precipitation method using urea as precipitator was used to coat a layer of binary mixture of SiO2-TiO2 with different weight ratios on the surface of the $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$ phosphor as described by Tonggang Qi et al. [9]. Scheme 1 [9] shows the coating sequential process diagram. In brief, tetraethyl orthosilicate (TEOS) dissolved in the mixture of distilled water and ethanol in the volume ratio of 1:1. Subsequently, nitric acid was added into the above mixed solution to adjust its pH value to 1. In next stage, the ammonium bicarbonate was added to increase the solution pH to 6. The phosphor and urea (urea to Si in TEOS was 10:1) were added to the above mentioned solution in a water bath at $95^{\circ}C$ with stirring condition. The reaction time was kept at 2 h and the final pH value was 8.The total weight ratio of coated layer (SiO2 in TEOS, TiO2 and their binary mix) to phosphor, was adjusted to 5.0% as optimum value [9]. Table 1 shows the SiO2-TiO2 weight ratios in binary mixtures.

# Results and Discussion

## Identification and Characteristics

Figure 1 shows the FT-IR spectra of the un-coated $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$ phosphor. As observed, the stretching vibration modes of $SrAl_2O_4$ were appeared at 646 (Sr-O), 782 (Al-O), 849 (Al-O) and 898 (Al-O) $cm^{-1}$ [9, 21]. The appeared peak at 3427 $cm^{-1}$ was attributed to stretching vibration of –OH group representing water as moisture in tested sample, un-coated phosphor [21]. However, another observed peak at 446$cm^{-1}$ was attributed to symmetric vibration of the O-Al-O. Figure 2 represents the FT-IR spectra for coated phosphor with silica (A100, Table 1). As shown, the Si-O peak was appeared around 1095 $cm^{-1}$. This peak was seen in the same position for the rest samples with various silica ratios in binary SiO2-

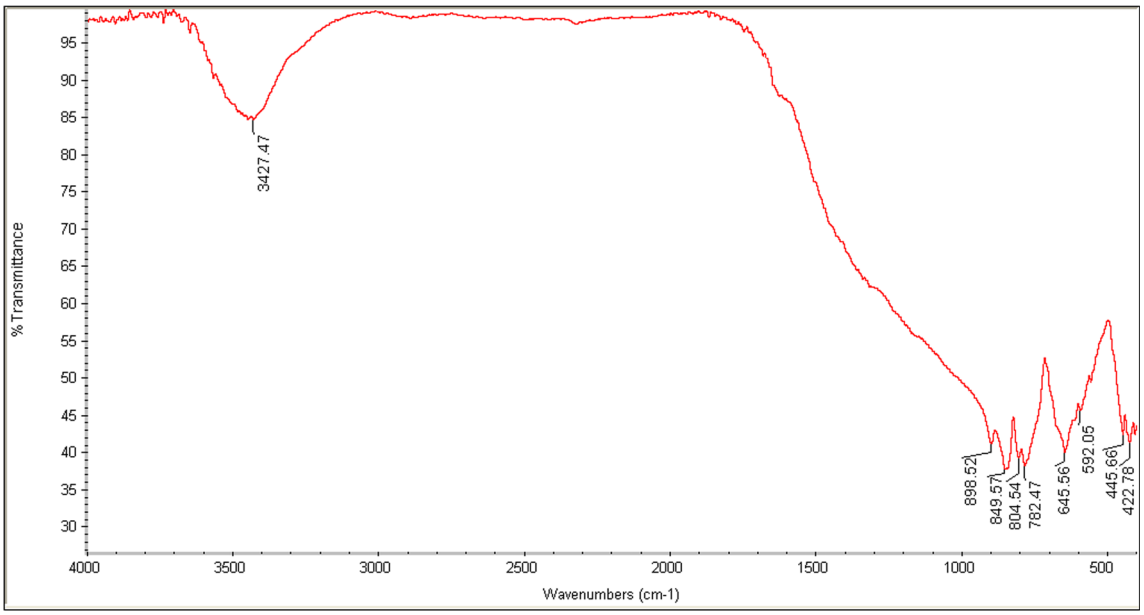



**Fig. 1** The FT-IR spectra of the un-coated $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$ phosphor

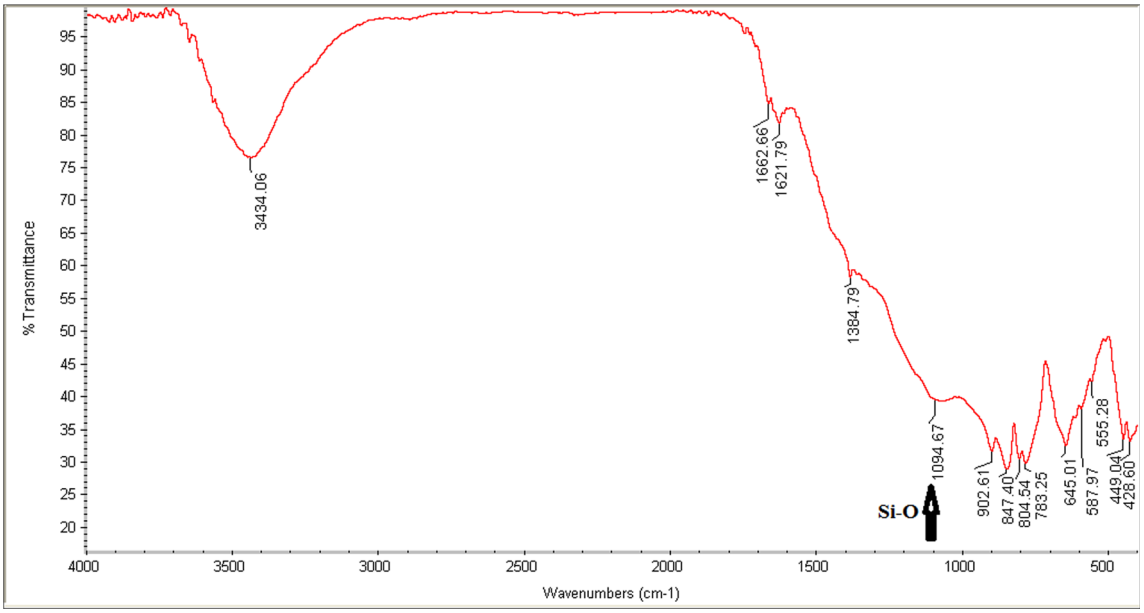



**Fig. 2** The FT-IR spectra of the coated $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$ phosphor by silica (sample A100, Table 1)

TiO2 mixtures (Fig. 3 for samples A90,A70, A50 and A30, Table 1). This is a good evidence for coating of the SiO2 on the phosphor surface. However, as expected, Si-O peak was not observed for the sample A0 with wholly coated phosphor with TiO2 (Fig. 4). Interestingly, comparing the stretching vibration intensities for the –OH group (water as moisture) for un-coated and coated phosphors with different SiO2-TiO2 ratios, clearly shows lower intensities for coated phosphors with a binary mixture of SiO2-TiO2 layer (compare appeared peaks around $3400cm^{-1}$ in Figs. 1, 2, 3 and 4). This is desirable because, it predicts lower moisture absorption by the coated phosphors [12]. This fact will be discussed in detail during water resistance consideration of the coated phosphors. The most distinguishable TiO2 peaks were appeared between 450 and $800cm^{-1}$[28]. However, due to the most of these peaks were overlapped by the stronger phosphor peaks in the same range, for detection of the Ti element in the sample, EDS analysis was performed. Table 2 shows the elements wt%'s for un-coated and selected coated phosphors obtained by EDS. Figure 5 also shows the EDS spectra for the un-coated phosphor and coated phosphors with various SiO2-TiO2 ratios in coated layer, A0, A100

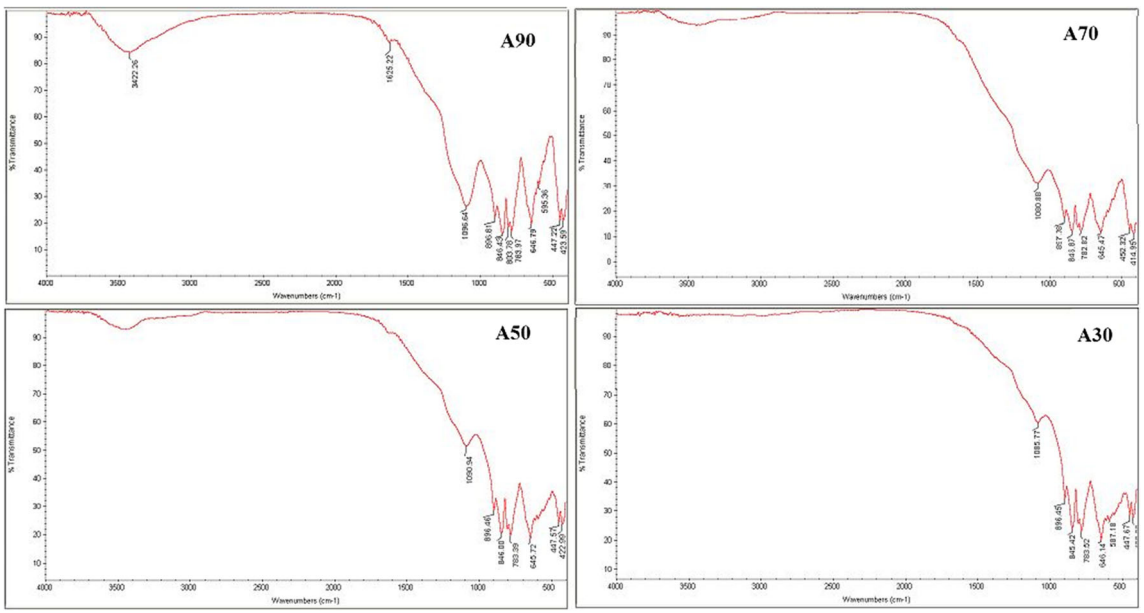



**Fig. 3** The FT-IR spectra of the coated $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$ phosphor by binary silica-titanium dioxide mixtures with different ratios (samples A90, A70,A50 and A30, Table 1)

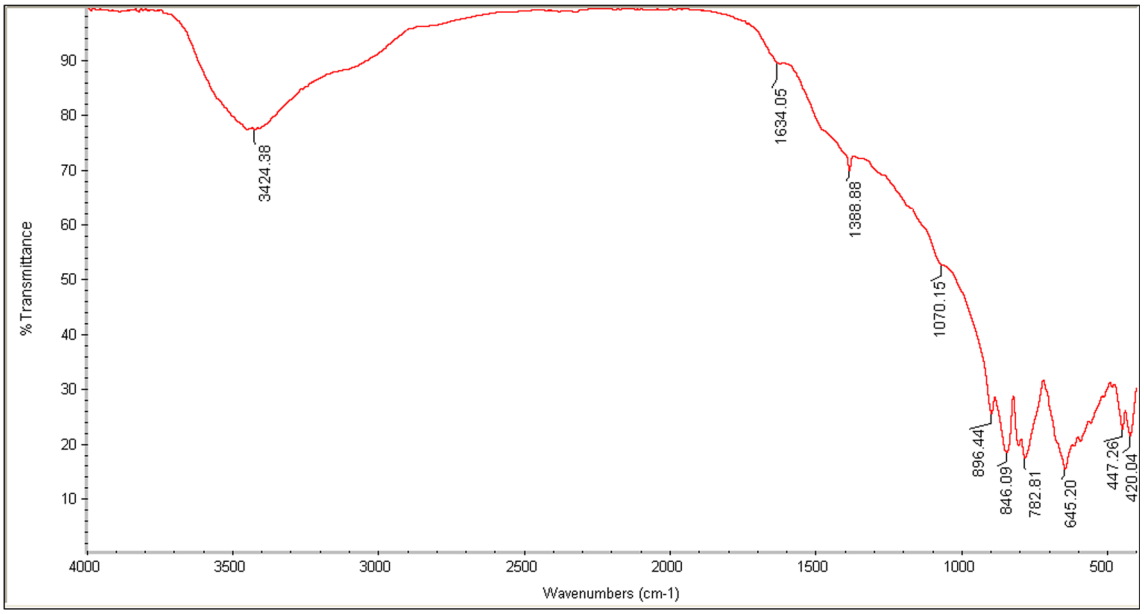



**Fig. 4** The FT-IR spectra of the coated $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$ phosphor by titanium dioxide (sample A0, Table 1)

and A50, respectively. As observed, the un-coated phosphor contains 40, 19 and 40 wt%, elemental oxygen, aluminum and strontium in composition, respectively. However, for 100% TiO2 coated phosphor (sample A0, Tables 1 and 2), 9% elemental Ti was observed. Figure 5 (for A0 and A50) shows three distinguished peaks attributed to Ti at 0.5, 4.5 and near 5 keV. This also was confirmed by another research [28]. With considering of the above observations, it was concluded a proper coating of the TiO2 on the used phosphor. For equal SiO2-TiO2 ratio (sample A50), 3 and 21%, Si and Ti, respectively, were observed in coating layer composition. The higher value for Ti shows the more trend of TiO2 for coating on the phosphor when compared with the SiO2. Table 2 also shows 5% Si available in coated phosphor with 100% SiO2 (Sample A100, Table 1). The corresponding Si peak was appeared near 2 keV (Fig. 5 for A0, A50 and A100). Our founds were in conformity with the others [9, 12–14]. Figure 6 represents the SEM micrographs of un-coated (a) and coated, A0 (b), A50 (c) and A100 (d) phosphors. As observed, the un-coated phosphor particles had sharp edges with rough surface. This is a typical characteristics of prepared $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$ phosphor grinded powder [9]. Moreover, the correspondent micrographs for coated $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$ phosphor particles showed that soft edges with smooth surfaces covered by SiO2, TiO2 and or SiO2-TiO2 binary mixture layer. The continuous and uniform SiO2-TiO2 layer proved the eligibility of the used precipitation method utilizing urea hydrolysis for efficient coating of the $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$ phosphor. It seems, the availability of the above mentioned coating layer improves the water resistance and afterglow properties of the coated phosphor as it will be discussed later in this text.

**Table 2** The elements wt%'s for un-coated and selected coated phosphors obtained by EDS

| Sample | O (wt%) | Al (wt%) | Sr (wt% | Si (wt%) | Ti (wt% |
|---|---|---|---|---|---|
| Un-coated | 40 | 19 | 40 | – | – |
| A0 | 56 | 17 | 18 | – | 9 |
| A100 | 48 | 18 | 28 | 5 | – |
| A50 | 47 | 11 | 17 | 3 | 21 |

Average crystallite size of a crystal was estimated according to the Scherrer's eq. [29] as follow:

$$D = \frac{k\lambda}{\beta\cos\theta} \quad (1)$$

Where K is the Scherrer constant, λ, the X-ray wavelength, β, the peak width of half maximum, and θ is the Bragg diffraction angle. Table 3 shows the average crystallite size (D) of the un-coated and selected coated $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$ phosphor crystals (A100, A50 and A0, Table 1) derived by XRD technique. As observed, the D values were 14.7 nm for un-coated and A100 samples which increased to 20 and 23 nm for equal ratios SiO2-TiO2 coated phosphor (A50) and wholly covered phosphor by TiO2 (A100). Apparently, the existence of the TiO2 in the coating layer had beneficial effect on the D value. The means SiO2 (TEOS) and TiO2 particle diameters (Particle size analyzer, Vasco3,Cordouan, France) were 385 and 454 nm respectively. The greater TiO2 particle size along with higher tendency for agglomeration when compared with SiO2 was the reason of higher D values for samples A50 and A0 with TiO2 in content.

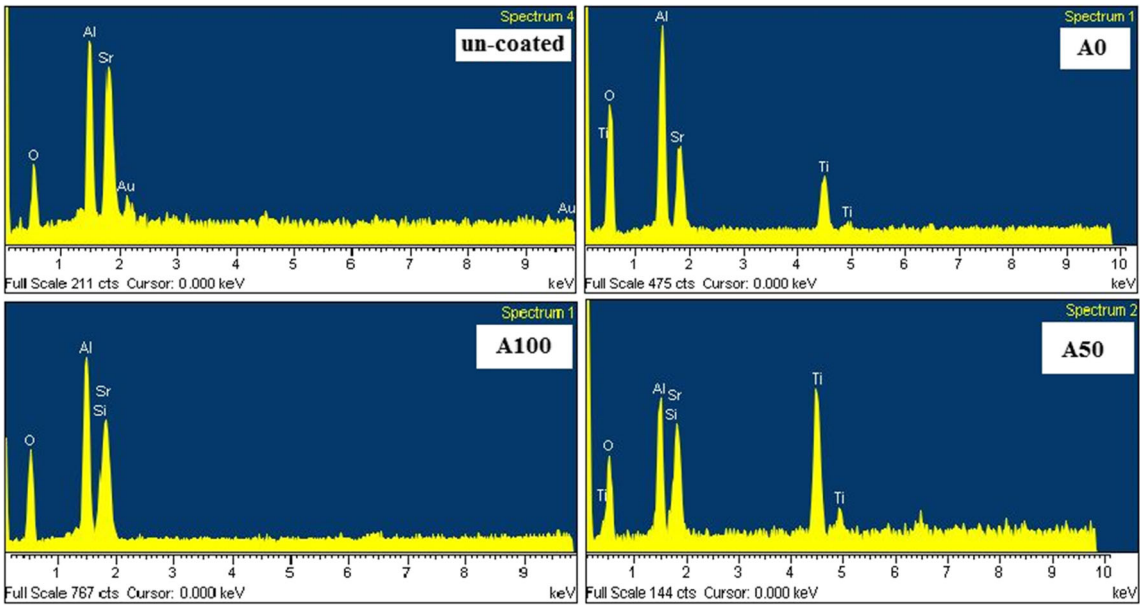



**Fig. 5** The EDS spectra for the un-coated and coated phosphors with various SiO2-TiO2 ratios in coated layer

The XRD patterns of the un-coated and coated phosphors were shown in Fig. 7. In general, the comparison between un-coated pattern with coated patterns revealed that the coating of the phosphor with SiO2 and TiO2 has not changed the phase structure of the phosphor sensitively. This found was in conformity with the other report [30]. Moreover, there were no sensitive differences between patterns of the un-coated with totally SiO2 coated phosphor (A100). The amorphous nature of the SiO2 prevents the appearance of the characteristic XRD peaks in the XRD patterns [9, 31].

## Water Resistance and Afterglow Properties

The un-coated SrAl2O4:$Eu^{2+}$, $Dy^{3+}$ phosphors hydrolyze in water easily. The hydrolyzed solutions represent alkaline behavior as shown in eq. 2 [9].

$$SrAl_2O_4 + 4H_2O \rightarrow Sr^{2+} + 8OH^- + 2Al^{3+} \quad (2)$$

After dispersion of the above mentioned phosphor in water, the pH will be increased because hydroxyl ion generation (eq. 2). Hence, monitoring the solution

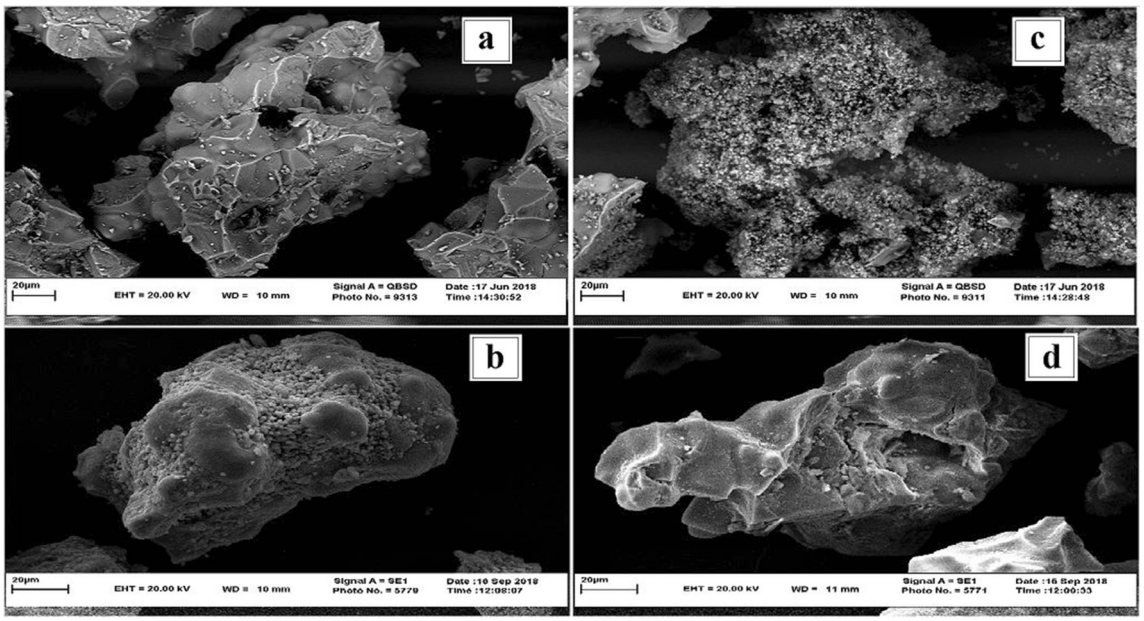



**Fig. 6** The SEM micrographs of un-coated (**a**) and coated, A0 (**b**), A50 (**c**) and A100 (**d**) phosphors

**Table 3** The average crystallite size of the un-coated and selected coated $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$ phosphor crystals derived by XRD technique

| Sample | β(degree) | 2θ (degree) | D (nm) |
|---|---|---|---|
| Un-coated | 0.55 | 29 | 14.7 |
| A100 | 0.55 | 29 | 14.7 |
| A50 | 0.41 | 29 | 20 |
| A0 | 0.35 | 29 | 23 |

pH with time will be a good criteria for evaluation and measurement of the water resistance of the un-coated and coated phosphors. Figure 8 shows and compares the dispersed phosphor solution pH versus time for un-coated, and coated phosphors, A100,A50 and A0. As observed the initial pH of all solutions were 6.1. However, for un-coated phosphor (A), it rapidly increased with a sharp slope to the value of 10.4 after 30 min. After 30 min, the slope reduced and eventually, the pH value reached to 11.7 after 7 h and curve reached to a plateau. This was evidenced as rapid hydrolyze of the un-coated phosphor [9]. The total pH changes for A, A100, A50 and A0 were 5.6, 1.5, 4.8 and 3.4, respectively. The related curves for A100, A50 and A0 reached to a plateau after 4, 2 and 8 h, respectively. As observed, the availability of the TiO2 in coated layer had beneficial for water resistance of the coated phosphor, although, in comparison with SiO2, it was less effective. With considering above observations, it observed that the SiO2 deteriorated the complete hydrolysis of the coated phosphor and reduced it from 7 h for A to 4 h for A100 while the TiO2 improved it from 7 h to 8 h for A0. It was concluded that the availability of the TiO2 in formulation of the coating layer protects the phosphor (pigment) from air moisture and water [22].

The emission (photoluminescence) spectra of the un-coated and selected coated phosphors represented in Fig. 9. As observed, because the ratio of Al/Sr in used phosphor was 2, the intensities at 531 nm was the highest for the tested phosphors and the emitted color was green [23]. The green light was the result of electron transfer from $4f^6 5d^1$ *to* $4f^7$ orbital of the $Eu^{+2}$ when SrAl2O4 was the host. Because the maximum intensities for all spectra were the same at 531 nm, it may conclude that the crystalline structure of the phosphor has not changed after coating as discussed earlier during study of the XRD patterns of coated phosphors. Surprisingly, the intensities of the TiO2 content coating layers were remarkably higher when compared with un-coated (A) and also totally coated phosphor with SiO2 (A100). The reason refers to relatively high refractive index of the used TiO2 white powder with the value of 2.71 when the corresponding value for SiO2 (TEOS) was 1.56. Fig. 9 also shows the availability of the SiO2 in coating layer deteriorated the emission of the phosphor. However, the emission increased with increasing the amount of the TiO2 in coating layer. Figure 10 compares intensity changes for un-coated and coated

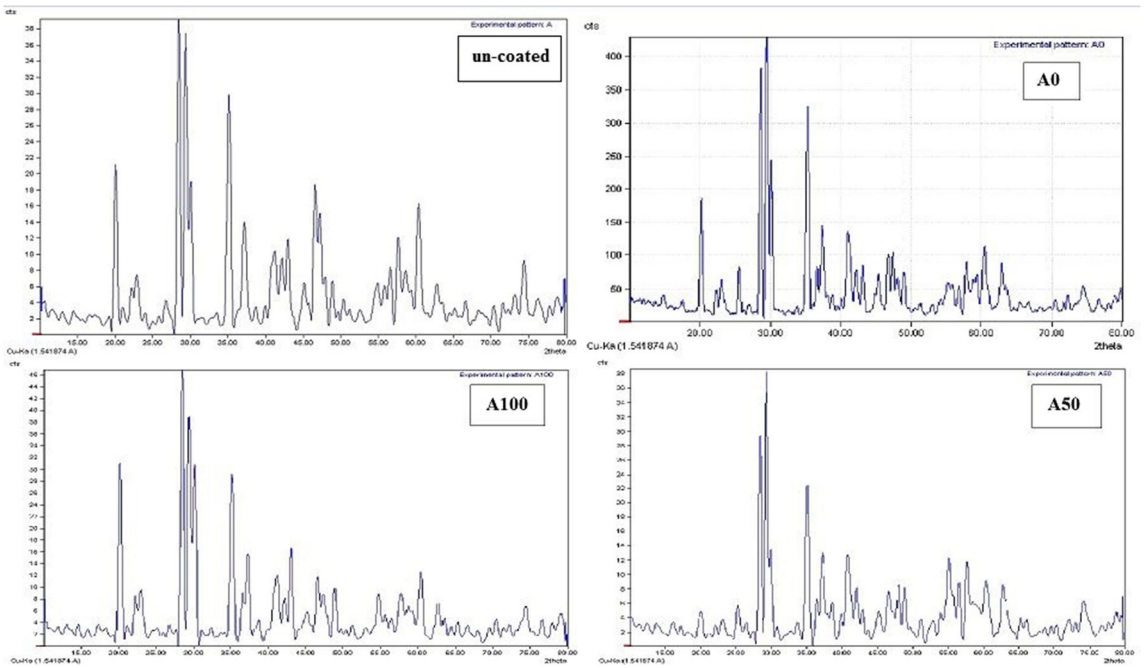



**Fig. 7** The XRD patterns of the un-coated and selected coated phosphors

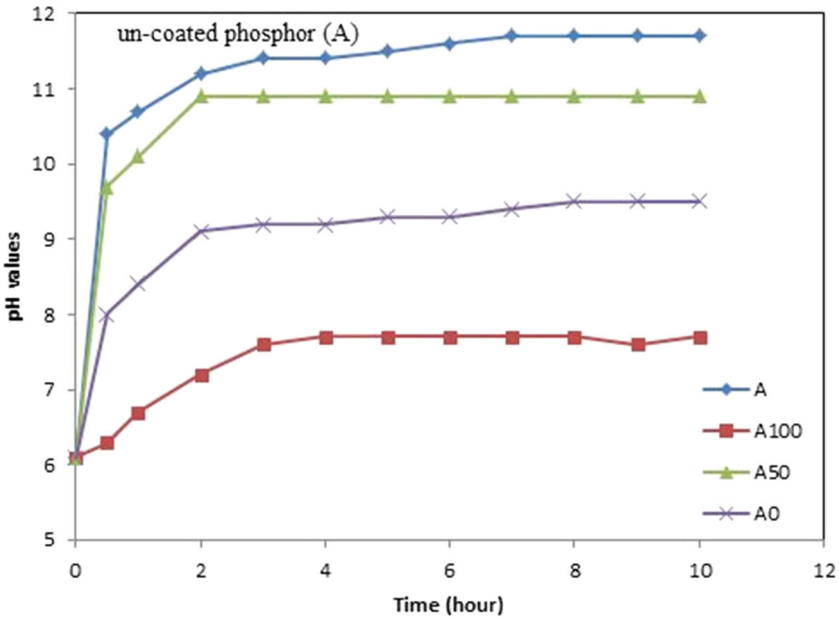



**Fig. 8** The dispersed phosphor solution pH versus time for un-coated, and coated phosphors, A100, A50 and A0

(A50) phosphors before and after hydrolysis in water for 10 h. As observed, this parameter was about twice for un-coated phosphor when compared with coated one. As a conclusion, coating the phosphor was beneficial for color emission stability of the phosphor. Our founds were in conformity with the other report [9, 22]. Figure 11 represents the afterglow brightness decay curves for un-coated and coated phosphors, A100, A90, A50 and A0. As observed, unlike of the un-coated and wholly coated with SiO2 phosphors, the phosphors with the TiO2 content in coating layer, had the minimum intensity decay versus time. Based on observed results from Figs. 9, 10 and 11, coated phosphor with equivalent SiO2-TiO2 ratio was selected as optimum sample. As an important conclusion, the existence of TiO2 in coating layer improved afterglow performance of the phosphors without considerable decay after aging. As mentioned above, the reason refers to high refractive index and photocatalytic property of the TiO2 [32]. Moreover, the increase of the phosphor particle size after encapsulation with TiO2 was an evidence for photoluminescence improvement [12].

## Paint Appearance

To evaluate the photoluminescence property of the un-coated and coated phosphors in a paint, the phosphor

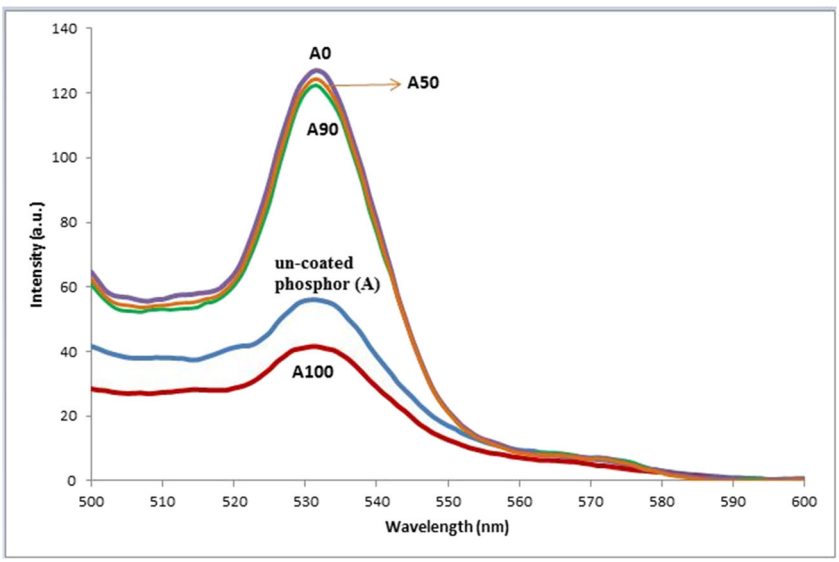



**Fig. 9** The emission spectra of the un-coated and selected coated phosphors

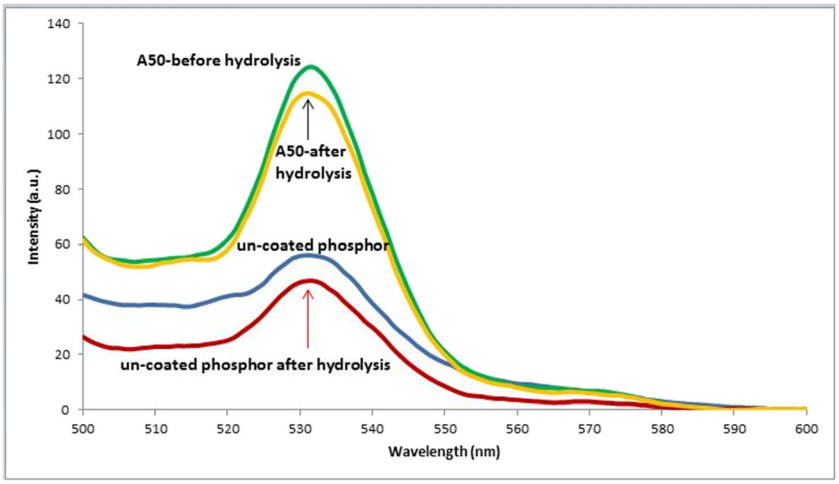



**Fig. 10** The intensity changes for un-coated and coated (A50) phosphors before and after hydrolysis in water for 10 h

(pigment) was added to a glassy beaker already contained a waterborne acrylic resin (New color paint company, Tehran) with the pigment-resin weight ratio of 30–100 and the mixture well stirred for 10 min. Subsequently, the prepared paints irradiated and exposed against a UV source at 390 nm for 15 min and their appearances were evaluated by taking photo from them. Tables 4, 5 and 6 show the appearances for paints contained un-coated phosphor, A100, A50 and A0 before irradiation, after 15 min UV irradiation and subsequent 1 h aging, respectively. As observed from Table 5, all irradiated samples showed suitable photoluminescence property. However, for totally SiO2 coated phosphor (A100) less photoluminescence was observed because the refractive index of the SiO2 was lower than the TiO2 as explained earlier. As expected, aging had inverse effect on photoluminescence of the samples but still after passing 1 h, acceptable photoluminescence was observed for all samples (Table 6).

## Conclusions

From this study it was concluded that SiO2 and TiO2 individually and in combination were precipitated on the studied commercial $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$ phosphor successfully. From the EDS spectra study, the higher trend of the TiO2 for coating on the phosphor when compared with the SiO2 was observed. The SEM micrographs showed a continuous and uniform SiO2-TiO2 layer on the coated phosphor. It was a good evidence for the eligibility of the used precipitation method utilizing urea hydrolysis for efficient coating of the $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$ phosphor. Based on XRD results, the existence of the TiO2 in the coating layer had beneficial effect on the average crystallite size values. The pH solution versus time showed that the availability of the TiO2 in coated layer improved the water resistance of the coated phosphor, although, in comparison with SiO2, it was less effective. It found that the coating of the phosphor increased color emission stability of the

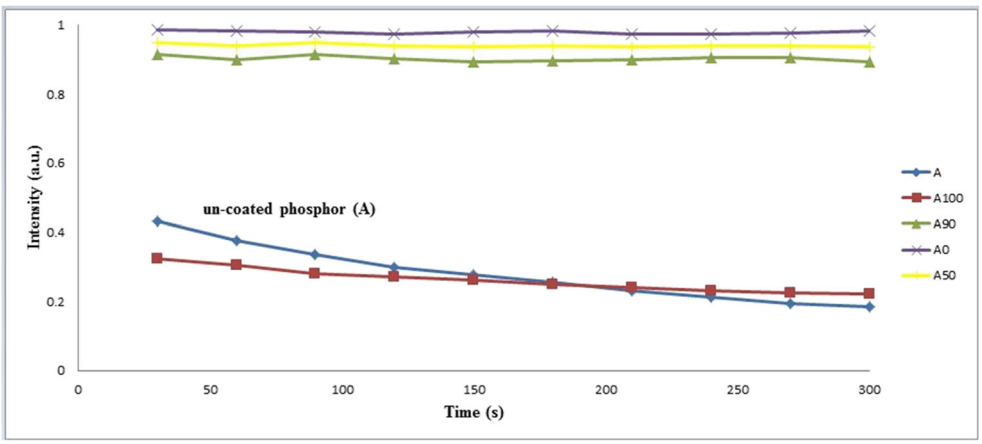



**Fig. 11** The afterglow brightness decay curves for un-coated and coated phosphors, A100, A90, A50 and A0

**Table 4** The appearances for paints contained un-coated phosphor, A100, A50 and A0 before irradiation

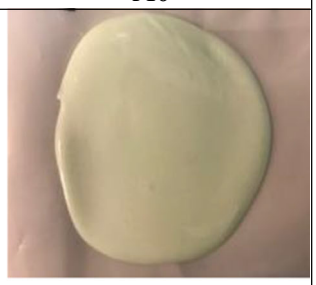
| Sample | | | |
|---|---|---|---|
| Un-coated | A100 | A50 | A0 |
|  |  |  |  |

**Table 5** The appearances for paints contained un-coated phosphor, A100, A50 and A0 after 15 min UV irradiation

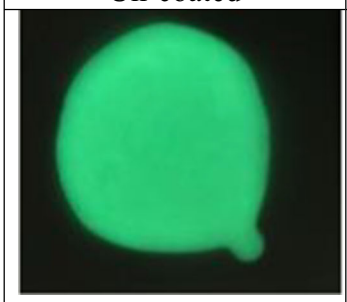
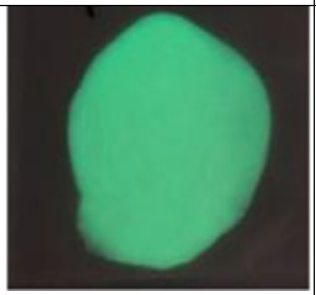
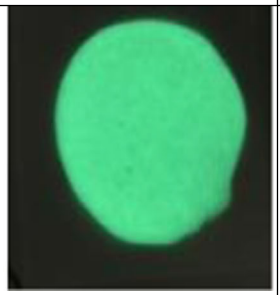
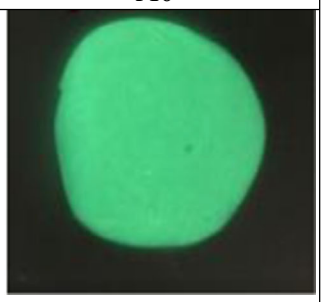
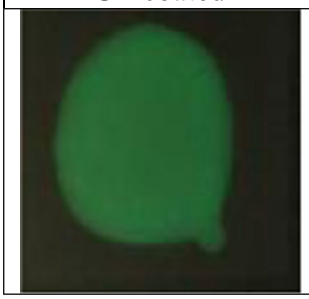
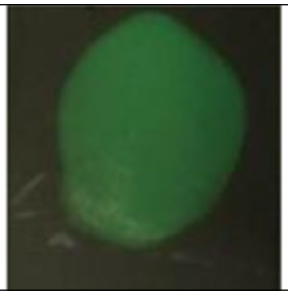
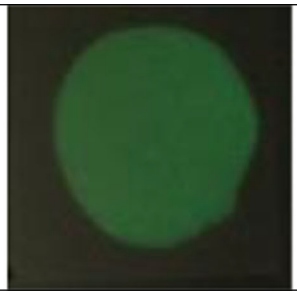
| Sample | | | |
|---|---|---|---|
| Un-coated | A100 | A50 | A0 |
|  |  |  |  |

**Table 6** The appearances for paints contained un-coated phosphor, A100, A50 and A0 after 15 min UV irradiation and subsequent 1 h aging

| Sample | | | |
|---|---|---|---|
| Un-coated | A100 | A50 | A0 |
|  |  |  |  |

phosphor. It observed, unlike of the un-coated and wholly coated with SiO2 phosphors, the phosphors with the TiO2 content in coating layer, had the minimum afterglow brightness decay. Therefore, the phosphor with TiO2 in coating layer was recommended as a suitable pigment for waterborne photoluminescence paints. Based on observed results, coated phosphor with equivalent SiO2-TiO2 ratio was selected as optimum sample.

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