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ORIGINAL PAPER

Inkjet Printable Luminescent Eu^{3+}-TiO_2 Doped in Sol Gel Matrix for Paper Tagging

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Abstract Europium (III) with different concentrations (0.2, 0.4 and 0.8 %)-TiO_2 doped silica composite systems were sensitized by sol–gel method. Different spectroscopic and microscopic tools characterized the composites. The Europium ion incorporated into the liquid silica–titania solution acts as red light emission center in the luminescent materials. This luminescent nano composite pigment has great potential of application in preparing luminescent ink. Inkjet printer loaded with the prepared ink to show its potential usage as tagging material performed the printing test on a white paper.

Keywords Nano composite · SiO_2-TiO_2 · Sol–gel method · Eu^{3+} ion · Luminescent ink · Ink-jet printing

Introduction

Recently, the inorganic – organic hybrid materials have shown great usefulness in the fields of material science and nanotechnology. The incorporation of lanthanide ions into inorganic hybrid host materials has been extensively explored in recent studies and the obtained materials have been found to show high improvements for their thermal, mechanical properties and chemical stability [1].

Silica–titania is an attractive hybrid inorganic glassy system suitable to incorporate rare-earth ions. It is characterized by the high thermal stability, chemical durability and mechanical strength in addition to an adjustable refractive index in a wide range. [2, 3].

The sol–gel technique provides an excellent way for the preparation of transparent inorganic–organic hybrid materials at room temperature, and offers the possibility to prepare the materials with an attractive improvement in their physical and chemical properties [1–7].

Europium (Eu) usually characterized by red emission ascribed to the $^5D^0$– $^7F^{0-6}$ transitions and with high luminescence efficiency under UV excitation [3, 7].

Synthetic fibers make luminescent using a europium (III) complex is present in certain Euro bank notes, which will show the typical red glow from europium complexes under UV lamp indicating that banknote is not a counterfeit.

It is worth noting that the newest methods of printing used by counterfeiters produce documents of such good quality that questioned documents examinations are more and more challenging and forgeries are harder to detect. What is more, the scourge of falsification and document alteration is growing rapidly in every public field and may affect most documents connected with such fields. There are thousands of documents with different types and levels of protection (watermarks, special inks or paper, invisible patterns, etc.), which can be counterfeited.

Furthermore, no less problematic is the increase in forged ink production, which, nowadays, has reached epidemic proportions. Counterfeit inks – not to be confused with off-brand compatible inkjet inks – can be found in just about every distribution channel imaginable.

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In the past few years, luminescent inks are potential for detecting any counterfeiting, alteration, and unauthorized trading. Obvious applications of these inks include banknotes, branded goods, drug packaging, fiscal stamps and food security. The security ink is invisible under visible light, but when being irritated with ultraviolet radiations, it emits light and the recorded information can be read.

Interest in ink-jet printing is growing fast because of its use in various applications and technical variations such as in electronics, biotechnology, and polymers, ceramics, and solar cells as well as in conventional graphic applications [8–10].

Inkjet printing process reveals a number of advantageous such as precise material deposition on paper or substrate at well-defined position, low material consumption, and less material wastage [7], the ability to dispense uniform droplets in the peculator range with high degree of accuracy, offer possibilities to deposit a variety of functional materials onto different types of carrier surfaces or substrates [10], excellent pattern quality, considerably little pollution, and especially fast response to the frequent shift of cloth fashion, ease with which it can be used in mass production, low costs of materials and equipment, and flexibility [9]. Furthermore, it is a noncontact technique that offers ease of patterning in various industrial processes. In this paper we prepare and characterize nano composite of different concentrations of Eu^{3+} ion -TiO_2 doped in sol–gel matrix. This nano composite will be used to prepare luminescent ink. Inkjet printer loaded with the newly prepared nano-ink will be used for printing test on white paper to explore exploitation as tagging material.

Expremental

Material and Reagents

Europium nitrate hexa-hydrate, $[Eu(NO_3)_3 \cdot 6H_2O]$,, Hydrochloric acid (HCl) and absolute ethanol, (C_2H_5OH) were purchased from Sigma Aldrich (99.9 % pure grade). Tetraethylorthosilicate (TEOS) and Titanium (iv)tetraisopropoxide Ti $[O(C_3H_7)]_4$ (TTIP) 98 %, were purchased from Fluka. 5,5'-Diethylene glycol, glycerol, urea, sodium hydroxide and poly vinyl alcohol were purchased from Fluka. we used paper A4 80gm^2 as a substrate for printing.

Characteristics of the used paper for printing process.

– PaperOne™ All Purpose is a premium quality home and office paper made in Indonesia for all printing and copying machines, made from renewable fiber. With its superior opacity, designed to fit in all kinds of equipment

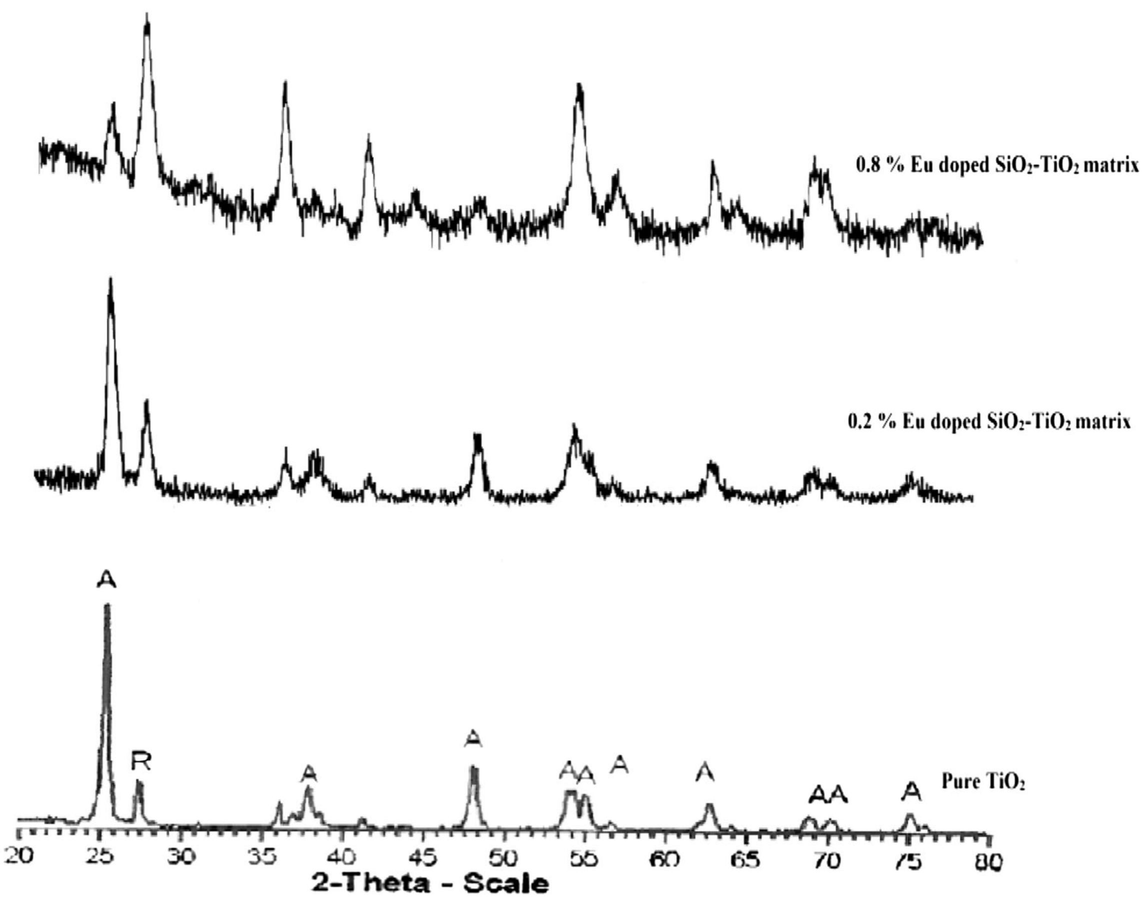

Fig. 1 X-ray diffraction pattern of pure TiO_2, 0.2 and 0.8 % Eu (Ш) doped (SiO_2-TiO_2) matrices

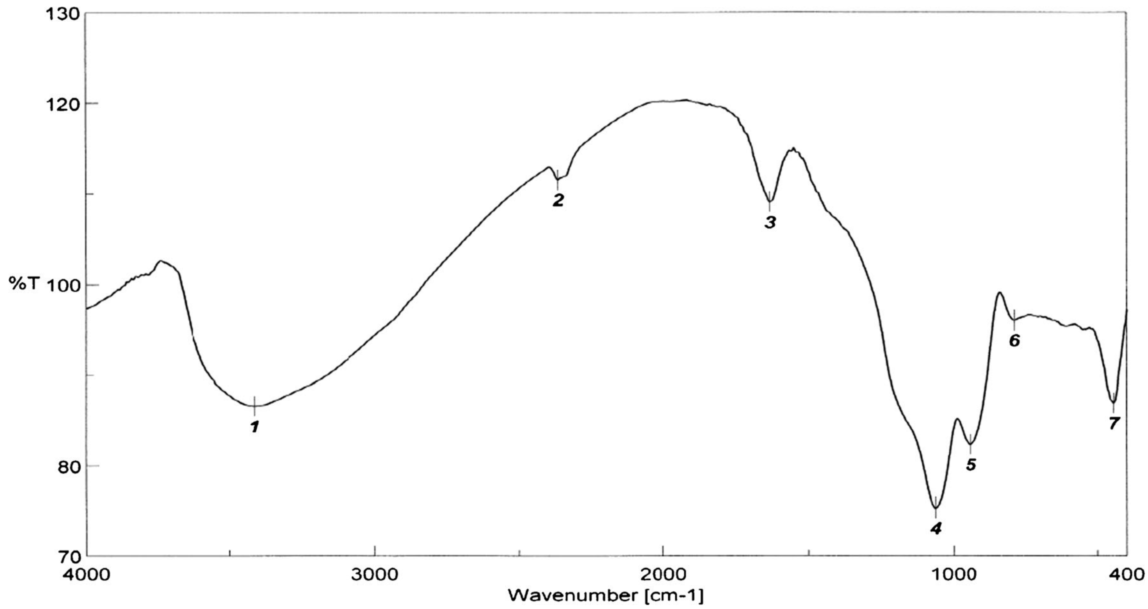

Fig. 2 FT-IR spectrum of the dried and annealed Eu: SiO_2TiO_2 sample

using inkjet and xerographic principles. Examples of usage areas are presentations, newsletters, proposal copies, graphics, memos, reports, resumes and letters.

– Made from 100 % plantation fiber.
– APRIL Acacia pulp has a low hemicellulose content that improves stability since less water is either added to the paper (offset) or removed from the sheet (copying). High number of fibbers also improves dimension stability. Better dimensional stability means less curling, wrinkling and thus less jamming.
– Acacia fibers have thinner fiber walls and thus more collapsed fibers, which results in a paper with inherently very low roughness. When combined with high number of fibers per gram with a very short fiber length, this produces excellent printing results in offset, xerography and ink-jet printing. Additionally, Acacia has a narrow fiber length distribution which is important for ink absorption, especially for offset and ink-jet printing.

Instrumentations

The morphology of samples was characterized using Transmission Electron Microscopy, (TEM JEOL JEM-1230) instrument, X-Ray Diffraction patterns (XRD) were measured using a Philips Analytical, X'Pert PRO, fourier transform infrared spectrum was detected using a Shimadzu with a shimadzu CVT-04 spectrophotometer using aperkin Elmer/1650, all luminescence measurements were recorded with a Meslo-PN (222–263000) Thermo Scientific Lumina fluorescence

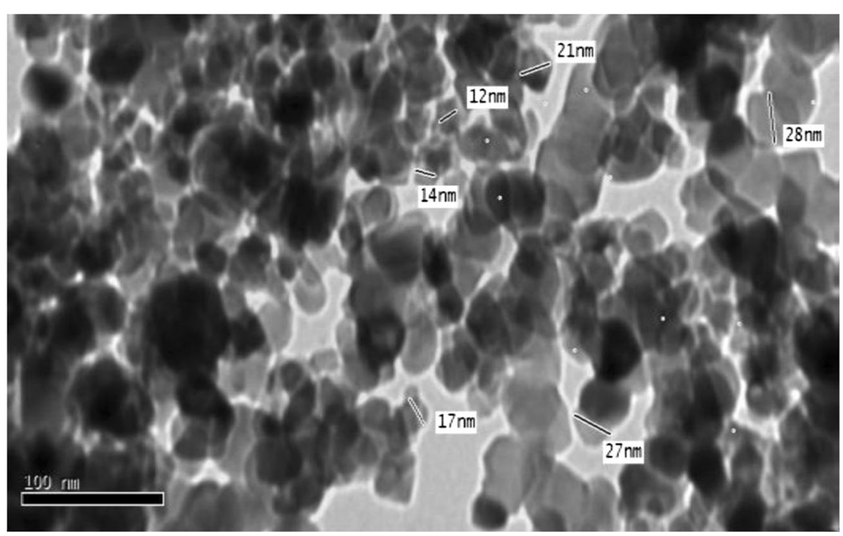

Fig. 3 TEM images of TiO_2

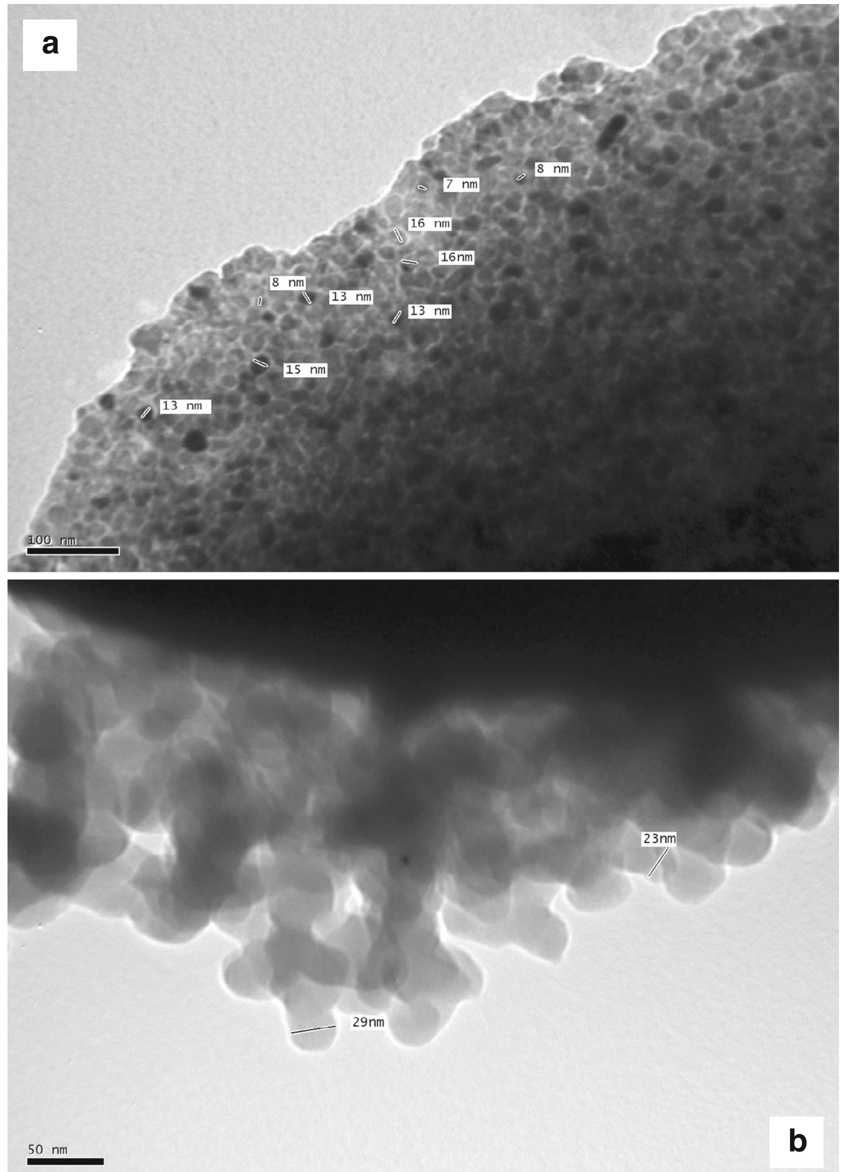

Fig. 4 TEM images of **A** 0.2 % Eu doped TiO_2/SiO_2. **B** 0.8 % Eu doped TiO_2/SiO_2

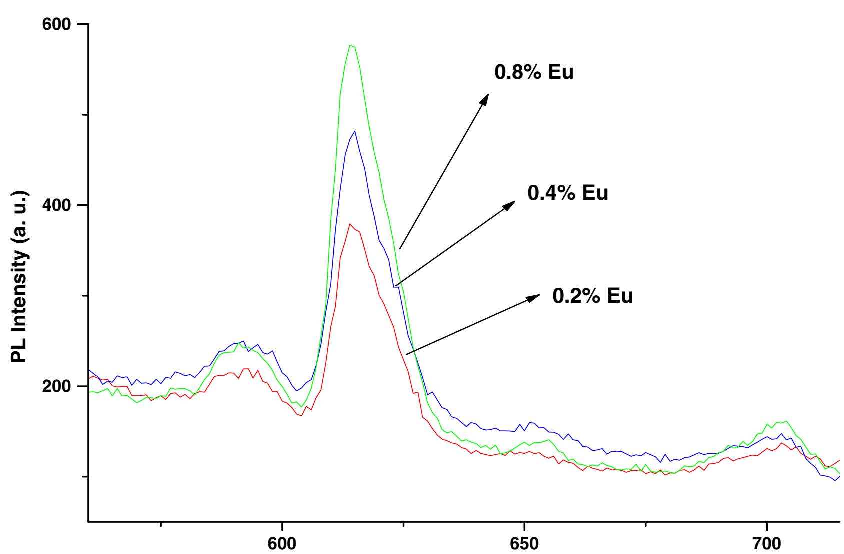

Fig. 5 Photoluminescence spectra of 0.2, 0.4 and 0.8 % Europium- doped silica- titania at λ_{ex}=380 nm

Spectrometer in the range (190–900 nm), dynamic Viscosity ( ) of the prepared inkjet inks measured using Brookfield Model Dv – 111, programmable R geometer, and Luminescence images of the printed Sample were investigated by Video Spectral Comparator (VSC 6000). ultrasonic (Sonics and materials inc model vcx 750 V 230 vac).

Preparation of Luminescent Europium Doped in Titania–Silica Matrix by Sol–gel Method

The Europium (III) doped $Ti[O(C_3H_7)]_4$ and TEOS nano crystals was prepared by doping Eu (III) into TiO_2 and silica using a sol–gel process. TEOS (5 mL) was added to 30 mL of absolute ethanol at room temperature with vigorous stirring followed by the calculated amount of Europium (dissolved in 10 ml of absolute ethanol), then added 3 mL of (TTIP) under vigorous stirring and covered by alumina foil and added few drops of HCl as a catalyst and reflux for 2 h. The resulting transparent colloidal suspension was put in refrigerator for 12 h till the formation of gel. The gel was dried at 353 K and then ground. The powder was calcinated at 1000 C for ½h.

Preparation of Ink Jet Inks

Two inkjet inks were prepared by varying the dispersed prepared luminescent nano composite 0.2 and 0.4 % Eu (III): TiO_2- SiO_2 with a pigment-to-polymer ratio of 2:1. The formulation in a weight basic for preparing the pigment ink jet inks is shown as follows: pigment dispersion 8 %, diethylene glycol 10 %, glycerol 10 %, urea 5 %, Polyvinyl alcohol (PVA) 4 % and de-ionized distilled water 63 %. The ink components were mixed together by ultrasonic at 100 rpm for 10 min or until a homogeneous solution was obtained. Then, sodium hydroxide (10 % by weight) was added to control the ink pH to a range of 7–9. The inks were later filtered through a 8 μm pore filtering sieve. After the inks had been prepared, they were stored in capped glass vessels and placed in a desiccators to avoid absorption of moisture from the air [11]. Then the inks were loaded into the inking unit of the modified printer (HP DeskJet 1050 A PRINT SCAN COPY).

Table 1 The viscosity and shearing for (0.4 % Eu) ink at different rates of shear

Rate of shear (s^{-1})	Shearing (d/Cm^2)	Viscosity (cP)±sd[a]
46.0	6.98	14±0.05
93.0	13.5	13.3±0.04
140	19.2	13±0.03
186	25.6	12.8±0.04
233	32.6	12.3±0.025

[a] *sd* is standard deviation for three measurements

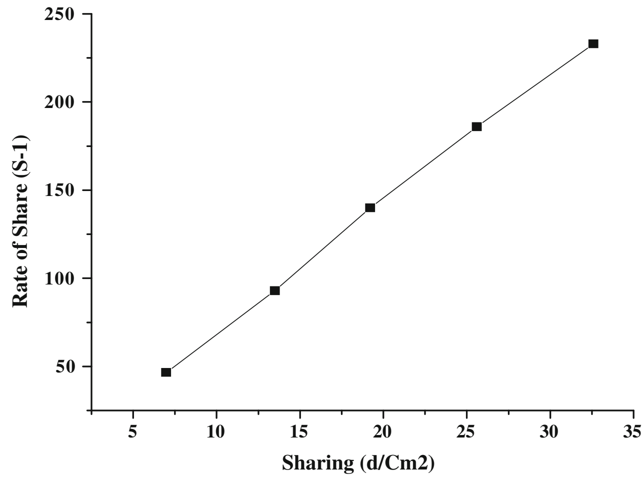

Fig. 6 Plot of rate of share (S^{-1}) as a function of sharing (d/C^2) for ink (0.4 % Eu)

Results and Discussion

The XRD patterns show that the peaks at 2 =25.17, 37.77, 48.03, 55.08 and 62.56° in the spectrum of pure TiO_2 is easily identified as the crystal of anatase form and a very low peak intensity at 2 =27.40° which is easily taken as the crystal of rutile form. The analytical results showed that the relative intensity of peak at 2 =25.17 decreased significantly in doped TiO_2 with respect to the un-doped TiO_2 nanocrystal. These results indicate that Eu doping inhibits the phase transformation from amorphous to anatase in the solid, leading to higher thermal stability [5], Fig. 1. There is a broad peak centered at 2 =23° which is characteristic to amorphous SiO_2 [6].

The FT-IR spectrum of the dried and annealed Eu: SiO_2TiO_2 sample is shown in Fig. 2. The transmission peak at 740 and 790 cm^{-1} are originated from the Si–O–Si symmetric and asymmetric stretching vibration modes [3]. The band at 940 cm^{-1} is attributed to Si–O–Ti vibration modes and

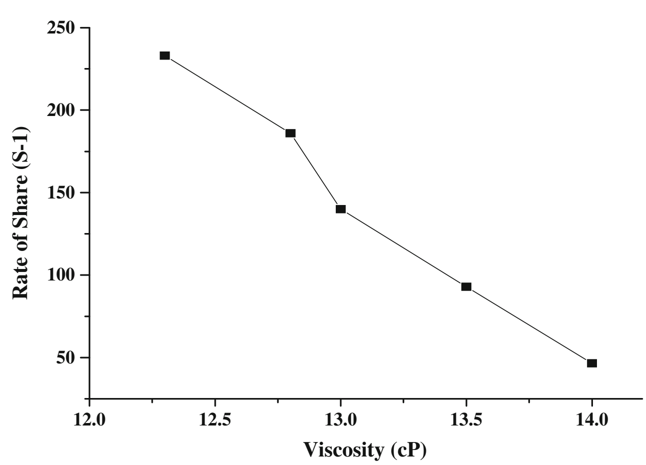

Fig. 7 Plot of rate of share (S^{-1}) as a function of viscosity (cP) for ink (0.4 % Eu)

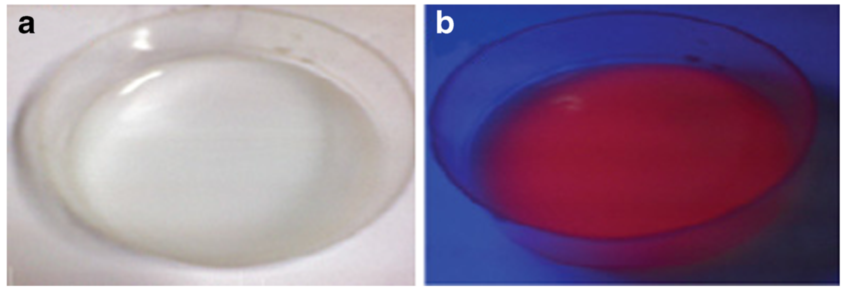

Fig. 8 Picture of luminescent Eu^{3+} doped silica – titania matrices **A** without UV illumination and **B** under UV illumination

Si–OH groups, which indicates that titania ions enter into the glass network. The strongest transmission peak at 1040 cm^{-1} is assigned to the asymmetric stretching vibration of Si–O–Si bonds. Also two bands are observed at 1650 and 3400 cm^{-1} due to –OH bending and stretching vibration modes of adsorbed water respectively [5]. The weak absorption bands 2400 cm^{-1} is due to the asymmetric stretching vibration of atmospheric CO_2.

The FTIR analysis confirmed the proper linkages of Si–O–Ti and Ti–OH and the formation of titanosilicate matrix. Since the Eu^{3+} ion only weakly interact with the SiO_2-TiO_2 matrix during the densification process, these ions can position themselves at the pore sites of the matrix. This is supported by the FTIR spectrum which shows no bonding between the Eu $^{3+}$ ion with SiO_2-TiO_2 matrix. The proof for the non-bonding of Eu^{3+} ion with SiO_2-TiO_2 matrix has already been reported by other works [6].

Figure 3 shows a Transmission electron microscopy (TEM) images of pure TiO_2 morphology with average particle diameter 23 nm. Figure 4A and B show the TEM morphologies of the prepared 0.2 and 0.8 % Eu (Ш): SiO_2-TiO_2 materials, which reveals that the prepared materials are nano particles with different shapes with average particle diameter 9.75 and 26 nm, respectively.

It can be clearly seen that doping with 0.2 % Eu (Ш) gives nano disks which have cubic shape with the

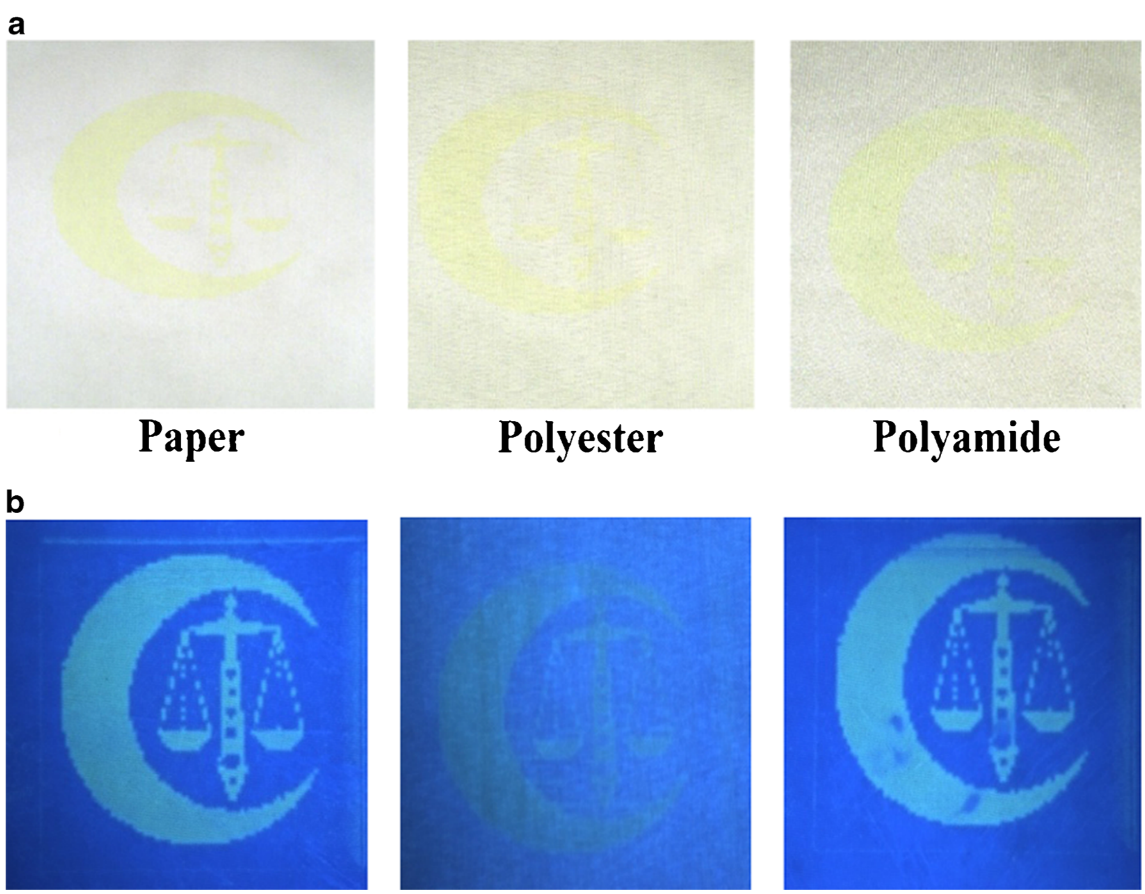

Fig. 9 **a**- printed samples under day-light are included for comparison. **b** - Luminescent Logo of the ministry of justice under UV-A is sharply appeared in case of paper and polyamide samples (Printed ink 0.4 % Eu Doped SiO_2-TiO_2)

uniform size, But doping with 0.8 % Eu (Ш) gives nano disks with spherical shape as shown in (Fig. 4 A and B), this may be due to increasing of Eu (Ш) content, which indicates that the Eu (Ш) ions are isolated from the SiO_2-TiO_2 matrices.

The emission spectra of (0.2, 0.4 and 0.8 %) Eu doped Silica – Titania matrix samples at λ_{ex}=380 nm gives the characteristic emission peaks of Eu ion due to Eu^{3+} transitions from $^5D_0$ excited level to ^7F_J manifolds of the $4f^6$ configuration were detected in the spectra of samples, Fig. 5.

Beside a strong emission attributed to the $^5D_0\rightarrow{}^7F_2$ transition of Eu^{3+} (around 615 nm), additional bands attributed to the transitions $^5D_0\rightarrow{}^7F_0$ (around 580 nm), $^5D_0\rightarrow{}^7F_1$ (around 595 nm), $^5D_0\rightarrow{}^7F_3$ (around 652 nm) and $^5D_0\rightarrow{}^7F_4$ (around 700 nm) were observed. The red colour of the strong luminescence signal is seen by the naked eye, due to the $^5D_0\rightarrow{}^7F_2$ transition implying the satisfactory color purity. Also the $^5D_0$–$^7F_0$ transition (580 nm) consists of one peak, which gives a strong indication that all the europium (III) ions occupy a site of the same symmetry [5].

After the calcinations at 1000 °C, it was possible to individuate only the main peak at about 615 nm and it was evident that the intensity of this red emission peak decreased probably due to the well-known phase transformation of titania at such a high calcination temperature.

It is clear from Fig. 5 that the PL intensity initially increases with increasing in the fraction of Eu. The highest intensity was observed at Eu concentration of 0.8 % [7].

It is generally accepted that inkjet inks should have low dynamic viscosity to be suitable for digital printing application, making the substrate properties very important for controlling ink spreading and reaching sufficient levels of print definition and performance [10–13]. We used diethylene glycol (DEG) and glycerol in the preparation of inkjet inks as a viscosity modifier and moisturizer [11].

The viscosity of 0.4 % Eu ink was found to be 14 mPa s (cP) measured at 46.0 s^{-1} and 12.3 mPa s (cP) measured at 233 s^{-1}. Also, the viscosity, rate of shear and shearing at different shearing rates are shown in Table 1 and plotted the rate of shear as a function of viscosity and shearing as shown in Figs. 6 and 7, Which indicated that viscosity decreased and shearing increased by increasing the rate of shear for the prepared ink.

Figure 8 A is the picture of Eu (III) doped in silica titania matrices in gel form without UV illumination, and Fig. 8 B is the same gel under UV irradiation. under UV irradiation the red luminescent emitted by the gel . The appearance color is homogeneous, indicating the particles are dispersed homogeneously. Figure 9 show the luminescence images of the printed paper before and after UV illumination.

Conclusion

The prepared and characterized luminescent Eu (III) doped SiO_2-TiO_2 nano composites were used in preparing inkjet emulsion inks and successfully printed as luminescent tagging for paper.

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