Forensic Science International 183 (2009) 45–49

Contents lists available at ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

The effectiveness of strong afterglow phosphor powder in the detection of fingermarks

Li Liu [a,b,*], Zhongliang Zhang [b], Limei Zhang [b], Yuchun Zhai [a]

[a] School of Materials & Metallurgy, Northeastern University, China
[b] Department of Forensic Science & Technology, China Criminal Police University, China

ARTICLE INFO

Article history:
Received 19 August 2008
Received in revised form 6 October 2008
Accepted 7 October 2008
Available online 20 November 2008

Keywords:
Afterglow
Phosphor
Fingermarks
Detection

ABSTRACT

There are numerous types of fluorescent fingermark powders or reagents used with the visualization of latent fingermarks deposited on multicolored substrate surfaces that can present a contrast problem if developed with regular fingermark powders. The developed fingermarks can show bright fluorescence upon exposure to laser, ultraviolet light and other light sources. These kinds of methods share a common concern, where surfaces and other substrates may fluoresce also. To overcome this concern, we have developed a phosphor powder which offers a strong afterglow effect which aid in the establishment of better fingermark detection. With the advent of a phosphor powder no special devices are required and the results obtained from fresh or a few days aged latent fingermarks left on: non-porous; semi-porous and also on some porous surfaces have been good. The strong afterglow effect offered by phosphor powder is also applicable for cyanoacrylate fumed fingermarks. Lift off and photography procedures of the developed fingermarks are incorporated in this paper.

1. Introduction

Europium doped strontium aluminate phosphors (ESAs) have shown great promise due to their long afterglow properties. Compared with sulfides europium doped strontium aluminate phosphors have shown: excellent photo-resistant; chemical stability; endurance in storage; no radiation was detected; as well as robustness in different environmental conditions. The success of this application has seen a wider acceptance of the use of these phosphorescent phosphors in many fields [1–9]. The use of phosphor materials in forensic applications in latent fingermark detection however has not previously been fully explored.

For the most part powder dusting continues to be the most widely used and is without doubt the most convenient method in the detection of the latent fingermarks at a crime scene. There is a long list of available fingermark powders, such as: grey powder; black powder; fluorescence powders; etc. [10,11]. These powders are usually selected depending on the color of the substrate where the suspect fingermarks may have been left, i.e. for light color surfaces, black or other dark colored powders are preferred as opposed to dark colored surfaces where grey or light colored powders are applied. When primary colors do not necessarily apply and the surface is more colorful then the use of fluorescence fingermark powders can aid us to observe and photograph using UV light to eliminate background effects. However, as more and more substrates and their fluoresce properties evolve, traditional fluorescent powder methods may not provide us with satisfactory results and therefore the use of special devices and/or techniques maybe required to develop the image needed for the detection of fingermarks, i.e. the time-resolved method as well as the other modified methods [12–14].

The use of europium doped strontium aluminate phosphor powder to eliminate background completely for the purposes of latent fingermark detection was the main goal of this exploratory study.

Rare earth europium doped strontium aluminate phosphor was prepared by hydrothermal method [15–18]. The rare earth doped phosphor was ground into fine powder as the dusting agent for latent fingermark detection. This phosphor powder was found to detect unfumed as well as cyanoacrylate fumed fingermarks on various forensic relevant materials including: metal foil; glass; porcelain; a plastic bag; paper; raw wood; fabric; etc. The rare earth doped phosphor powder had the effect of offering strong phosphorescence and an extended afterglow effect. The results suggest that europium doped strontium aluminate phosphor represents a new and useful class of phosphor powder for latent fingermark detection.

* Corresponding author at: Department of Forensic Science & Technology, China Criminal Police University, No. 83 Tawan Street, Huanggu District, Shenyang, Liaoning 110035, China. Tel.: +86 13804060856.
E-mail address: liliu_ccpu@yahoo.com (L. Liu).

0379-0738/$ – see front matter © 2008 Elsevier Ireland Ltd. All rights reserved.
doi:10.1016/j.forsciint.2008.10.008

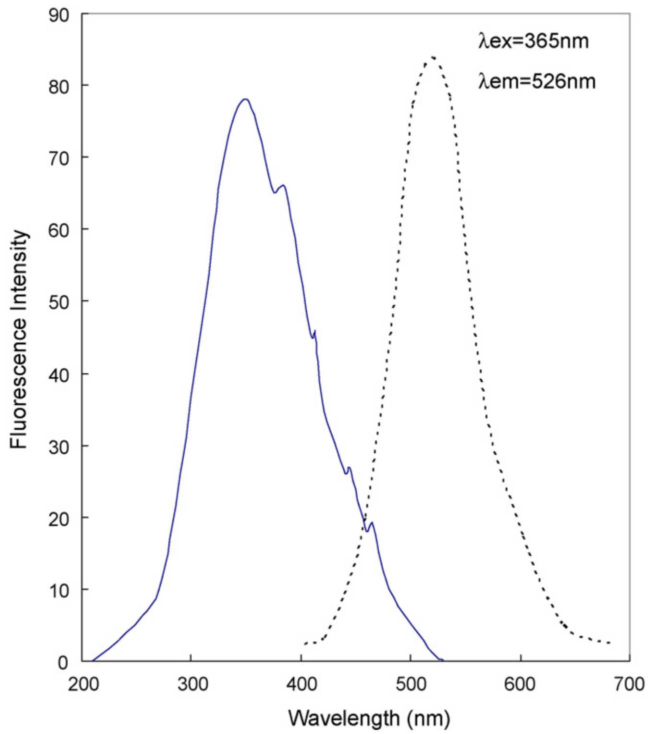

Fig. 1. Luminescence excitation and emission spectra of ESA.

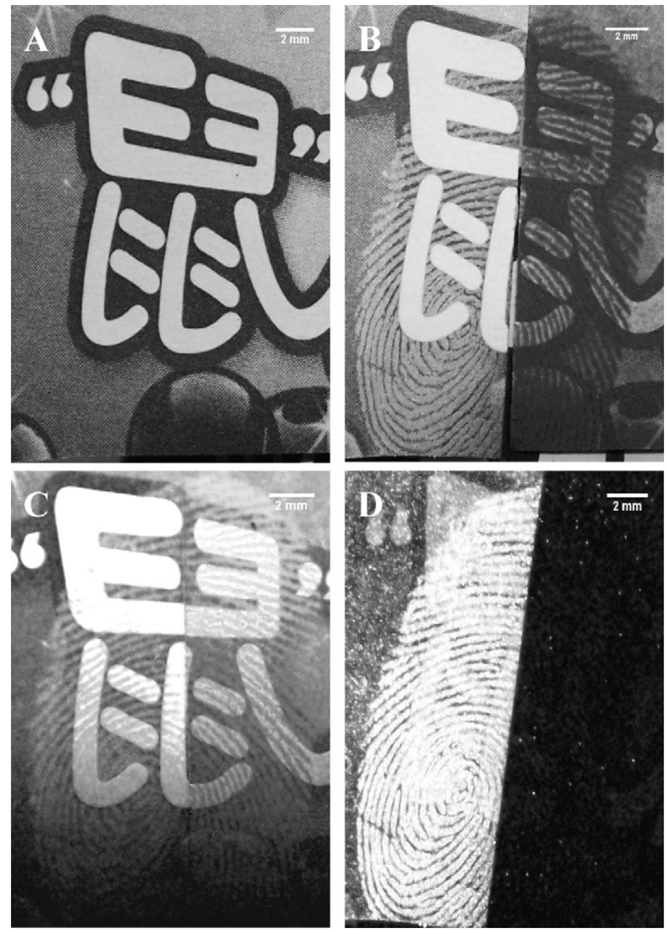

Fig. 2. Fingermark images detected using ESA powder and fluorescent powder on colored paper. The images of panels A and B were taken under white light; the image of panel C was taken under UV light; and the image of panel D was taken in the dark after a 2 min excitation under long UV light. All the images shown here appear as Figs. 3–5 which appear as 8-bit green-channel images of 24-bit-color images [24].

2. Materials and methods

2.1. Chemicals

Aluminium oxide, strontium carbonate, barium carbonate, basic magnesium carbonate, magnesium borate and europium oxide were purchased from the Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All chemicals were of analytical grade quality and presented a low risk of toxicity during the study.

2.2. Preparation of phosphor powder

The phosphor sample was prepared using the hydrothermal method. In this study, appropriate oxides and carbonates were used as starting materials. They were milled into a well-mixed composition and placed in an alumina crucible and sintered at around 1300 °C for 2–4 h in a mildly reducing atmosphere producing the desired phosphor material. The required reducing atmosphere was achieved using N_2 vapor containing 20% H_2 around the sample. After allowing the europium doped strontium aluminate phosphor to cool down the sample was ball-ground into fine powder, and identified as ESA powder.

2.3. The detection of fingermarks using ESA powder

A multitude of surface substrates were selected for fingermark experiments. The earlier tests were conducted on non-porous surfaces such as: aluminum foil; glass; porcelain; and plastic and were then applied to semi-porous and porous surfaces such as: leather; fabric; paper; and wood. All the fingermarks were obtained from the same donor and pressed onto the different substrates. Fingermarks from different donors were also tested and similar results were obtained. Then an additional set of 'fresh fingermarks' was used to test for 'aged fingermarking'. In these tests all of the fingermarks were left in the open air for various periods of time in the laboratory. All samples were stored at room temperature and all cyanoacrylate fumed fingermarks tests [11] were performed at the AFC-II cyanoacrylate chamber (Institute of Forensic Science, Ministry of Public Security, PR China). The application of the Phosphor powder was carried out using a Squirrel hair brush to dust the fingermarks. The developed fingermarks were excited under UV400-1 long wavelength (365 nm) UV Lamp (Institute of Forensic Science, Ministry of Public Security, China) for 2 min. The developed fingermarks were then imaged within 3 min after removal from the excitation light. All images were acquired by a 6.1 megapixel Kodak (Easy Share Z650) digital camera.

2.4. Spectroscopic measurements

Photoluminescence spectra were recorded using a FLUOROLOG-2 luminescence spectrophotometer (SPEX, USA). The excitation spectra were obtained by scanning the excitation wavelength from 200 to 500 nm while monitoring the luminescence emission at a fixed wavelength of 526 nm. For the emission spectra, the excitation was fixed at 365 nm but with an emission wavelength that varied between 400 and 700 nm.

3. Results

3.1. Luminescence excitation and emission spectra

The excitation and emission spectra were examined. In Fig. 1, a broad peak was shown at 365 nm in the excitation spectra. Lower and narrower excitation peaks were detected at 385, 413, 445 and 465 nm. It proved that the phosphor sample was excited by both visible light and UV light. For the emission spectra the main emission peak occurred at 526 nm and thus the afterglow presented as green in the dark.

The broad emission band peaking is attributable to the typical $4f^6 5d^1$ to $4f^7$ transitions of Eu^{2+} [19–23]. The 5d orbits lay the outside ions and are therefore strongly affected by the environment. Consequently, the positioning of the various associated energy levels may vary considerably. Thermal vibrations of the surrounding ions and local vibrations in the lattice structure may result in luminescence spectra with no sharp lines within a relatively broad band.

3.2. A comparison of fingermark detection between phosphorescent powder and fluorescent powder

Fig. 2 shows the comparison of ESA powder with fluorescent powder on colored paper. The paper with a mix of color covering red, white and yellow (panel A) was printed and cut into two parts. The left part of the print was labeled using ESA powder, while the right part was labeled with fluorescent powder. Only parts of the ridges of the paper were shown on both sides under white light because of the disturbance of the colored background (panel B). Then the detected paper was observed under UV light (panel C). The UV light did not help much either because of the background fluoresce effect, however after all the lights were turned off a very good ridge contrast on the left side of the paper, which had previously been dusted using ESA powder and excited after a 2 min under long UV light was obtained (panel D). It showed that ESA powder is more effective than traditional fluorescent powder because it eliminates unwanted background with its strong afterglow effect.

3.3. Detection of fingermarks on non-porous substrates by ESA powder

The fingermarks on different substrates such as: glass; aluminium foil; porcelain; plastic were tested. The ESA powder was able to detect the latent fingermarks on all of these non-

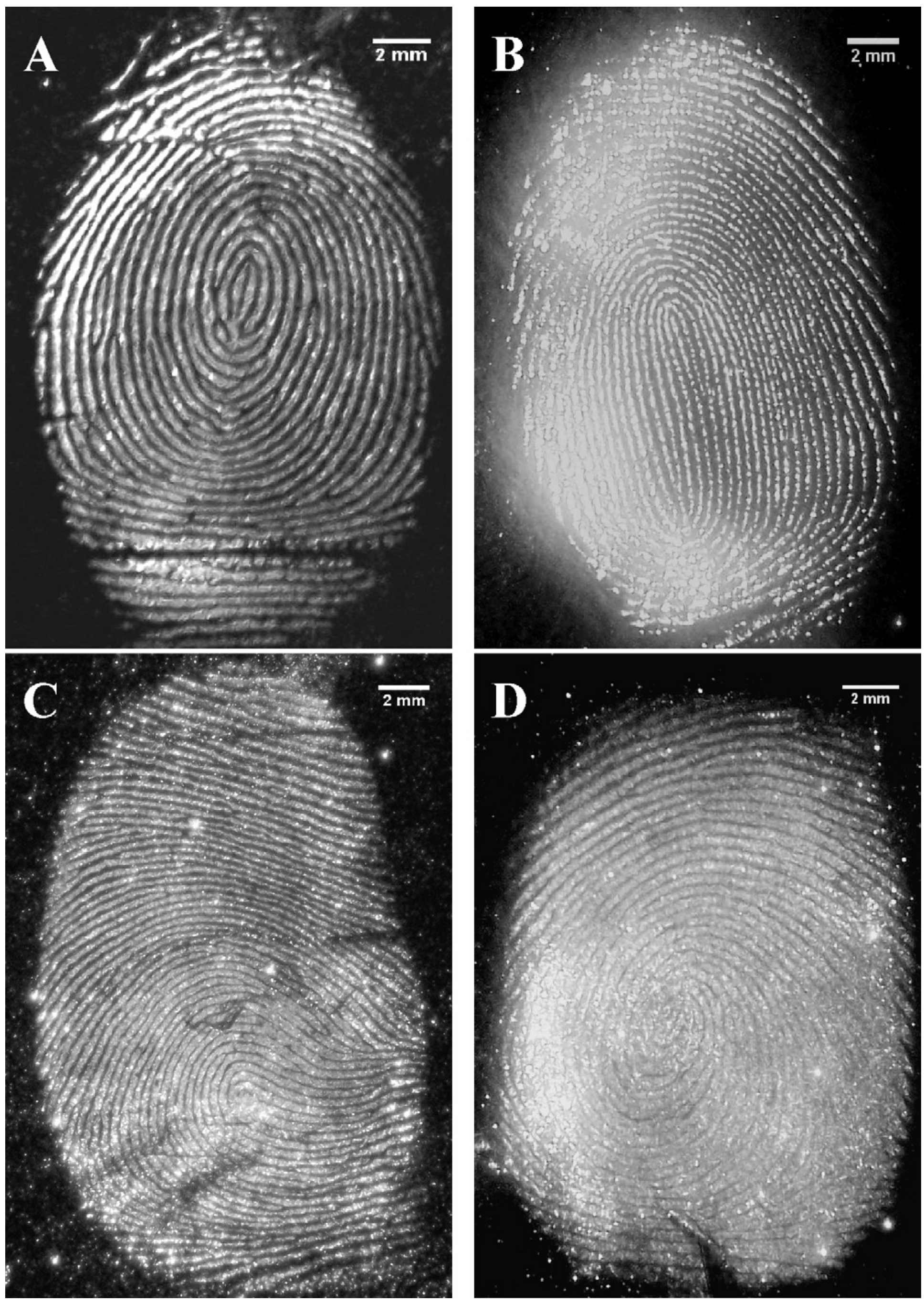

Fig. 3. Images of fingermarks detected by ESA powder on different non-porous substrates such as: foil (A); glass (B); porcelain (C); and a plastic bag (D). All of these experiments were performed using fresh fingermarks. All the images were taken in the dark after the labeled prints were excited under UV light for 2 min.

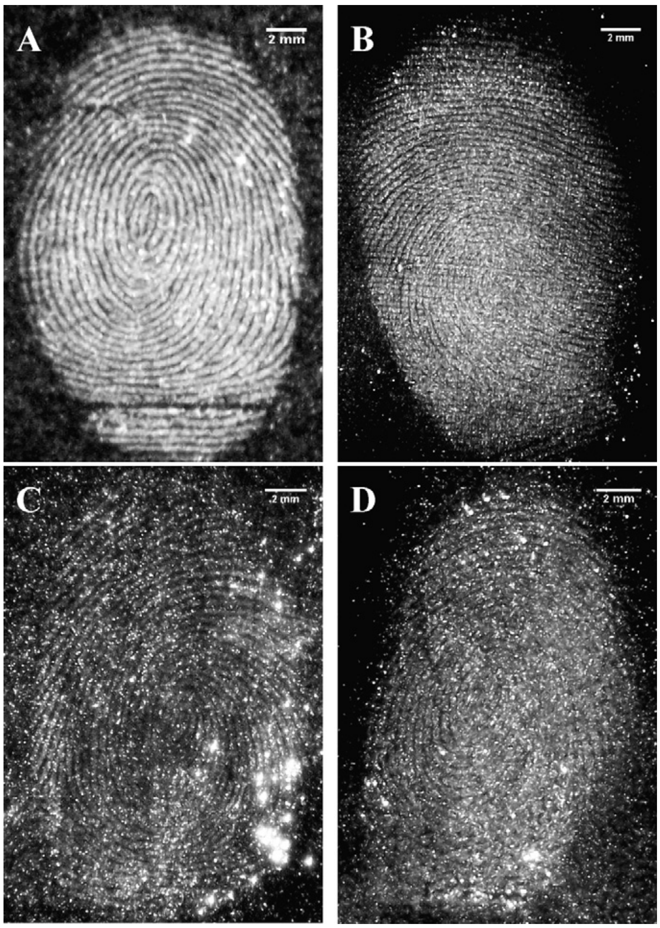

Fig. 4. Fingermark images detected by ESA powder on different semi-porous and porous substrates and the fingermarks images taken were of fingermarks placed on paper (A); fabric (B); wood (C); and leather (D). All of these experiments were performed using fresh fingermarks. All the images were taken in the dark after the labeled prints were excited 2 min under long UV light.

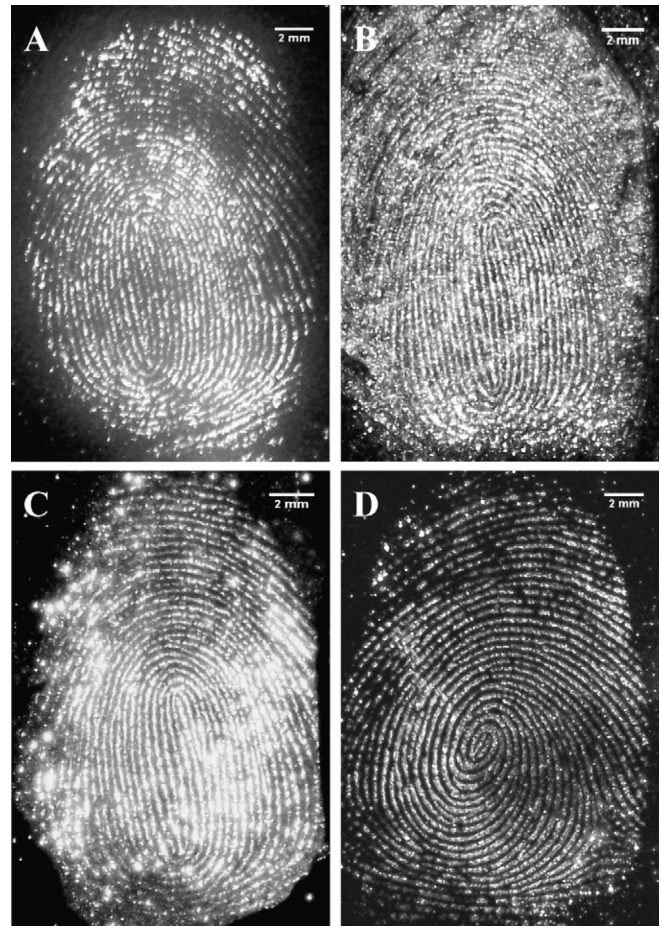

Fig. 5. 7-day-aged fingermark images detected using ESA powder. These 'aged fingermarks' were on: glass (A); a plastic bag (B); porcelain (C); and foil (D). All the images were taken in the dark after the labeled prints were excited under long UV light for 2 min.

porous surfaces. Fig. 3 shows the labeled fingermark on: foil (panel A); glass (panel B); porcelain (panel C); and a plastic bag (panel D).

3.4. Detection of fingermarks on semi-porous or porous substrates by ESA powder

ESA powder is used to detect fingermarks on some semi-porous and porous surfaces showed reasonable detail including: paper (panel A); fabric (panel B); wood (panel C); and leather (panel D) as shown in Fig. 4. All of these experiments were performed using fresh fingermarks.

3.5. Effect of fingermark aging using ESA powder labeling

Whether or not the ESA powder can be useful for aged fingermarks was also part of this study. The result showed that the phosphor powder can successfully detect fingermarks even though they have been left weeks earlier. Fig. 5 shows the labeled 7-day-old fingermarks on: glass (panel A); a plastic bag (panel B); porcelain (panel C); and foil (panel D). The labeling effectiveness depends largely on the component of the fingermark residue. During the course of this study we have also detected some 2-month-aged lipid fingermarks successfully.

3.6. Labeling as phosphorescent stain following cyanoacrylate fuming for the detection of fingermarks

In some cases cyanoacrylate fuming maybe needed to label the fingermarks. ESA powder can then be used for enhancement purposes on the fumed fingermarks also shown in Fig. 6 where the imaged fingermarks using cyanoacrylate fuming only (panel A) and using ESA powder dusting after cyanoacrylate fuming (panel B) applied on a plastic board.

3.7. Lifting of the fingermarks developed by ESA powder

ESA powder developed fingermark can be lifted by fingermark tape and preserved in the evidence bag. The developed fingermarks can be re-excited as many times as needed because our studies reveal that there were no obvious differences observed in the phosphorescence of the labeled fingermarks when re-excited.

4. Discussion

Eu^{2+} doped strontium aluminate phosphor was successfully prepared using the hydrothermal method. When ESA was excited by white or UV light, the luminescent center within the phosphor captures some energy and transfers it to another luminescent center. When the excitation light cut off the captured energy was

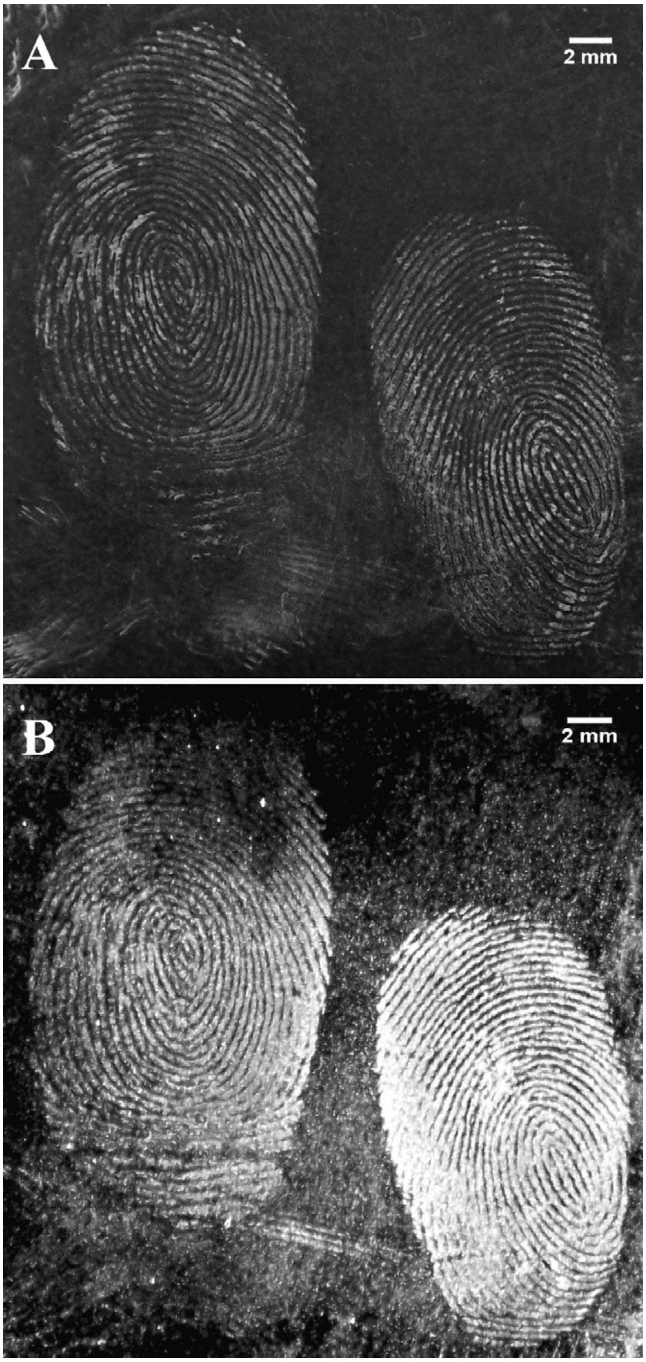

Fig. 6. Comparison of unlabeled (A) and labeled (B) cyanoacrylate fumed fingermarks by cyanoacrylate placed on a plastic board.

released as a visible light and thus the phosphorescence can be seen. The phosphorescence properties remained in tack as the ESA was held in storage along with the labeled prints for several months in a stable environment within the research laboratory. All the indicators suggest that our phosphor powder is useful as fingermark labeling agent. It was used to label all fresh prints on forensic relevant substrates including: foil; glass; porcelain; plastic; paper; etc. It was also effective in the labeling of 'aged' as well as 'cyanoacrylate fumed' fingermarks.

There were no toxicity or residual effects found in this research and the normal protocols used in fingermark detection were followed. Procedurally, DNA investigations would ordinarily take priority over fingermark detection.

In conclusion, this exploratory study indicates that ESA powder is a useful fingermark detection powder due to its strong afterglow effect and other phosphorescence properties, which can be applied to most porous, semi-porous or non-porous surfaces. It is an easy, efficient and effective powder dusting method that can eliminate background substrates with the advent of a squirrel hair brush and an ordinary camera with no special instruments or light sources needed.

Acknowledgement

This work was supported by the Ministry of Public Security of China, Foundation of Application of Innovation (2007YYCXXJXY104).

References

[1] S.R. Jansen, J.M. Migchels, T.H. Hintzen, R. Metselaar, Eu-doped barium aluminium oxynitride with the β-aluminium-type structure as new blue-emitting phosphor, J. Electrochem. Soc. 146 (1999) 800–806.
[2] J.T. Randall, M.H.F. Wilkins, Phosphorescence and electron traps, Proc. R. Soc. London Ser. 184 (1945) 366–407.
[3] R. Sakai, T. Katsumata, S. Komuro, T. Morikawa, Effect of composition on the phosphorescence from BaAl2O4:Eu2+, Dy3+ crystals, J. Lumin. 85 (1999) 149–154.
[4] K. Kaiya, N. Takahashi, T. Nakamura, T. Matsuzawa, G.M. Smith, P.C. Riedi, EPR studies of europium (II)-doped strontium aluminate phosphors, J. Lumin. 87–89 (2000) 1073–1075.
[5] G. Blasse, W.L. Wanmalcer, J.W. ter Vrygt, A. Bril, Fluorescence of Eu2+ activated silicates, Philips Res. Rept. 23 (1968) 189–200.
[6] B. Smets, J. Rutten, G. Hoeks, J. Verlijsdonk, 2SrO·3Al2O3:Eu2+ and 1.29 (Ba, Ca) O 6Al2O3:Eu2+ two new blue-emitting phosphors, J. Electrochem. Soc. 136 (1989) 2119–2123.
[7] E. Nakazawa, T. Mochida, Traps in SrAl2O4:Eu2+ phosphor with rare-earth ion doping, J. Lumin. 72–74 (1997) 236–237.
[8] Q. Li, X. Teng, W. Zhang, X. Huang, C. Zhao, Progress of studies on multi-color long afterglow luminescence materials, Chin. Rare Earth 26 (2005) 62–67.
[9] W. Hoogenstraaten, Electron traps in zinc-sulfide phosphors, Philips Res. Rept. 13 (1958) 515–693.
[10] G.S. Sodhi, J. Kaur, Powder method for detecting latent fingerprints: a review, Forensic Sci. Int. 120 (2001) 172–176.
[11] H.C. Lee, R.E. Gaensslen, Advances in Fingerprint Technology, 2nd edition, CRC Press, New York, 2001, pp. 108–112.
[12] R.H. Murdock, E.R. Menzel, A computer-interfaced time-resolved luminescence imaging system, J. Forensic Sci. 38 (1993) 521–529.
[13] E.R. Menzel, M. Pleil, S. Gangopadhyay, W. Borst, Enhancement of fluorescent fingerprints by time-resolved imaging, Proc. SPIE 743 (1987) 198–202.
[14] I.M. Alaoui, E.R. Menzel, M. Farag, K.H. Cheng, R.H. Murdock, Mass spectra and time-resolved fluorescence spectroscopy of the reaction product of glycine with 1,2-indanedione in methanol, Forensic Sci. Int. 152 (2005) 215–219.
[15] T.R.N. Kutty, R. Jagannathan, Luminescent of Eu2+ in strontium aluminates prepared by the hydrothermal method, Mater. Res. Bull. 25 (1990) 1355–1362.
[16] J. Chen, Q. Song, A new type phosphor SrAl2O4:Eu with long afterglow luminescence, J. Appl. Sci. 14 (1996) 108–112.
[17] X. Zhang, Y. Zhai, S. Wu, Synthesis of night-luminous phosphors with high luminescence and slow luminescent decay, Eng. Chem. Metall. 19 (1998) 109–112.
[18] S. Guo, Q. Zeng, Research developments of europium-doped strontium aluminates luminescent materials, Chem. Res. Appl. 16 (2004) 6–10.
[19] H. Yamamoto, T. matsuzawa, Mechanism of long phosphorescence of SrAl2O4:Eu2+, Dy3+ and CaAl2O4:Eu2+, Nd3+, J. Lumin. 72–74 (1997) 287–289.
[20] F.C. Palilla, A.K. Levine, M.R. Tomkus, Fluorescent properties of alkaline earth aluminates of the type MAl2O4 activated by divalent europium, J. Electrochem. Soc. 115 (1968) 642–644.
[21] D. Haranath, V. Shanker, H. Chander, P. Sharma, Tuning of emission colours in strontium aluminate long persisting phosphor, J. Phys. D: Appl. Phys. 36 (2003) 2244–2248.
[22] J.M.P.J. Verstegen, J.L. Sommerdijk, A. Bril, Short communication line emission of SrAl12O19:Eu2+, J. Lumin. 9 (1974) 420–423.
[23] Y. Meng, D. Wang, L. Li, Z. Shi, Effect of Sr/Al ratios on phases and luminescent properties of strontium aluminate doped with rare earths, J. Chin. Rare Earth Soc. 23 (2005) 277–280.
[24] L. Liu, S.K. Gill, Y. Gao, L.J. Hopeweeks, K.H. Cheng, Exploration of the use of novel SiO2 nanocomposites doped with fluorescent Eu3+/sensitizer complex for latent fingerprint detection, Forensic Sci. Int. 176 (2008) 163–172.