HHS Public Access
Author manuscript
ACS Appl Mater Interfaces. Author manuscript; available in PMC 2016 December 30.

Published in final edited form as:
ACS Appl Mater Interfaces. 2015 December 30; 7(51): 28110–28115. doi:10.1021/acsami.5b09320.

Rare Earth Fluorescent Nanomaterials for Enhanced Development of Latent Fingerprints

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Abstract

The most commonly found fingerprints at crime scenes are latent and, thus, an efficient method for detecting latent fingerprints is very important. However, traditional developing techniques have drawbacks such as low developing sensitivity, high background interference, complicated operation, and high toxicity. To tackle this challenge, we have synthesized two kinds of rare earth fluorescent nanomaterials, including the fluoresce red-emitting YVO_4:Eu nanocrystals and green-emitting $LaPO_4$:Ce,Tb nanobelts, and then used them as fluorescent labels for the development of latent fingerprints with high sensitivity, high contrast, high selectivity, high efficiency, and low background interference, on various substrates including noninfiltrating materials, semi-infiltrating materials, and infiltrating materials.

Graphical Abstract

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Notes

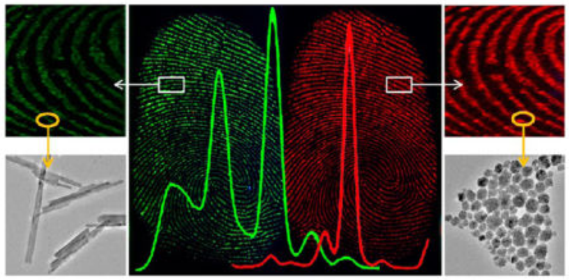
The authors declare no competing financial interest.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b09320.

Detailed experimental procedures, as well as images of latent fingerprints labeled by rare earth fluorescent nanomaterials and corresponding bulk rare earth fluorescent powders (PDF)

Movie S1 (AVI)



Keywords

rare earth; fluorescent; nanocrystals; nanowires; fingerprint

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A fingerprint, constituting a partial representation of the ridge pattern of skin on the human finger, has been established as one effective trace that can be used as important evidence for individual identification.' Latent fingerprints are the most commonly encountered forms of the fingerprints at crime scenes, which are invisible to naked eyes and required to develop the visualization techniques. At crime scenes, powder dusting method is the simplest and most commonly used method for the development of latent fingerprints due to its high efficiency and ease in use. There are two major types of powders used in powder-dusting method, including metal powders and magnetic powders. Although the powder dusting method using these traditional powders is effective in the development of latent fingerprints under some ordinary circumstances, it is increasingly challenged by the following problems: (i) low contrast due to the nonfluorescence of the powders; (ii) low selectivity due to the nonuniform size and unsuitable adsorptive property of the powders; and (iii) high background interference due to the complex colors or complicated patterns of the substrates. To the end, the development of latent fingerprint with high efficiency, high contrast, high selectivity, and low background interference remains a major challenge in the areas of forensic sciences.

In the past ten years, the use of fluorescent nanomaterials for latent fingerprints in forensic science has attracted significant research interest, due to their excellent chemical and physical properties, such as large surface area and high fluorescent intensity.– Nanomaterials, such as quantum dots, which can emit strong visible fluorescence by the excitation of ultraviolet lights, are the most widely studied fluorescent nanomaterials at present for the development of fingerprints.– By using the nanomaterials for the development of fingerprints, an increased contrast and decreased background interference could be achieved due to the strong fluorescent emission. In addition, the surface modification technology of the nanomaterials is advanced and flexible, ensuring a high selectivity in fingerprint development.– However, the nanomaterials colloidal solution is not very suitable to use in actual crime scenes, for its complex operation and low efficiency. Therefore, new types of fluorescent nanomaterials for the development of latent fingerprints with high contrast, high selectivity, low background interference, and high efficiency are still needed in the area of forensic sciences.

Moreover, rare earth fluorescent nanomaterials, which possess the advantages of small particle size, large surface area, high quantum yields, high fluorescent intensity, narrow emission peak, and good optical stability, are suitable as effective fluorescent labels for the development of latent fingerprints in recent years., Due to the use of rare earth fluorescent nanomaterials for developing the latent fingerprints, the papillary ridge details of fingerprints on various smooth substrates could be clearly defined under the excitation of 254 nm UV light, resulting in high efficiency, high contrast, high selectivity, and low background interference for enhanced fingerprint development.

Inspired by aforementioned concepts, we have reported YVO_4:Eu and $LaPO_4$:Ce,Tb rare earth fluorescent nanomaterials as effective fluorescent labels for the enhanced development of latent fingerprints. Moreover, we have successfully used the rare earth YVO_4:Eu nanocrystals and $LaPO_4$:Ce,Tb nanobelts to clearly image latent fingerprints on various smooth substrates. The high contrast, sensitivity, and background interference of the fluorescent nanomaterials in latent finger-print development are also investigated in detail. Thus, our results demonstrate that the two kinds of rare earth fluorescent nanomaterials hold great promise for latent fingerprint imaging applications in forensic sciences.

In this research, we used a typical hydrothermal method to chemically synthesize YVO_4:Eu and $LaPO_4$:Ce,Tb fluorescent nanomaterials (detailed synthetic procedures were described in the Supporting Information). Then, the two fluorescent nanomaterials are characterized by TEM images and XRD. The TEM images of YVO_4:Eu and $LaPO_4$:Ce,Tb fluorescent nanomaterials are shown in Figure 1a, a′, respectively. It could be clearly observed that both of the two fluorescent nanomaterials were well-dispersed. The YVO_4:Eu samples were nanocrystals with about 40 nm (Figure 1a), whereas the $LaPO_4$:Ce,Tb samples were nanobelts with an average diameter of about 19 nm and an average length of about 340 nm (Figure 1a′). Such small size of these synthetic fluorescent nanomaterials was very suitable for observing the detailed features in latent fingerprint development to obtain a high developing sensitivity. The XRD patterns of YVO_4:Eu and $LaPO_4$:Ce,Tb fluorescent nanomaterials are shown in Figure 1b, b′, respectively. The XRD patterns of YVO_4:Eu and $LaPO_4$:Ce,Tb fluorescent nanomaterials matched closely with the calculated values for tetragonal phase YVO_4 (Figure 1c, JCPDS No. 72–0861) and monoclinic phase $LaPO_4$ (Figure 1c′, JCPDS No. 84–0600), respectively, indicating that both of the two fluorescent nanomaterials were of pure phase and well-crystallized. To further assess the optical properties, the samples are characterized by fluorescence spectra measurement. The fluorescence spectra of YVO_4:Eu and $LaPO_4$:Ce,Tb fluorescent nanomaterials are shown in Figure 1d, e and Figure 1d′, e′, respectively. For YVO_4:Eu fluorescent nanomaterials, the excitation spectrum monitored at 619 nm emission was composed of an intense broad band peaking at 277 nm (Figure 1d), which corresponded to the absorption of VO_4; the emission spectrum under 277 nm excitation consisted of four intense band peaking at 539 nm, 594 nm, 619 nm, 653 nm (Figure 1e), which belong to the $^5D_1 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_4$ transitions of Eu^{3+}. For $LaPO_4$:Ce,Tb fluorescent nanomaterials, the excitation spectrum monitored at 541 nm emission was composed of an intense broad band peaking at 262 nm (Figure 1d′), which corresponded to the 4f–5d transition of Ce^{3+}; the emission spectrum under 262 nm excitation consisted of four intense band peaking at 485, 541, 581, 617 nm (Figure 1e′), which belong to the $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, $^5D_4$

$\rightarrow {}^7F_3$ transitions of Tb^{3+}. It could be seen from the insets of Figure 1d, e and Figure 1d′, e′ that the YVO_4:Eu and $LaPO_4$:Ce,Tb fluorescent nanomaterials could emit strong red and green fluorescence under 254 nm UV irradiation, respectively. Such strong UV-induced visible fluorescence from these synthetic fluorescent nanomaterials was very suitable for the latent fingerprint development with high developing contrast and low background interference.

Our developing process using rare earth fluorescent nanomaterials was relatively simple, fast and effective, which mainly involved a light brushing action (detailed procedures of latent fingerprint development are described in the Supporting Information). Here, a soft feather brush consisted of many fine flexible tendrils was used to minimize the damage of the latent fingerprints, and it is proved that the latent fingerprints could not be easily damaged by a soft feather brush (Figure S1). To ensure a high contrast and low background interference for latent fingerprint development, the fluorescence intensity of the nanomaterials should be high enough. To obtain a high sensitivity and selectivity, the size of the nanomaterials should be small and the adsorptive property of the nanomaterials should be suitable. In this research, YVO_4:Eu and $LaPO_4$:Ce,Tb fluorescent nanomaterials were used for developing latent fingerprints on various substrates, including noninfiltrating materials, semi-infiltrating materials, and infiltrating materials. In addition, the developing sensitivity, contrast, selectivity, and the background interference were investigated in detail.

To determine the sensitivity in latent fingerprint development using YVO_4:Eu and $LaPO_4$:Ce,Tb fluorescent nanomaterials as fluorescence labels, transparent glass was chosen a smooth substrate. In addition, as control labeling powders, bulk powders of YVO_4:Eu and $LaPO_4$:Ce,Tb were also used to develop the latent fingerprints. As shown in Figure S2, detailed features of the fingerprints as well as the sweat pores could be observed clearly using YVO_4:Eu and $LaPO_4$:Ce,Tb fluorescent nanomaterials (Figure 2a, b), because of their small particle size and suitable affinity, which was almost impossible to achieve using corresponding bulk powders (Figure S2a′, b′). Therefore, our YVO_4:Eu and $LaPO_4$:Ce,Tb fluorescent nanomaterials could be used for developing the latent fingerprints with high sensitivity.

To determine the contrast and selectivity in latent fingerprint development using YVO_4:Eu and $LaPO_4$:Ce,Tb fluorescent nanomaterials as fluorescence labels, we chose transparent glass as a smooth substrate. In addition, as control labeling powders, conventional red and green fluorescent powders were also used to develop the latent fingerprints. As shown in Figure 2, when the background color was pure black, the fingerprints labeled with fluorescent nanomaterials (Figure 2a, d) and conventional fluorescent powders (Figure 2a′, d′) showed a medium contrast between the background and the powder-labeled fingerprints. When excited by 254 nm UV irradiation, the contrast was enhanced markedly by the red (Figure 2b, b′) or green (Figure 2e, e′) fluorescence. However, it could be seen clearly from the expanded images (Figure 2c′, f′) that not only the papillary ridges but also the furrows were labeled with the conventional fluorescent powders, and the papillary ridges of the resultant fingerprints seemed to be ambiguous, resulting a low developing selectivity. When fluorescent nanomaterials were used, clear and well-defined papillary ridges of the fingerprints were revealed clearly with sharp edges under 254 nm UV irradiation, resulting a high selectivity. These results clearly showed that using both the fluorescent nanomaterials and the conventional fluorescent powders in latent fingerprint development could exhibit high contrast, due to their strong fluorescence emissions under 254 nm UV irradiation. However, compared with the fingerprints labeled by conventional fluorescent powders, the selectivity of the fingerprints labeled by fluorescent nanomaterials was obviously increased because of their small size and suitable adsorptive property. Therefore, our YVO_4:Eu and $LaPO_4$:Ce,Tb fluorescent nanomaterials could be used for developing the latent fingerprints with high contrast and high selectivity.

To determine the background interference in latent finger-print development using YVO_4:Eu and $LaPO_4$:Ce,Tb fluorescent nanomaterials as fluorescence labels, plastic cards with background colors were chosen as smooth substrates. As shown in Figure 3, fingerprints labeled with both YVO_4:Eu (Figure 3a) and $LaPO_4$:Ce,Tb (Figure 3b) fluorescent nanomaterials showed low contrast due to serious background interference, resulting a low sensitivity. These powders without fluorescence were seriously restricted by the background color of the substrate. When excited by 254 nm UV irradiation, the contrast was enhanced markedly by the red (Figure 3a′) or green (Figure 3b′) fluorescence. Thus, clear and well-defined fingerprint images with high contrast, sufficient quality, and strong fluorescence could be captured under 254 nm UV irradiation, with low background interference. Therefore, our YVO_4:Eu and $LaPO_4$:Ce,Tb fluorescent nanomaterials could be used for developing the latent fingerprints with low background interference.

To determine the applicability of using YVO_4:Eu and $LaPO_4$:Ce,Tb fluorescent nanonaterials to develop of the fingerprints on smooth objects, a series of noninfiltrating materials (e.g., aluminum alloys sheets), semi-infiltrating materials (e.g., ceramic tiles, marbles, painted wood, and wood floor), and infiltrating materials (e.g., printing papers) were chosen as smooth substrates. As shown in Figure 4, clear and well-defined papillary ridges of the fingerprints could be clearly observed on all of the samples with high contrast, high selectivity, and no or low background interference. It should be noted that the whole procedure was fast and could be finished in approximately 30 s for trained investigators. Therefore, our YVO_4:Eu and $LaPO_4$:Ce,Tb fluorescent nanomaterials could be used for developing the latent fingerprints with high sensitivity and high efficiency on virtually all of the smooth substrates.

In summary, we report two kinds of rare earth fluorescent nanomaterials including red-emitting YVO_4:Eu nanocrystals and green-emitting $LaPO_4$:Ce,Tb nanowires, which are synthesized via a hydrothermal approach, as effective fluorescent labels in developing the latent fingerprints. The fluorescent nanomaterials were then successfully used as effective fluorescent labels for the high-sensitivity development of latent fingerprints on various substrates, including glass, ceramic tiles, marbles, aluminum alloys sheets, polymer materials, wood materials, and papers. The development nanomaterials exhibited outstanding performance with high sensitivity, high contrast, high selectivity, and low background interference. We demonstrated that the robustness of YVO_4:Eu nanocrystals and $LaPO_4$:Ce,Tb fluorescent nanowires as versatile fluorescent label for imaging of fingerprints on several other substrates. The rare earth nanomaterials are promising candidates for potential applications in forensic sciences.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work is supported by the National Science Foundation of China (21205139), the Application and Innovation Project of Chinese Ministry of Public Security (2012YYCXXJXY127), and the Program for Liaoning Excellent Talents in University (LJQ2014130). J.W. thanks the financial support from National Science Foundation of China (51302282). C.B.M. would like to thank the financial support from National Institutes of Health (EB015190), National Science Foundation (CMMI-1234957 and DMR-0847758), Department of Defense Peer Reviewed Medical Research Program (W81XWH-12-1-0384), Oklahoma Center for the Advancement of Science and Technology (HR14-160), and Oklahoma Center for Adult Stem Cell Research (434003).

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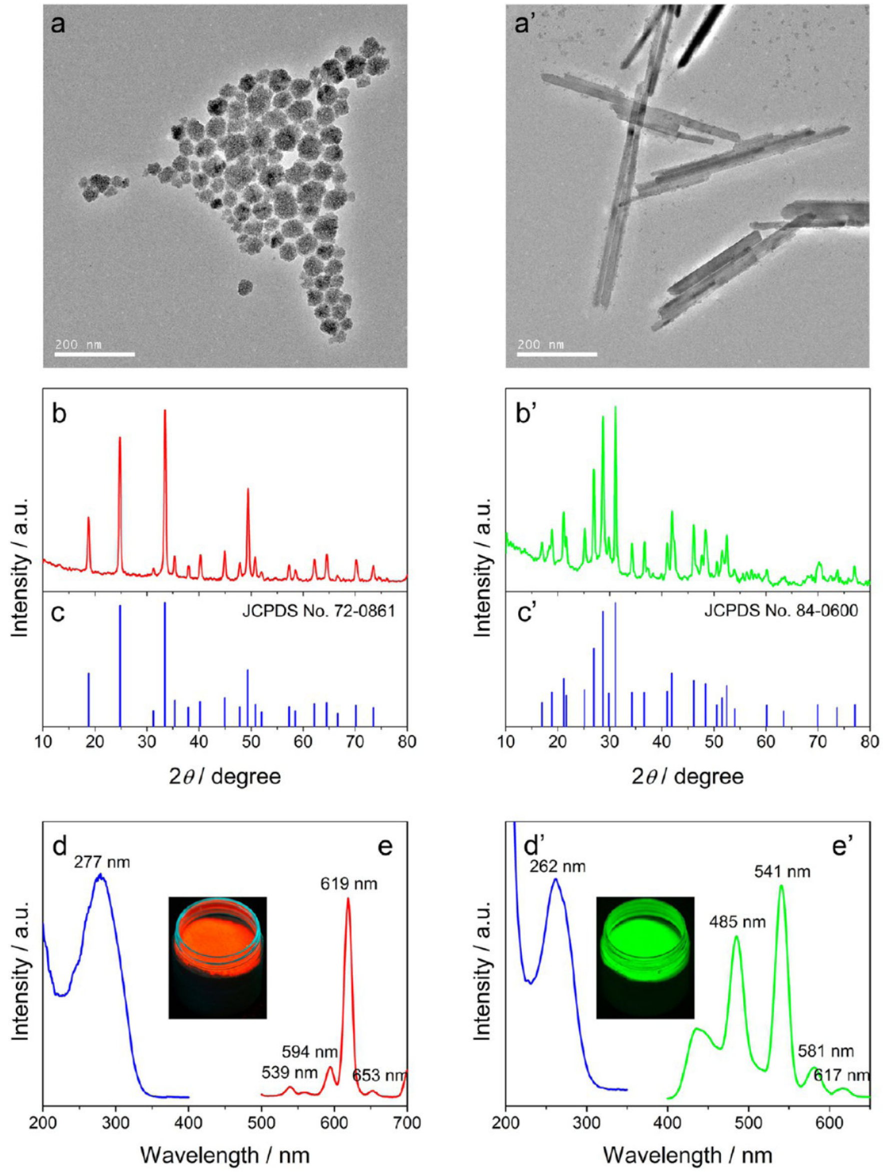

Figure 1.

(a–e) Characterization of YVO_4:Eu nanocrystals and (a′–e′) $LaPO_4$:Ce,Tb nanobelts: (a, a′) TEM images, (b, b′) powder XRD patterns, (c, c′) calculated XRD line patterns, (d, d′) excitation spectra, and (e, e′) emission spectra. Insets are photographs of the fluorescent powders in dark field, excited under 254 nm excitation.

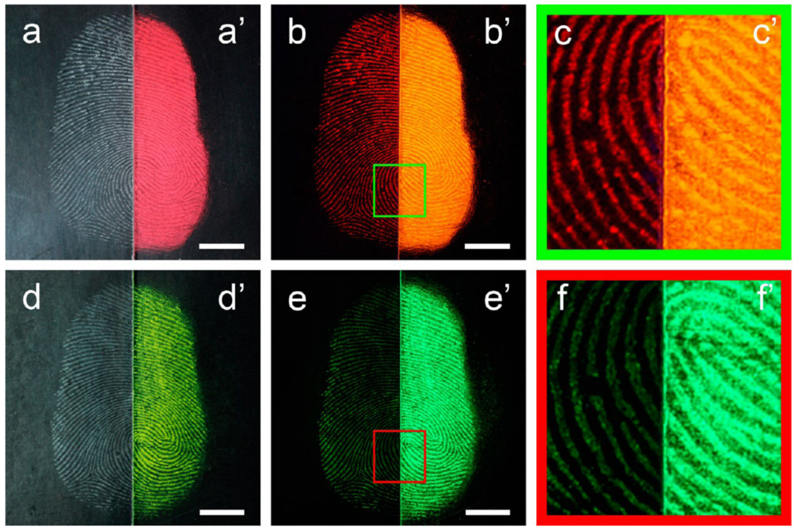

Figure 2.
Latent fingerprints on glass labeled by (a–c) YVO_4:Eu nanocrystals and (d–f) $LaPO_4$:Ce,Tb nanobelts as well as conventional (a′–c′) red and (d′–f′) green fluorescent powders, and then detected by 254 nm UV irradiation: (a, a′, d, d′) images in bright field without 254 nm UV irradiation, (b, b′, e, e′) fluorescent images in dark field under 254 nm UV irradiation, and (c, c′, f, f′) magnified images for the small box in b, b′, e, e′. The scale bar corresponds to 5.0 mm.

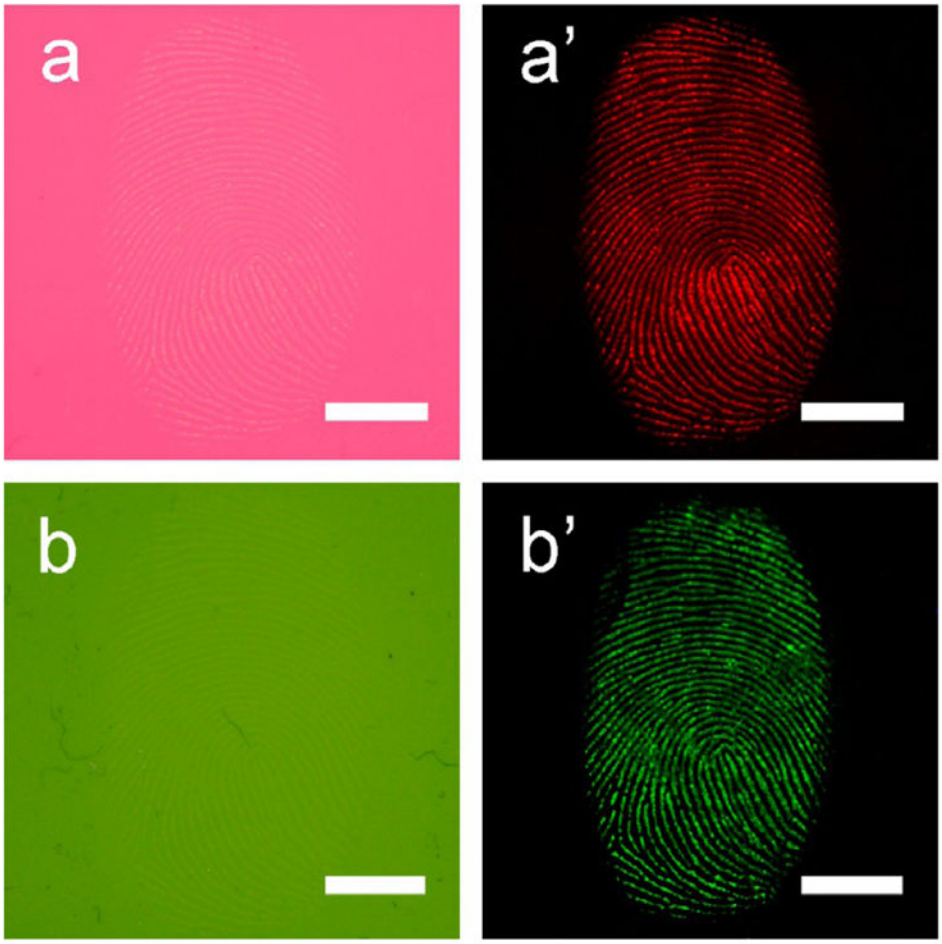

Figure 3.

Latent fingerprints on plastic cards with background colors labeled by (a, a′) YVO_4:Eu and (b, b′) $LaPO_4$:Ce,Tb fluorescent nanomaterials, and then detected by 254 nm UV irradiation: (a, b) images in bright field without 254 nm UV irradiation, (a′, b′) fluorescent images in dark field under 254 nm UV irradiation. The scale bar corresponds to 5.0 mm.

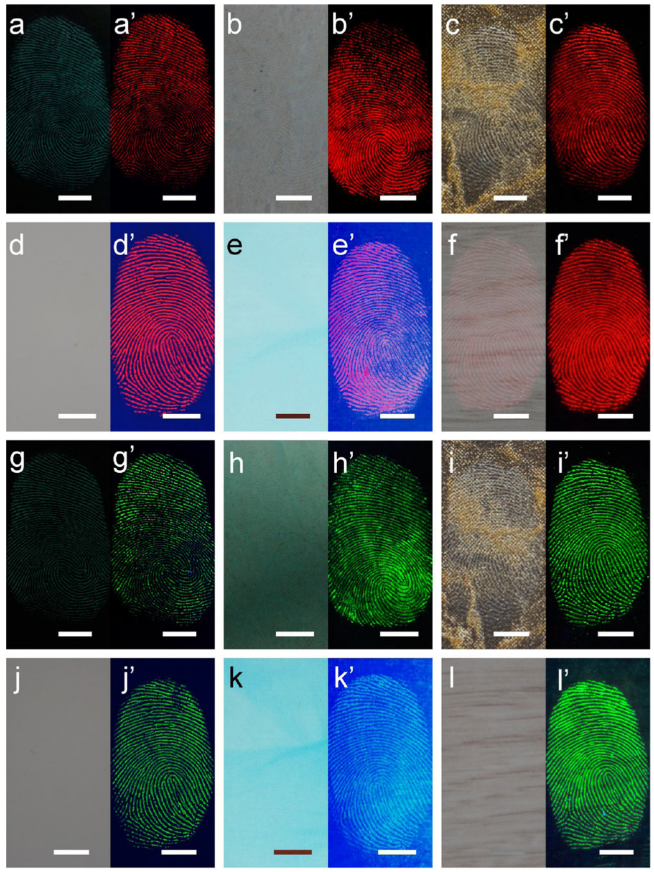

Figure 4.

Latent fingerprints on various substrates labeled by (a–f) YVO_4:Eu and (g–l) $LaPO_4$:Ce,Tb fluorescent nanomaterials in bright field, and then (a′–l′) detected by 254 nm UV irradiation in dark field: (a, a′, g, g′) aluminum alloys sheets, (b, b′, h, h′) ceramic tiles, (c, c′, i, i′) marbles, (d, d′, j, j′) painted wood, (e, e′, k, k′) printing papers, and (f, f′, l, l′) wood floor. The scale bar corresponds to 5.0 mm.