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NIR-induced highly sensitive detection of latent finger-marks by NaYF₄:Yb,Er upconversion nanoparticles in a dry powder state

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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 detection sensitivity, high background interference, complicated operation, and high toxicity. To tackle this challenge, we employed fluorescent NaYF₄:Yb,Er upconversion nanoparticles (UCNPs), which can fluoresce visible light when excited by 980 nm human-safe near-infrared light, to stain the latent fingerprints on various substrate surfaces. The UCNPs were successfully used as a novel fluorescent label for the detection of latent fingerprints with high sensitivity, low background, high efficiency, and low toxicity on various substrates including non-infiltrating materials (glass, marble, aluminum alloy sheets, stainless steel sheets, aluminum foils, and plastic cards), semi-infiltrating materials (floor leathers, ceramic tiles, wood floor, and painted wood), and infiltrating materials such as various types of papers. This work shows that UCNPs are a versatile fluorescent label for the facile detection of fingerprints on virtually any material, enabling their practical applications in forensic sciences.

Keywords

upconversion; nanoparticles; fingerprint; development

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1 Introduction

A fingerprint is one of the most powerful traces that can be exploited as evidence for the identity of individuals since it represents the unique ridge skin pattern of an individual's finger. The most commonly found fingerprints at crime scenes are typically latent. Namely, they are normally invisible or less visible to investigators and can only be visualized by certain developing techniques. To date, many fingerprint developing techniques have been studied and used by fingerprint scientists, including powder (metallic, magnetic, or fluorescent powder) dusting [1], ninhydrin spraying [2], iodine fuming, cyanoacrylate fuming [3–5], and silver nitrate soaking. However, these traditional techniques are still associated with serious problems in developing latent fingerprints, such as low detection sensitivity, high background interference, complicated operation, and high toxicity. Therefore, there is a pressing need to create a simple method in developing latent fingerprints with high sensitivity, low background, high efficiency, and low toxicity, which is the long-term goal for forensic scientists.

Recently, new techniques such as electrochemiluminescence and nanotechnology have been applied toward the enhanced development of latent fingerprints [6–11]. In particular, the use of fluorescent nanoparticles (NPs), such as quantum dots (QDs), for the development of latent fingerprints has attracted significant research interest in forensic science [12–18]; this is because of their unique physical and chemical properties such as small particle size, large surface area, good photochemical stability, and high fluorescent intensity. The integration of QDs in latent fingerprint development provides a variety of advantages including increased sensitivity, enhanced contrast, and improved selectivity [19–26]. When excited by ultraviolet (UV) radiation, QDs can emit strong visible fluorescence to enhance fingerprint contrast. However, UV light is needed to excite QDs and other fluorescent NPs, resulting in many drawbacks including the following: high background interference owing to the significant autofluorescence from the substrates, photo damage to the skin and eyes of the operators, and the possibility of severe irradiation-induced damage of DNA in fingerprint residue, resulting in the subsequent DNA analysis failing. Furthermore, increasing concerns on the inherent toxicity of QDs limit their long-term use [27–29]. Therefore, a novel type of fluorescent NPs with high sensitivity, low background, high efficiency, and low toxicity is needed for the development of latent fingerprints in the field of forensic chemistry.

Fluorescent upconversion (UC) NPs (UCNPs) can convert a longer wavelength radiation (e.g., near-infrared (NIR) light) into a shorter wavelength emission (e.g., visible light) via a two-photon or multi-photon mechanism [30, 31]. They can emit strong visible fluorescence, suggesting they can reach a high sensitivity and a high contrast in latent fingerprint development through fluorescence imaging [32–36]. The excitation of UCNPs often requires NIR radiation (e.g., 980 nm); this low energy radiation cannot cause autofluorescence from the substrates, and thus background interference can be avoided in the detection of fingerprints [36]. Compared with UV radiation, lower-energy NIR radiation is non-toxic and often desired in biomedical imaging, because it is less harmful to the skin and eyes of the operators as well as the DNA in fingerprint residue. In addition, UCNPs have other prominent advantages, such as a narrow emission peak, large Stokes shifts, good chemical/physical stability, and low toxicity [37–40]. Therefore, UCNPs are promising alternatives to

traditional fluorescent NPs, such as QDs, for latent fingerprint development. Recently, it was reported that commercially available $\text{NaYF}_4:\text{Yb},\text{Er}$ UC fluorescent particles could be used for the development of latent fingerprints [41]. However, the commercial particles used were not well dispersed and uniform in shape, having a large size range from ~ 0.2 to $2\ \mu\text{m}$. Such large particles with nonuniform shapes could interfere with the affinity between the particles and the fingerprint; even detailed features of the fingerprints, such as sweat pores, could be covered by the larger particles, leading to decreased detection sensitivity.

Hence, for the first time we report the use of nano-sized $\text{NaY}_{0.78}\text{F}_4:\text{Yb}_{0.20},\text{Er}_{0.02}$ dry powder as a novel UC fluorescent label for completely developing whole latent fingerprints. We successfully used UCNPs to clearly image latent fingerprints on various smooth substrates, including glass, ceramic tiles, floor leathers, marble of different surface textures, metallic materials (aluminum alloy sheets, stainless steel sheets, and aluminum foils), polymeric materials (plastic cards), wood materials (wood floor and painted wood), and various papers (train tickets, printing papers, magazine covers, and note papers). Owing to the use of UCNP powder to develop fingerprints, the friction ridge details of fingerprints on various smooth substrates could be clearly defined without background interference or color distraction under the excitation of human-safe NIR light, resulting in good contrast for enhanced fingerprint development.

2 Experimental

2.1 Materials

The rare earth oxides used in this work, including yttrium oxide (Y_2O_3), ytterbium oxide (Yb_2O_3), and erbium oxide (Er_2O_3), were all of 99.99% purity. Sodium fluoride (NaF), stearic acid ($\text{C}_{17}\text{H}_{35}\text{COOH}$), oleic acid ($\text{C}_{17}\text{H}_{33}\text{COOH}$), sodium hydroxide (NaOH), and nitric acid (HNO_3) were of analytical grade. Triple-distilled water was used throughout the experiments.

2.2 Characterization

The size and morphology of as-prepared UCNPs were observed with a transmission electron microscope (TEM) using an accelerating voltage 200 kV. X-ray diffraction (XRD) measurements were performed on an X'Pert Pro diffractometer (PANalytical Co., Holland) at a scanning rate of $8^\circ/\text{min}$ in the 2θ range of 10 to 80° , with graphite monochromatized $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15406\ \text{nm}$). UC fluorescent spectra of the dried NP powder were measured on an LS-55 fluorescence spectrophotometer (Perkin Elmer Co., USA) attached with an external 980 nm laser (Beijing Hi-Tech Optoelectronic Co., China) instead of an internal excitation source. The UCNP labeled fingerprints were irradiated by a 980 nm laser (Suzhou Xiaosong Technology Development Co., Ltd. China) equipped with a beam expander. The power of the 980 nm laser was 15 W and the power density was $1.67\ \text{W}/\text{cm}^2$. The fingerprint images were photographed *in situ* by using a Nikon D800 digital camera equipped with an AF-S Nikkor 24–70 mm f/2.8G ED lens.

2.3 Synthesis of NaYF₄:Yb,Er upconversion nano-particles

We followed our reported oleic acid-based solvothermal method with a minor modification [42, 43]. In this synthesis, rare earth stearate was used as a precursor. A mixture of 0.8807 g of Y₂O₃, 0.3941 g of Yb₂O₃, and 0.0383 g of Er₂O₃ was dissolved in nitric acid by heating to form the rare earth nitrates; the nitrate powder was obtained after solvent evaporation. The as-prepared powder and 8.5344 g of stearic acid were dissolved in 150 ml ethanol in a three-neck flask with vigorous stirring at 50 °C. Subsequently, the temperature was elevated to 78 °C. Then another solution containing 1.1900 g of NaOH and 20 ml of ethanol was added dropwise into the flask. The resulting mixture was refluxed at 78 °C for another 40 min. Precipitates from the reaction mixture were filtrated under decompression and washed with ethanol thrice. The precursor powder was obtained after the precipitates were dried at 60 °C for 12 h. Subsequently, 100 ml of water, 150 ml of ethanol, and 50 ml of oleic acid were mixed together under stirring to form a homogeneous solution, to which 9.5772 g of precursor powder and 2.0995 g of NaF were added. The resulting mixture was stirred under sonication for 15 min, transferred into a 500 ml autoclave, sealed, and then solvothermally treated at 180 °C for 24 h. After the autoclave was naturally cooled to room temperature, the UCNPs were deposited at the bottom of the vessel, and a mixture of chloroform and ethanol (1:6, v/v) was used to collect the precipitates. The UCNPs were purified by centrifugation, washed with a mixture of water and ethanol (1:2, v/v) three times, and dried at 60 °C for 12 h. NaYF₄:Yb,Er UCNPs were thus formed.

2.4 Detection of latent fingerprints using NaYF₄:Yb,Er upconversion nanoparticles

All the fingerprints were collected from the same donor. Firstly, hands were washed thoroughly with soap. The fingers were then gently wiped across the forehead. Finally, the fingers were pressed on the surfaces of different substrates at room temperature to obtain latent fingerprints. To develop the resultant latent fingerprints, the dry NaYF₄:Yb,Er UCNP powder was carefully applied to the surface of the substrates with a light brushing action. The excess powder was removed by dusting the substrate surfaces with a gentle, smooth motion until a fingerprint image was developed. The fingerprint images were photographed *in situ* with a Nikon D800 digital camera equipped with an AF-S Nikkor 24–70 mm f/2.8G ED lens and a 980 nm laser light for exciting the NaYF₄:Yb,Er UCNPs.

3 Results and discussion

3.1 Characterization of NaYF₄:Yb,Er upconversion nanoparticles

Synthesis methods for high-quality NaYF₄:Yb,Er UCNPs have been well established and widely reported, including the thermal decomposition method [44–46], hydrothermal method, and solvothermal method [47–49]. Here, we used an oleic acid-based solvothermal method to chemically synthesize NaYF₄:Yb,Er UCNPs. The as-prepared NaYF₄:Yb,Er UCNPs were then characterized by TEM, XRD, and fluorescence spectroscopy. It is known that there are two polymorphs in NaREF₄ (RE = rare earth) at ambient pressure: a cubic α -phase (metastable high-temperature phase) and a hexagonal β -phase (thermodynamically stable low-temperature phase). β -NaREF₄ can be obtained from α -NaREF₄ via a cubic-to-hexagonal phase transition process [50, 51]. The β -NaREF₄ phase is desired as it shows a strong UC fluorescence in comparison to α -NaREF₄. The TEM image (Fig. 1(a)) as well as

XRD patterns (Fig. 1(b)) collectively confirm that the obtained NaYF₄:Yb,Er UCNP are of pure β -phase with a regular spherical shape. The histogram of the particle diameter (Fig. S1 in the Electronic Supplementary Material (ESM)) reveals that the NaYF₄:Yb,Er UCNP are 62–89 nm in diameter, with an average value of 74.2 nm. The resultant NaYF₄:Yb,Er UCNP emitted strong green fluorescence under 980 nm irradiation (Figs. 1(c) and 1(d)). Such strong NIR-induced green fluorescence from synthetic β -phase NaYF₄:Yb,Er UCNP inspired us to use them for developing latent fingerprints on non-infiltrating materials (including glass, marble, aluminum alloy sheets, stainless steel sheets, aluminum foils, and plastic cards), semi-infiltrating materials (including floor leathers, ceramic tiles, wood floor, and painted wood), and infiltrating materials such as various types of paper.

3.2 Mechanism of latent fingerprint development by using NaYF₄:Yb,Er upconversion nanoparticles

The powder development method is essentially a physical phenomenon, which relies on the adherence of powder particles to the moisture (such as sweat) and oily components (such as grease and oil) in the fingerprint residue [1, 52]. Thus, it is expected that this attraction decreases with the evaporation of the fingerprint residue. Scheme 1 illustrates the general principle of latent fingerprint development by using NaYF₄:Yb,Er UCNP. NaYF₄:Yb,Er UCNP powder was first deposited onto the fingerprints. The sweat and grease in the fingerprint residue drove the quick physical adsorption of the UCNP onto the ridges produced on the substrate when the fingerprints were printed. 980 nm NIR light was then used to irradiate the fingerprints, exciting the UCNP to emit green light and consequently revealing the fingerprint image.

3.3 Latent fingerprint development by using NaYF₄:Yb,Er UCNP

To determine the effectiveness of NaYF₄:Yb,Er UCNP as fluorescence labels for the development of latent fingerprints on marble, traditionally used staining materials including magnetic iron oxide powder, TiO₂ powder, and commercial fluorescent powder were used as a control (Figs. 2(a)–2(c)). It was found that the magnetic powder and TiO₂ powder could not completely develop the latent fingerprints on marble (Figs. 2(a) and 2(b)). When the UV light was applied to the fingerprints stained by the traditional fluorescent powder, the friction ridges of the fingerprints could not be clearly resolved (Fig. 2(c)). However, when 980 nm NIR light was used to irradiate the fingerprints stained by UCNP, the friction ridges of the fingerprints were clearly revealed with sharp edges (Fig. 2(d)), showing that our NaYF₄:Yb,Er UCNP could be used as an effective powder for the development of latent fingerprints due to their enhanced strong green luminescence.

To determine the sensitivity of the UCNP-based fingerprint detection, a series of control experiments using traditional powders as well as micron-sized NaYF₄:Yb,Er UC powders were performed. The synthesis method used to obtain the micron-sized NaYF₄:Yb,Er UC powder is given in the ESM, and the scanning electron micrograph is shown in Fig. S2 in the ESM. As shown in Fig. 3, detailed features of the fingerprints, such as sweat pores, can be clearly observed with NaYF₄:Yb,Er UCNP (Figs. 3(a) and 3(b)), due to their small particle size, which is almost impossible to achieve with the micron-sized NaYF₄:Yb,Er UC powders (Figs. 3(c) and 3(d)). In the case of the fingerprints developed by traditional

powders, including bronze powder, magnetic iron oxide powder, and yellow fluorescent powder, detailed features, such as sweat pores could not be clearly observed (Fig. S3 in the ESM). These results clearly show that using UCNP for fingerprint detection can reveal more detailed features, leading to the high sensitivity of the developing method.

In order to demonstrate the practicality of the UCNP-based fingerprint detection method in forensic sciences, we conducted the fingerprint development experiments after the fingerprints had been aged for different periods of time. As shown in Fig. 4, the detection sensitivity decreased gradually with prolonged aging of the fingerprints, due to the gradual evaporation of the fingerprint. However, latent fingerprints aged for up to 1 year could still be developed with clear ridges, indicating that the sensitivity in the UCNP-based method was high enough for aged fingerprint development.

To determine the background interference of the UCNP-based fingerprint detection, various types of marble with complex surface patterns were chosen as a substrate, where fingerprints were printed, stained by UCNP powder, and then detected by NIR-induced green light emission from the UCNP (Fig. 5). As shown in Figs. 5(b')–5(f'), the well-defined friction ridges on the various types of marble with different textures could be clearly defined without background interference or color disruption after NIR light irradiation on the fingerprints, resulting in excellent contrast for enhanced fingerprint development. However, before NIR light irradiation, the fingerprints on the corresponding surfaces of the same marble were latent and almost invisible to the naked eye (Figs. 5(b)–5(f)). Similarly, excellent fingerprint images were detected on other non-infiltrating materials, such as glass, after NIR irradiation (Fig. 5(a')) in contrast to the hardly seen images before NIR irradiation (Fig. 5(a)). These results clearly show that the UCNP, used for fingerprint detection, can avoid the background interference, leading to the high sensitivity of the developing method.

In addition to the detection of the fingerprints on the surface of glass and marble, a series of development experiments using NaYF₄:Yb,Er UCNP were also carried out on the surfaces of a variety of other objects, including aluminum alloy sheets, stainless steel sheets, aluminum foils, plastic cards, floor leather, ceramic tiles, wood floor, and painted wood. Well-defined friction ridges of the fingerprints could be clearly observed on all of the samples (Fig. 6) without background interference, demonstrating that our developing method is versatile and can be applied to detect fingerprints on virtually all smooth objects.

We then proceeded with the evaluation of the use of UCNP in the detection of fingerprints printed on infiltrating materials such as various types of paper, including train tickets, printing papers, magazine covers, and note papers (Fig. 7). Surprisingly, the fingerprints on these materials could also be clearly detected, similar to the fingerprint development results on the non- or semi-infiltrating material (Figs. 5 and 6).

As shown by the aforementioned results, we have successfully employed NaYF₄:Yb,Er UCNP to detect fingerprints on a variety of different substrates. Our results show that dry NaYF₄:Yb,Er UCNP powder can image whole fingerprints with high efficiency (because the whole procedure was fast and could be finished in approximately 30 s for trained investigators), high sensitivity (because background interference can be avoided owing to the

use of NIR light as an excitation source, and sweat pores can be observed owing to the small particle size), and low toxicity (because NaYF₄:Yb,Er UCNP have proven to be biocompatible and NIR light is human-safe). Namely, the whole procedure is facile and rapid; an investigator only needs to apply pre-synthesized NaYF₄:Yb,Er UCNP powder onto the fingerprints, immediately followed by imaging the fingerprints under a fluorescence microscope with a 980 nm NIR light source. Moreover, NaYF₄:Yb,Er UCNP can be stored for a long duration without losing their UC fluorescence capability, allowing investigators to use pre-synthesized UCNP. Fingerprints also contain biomolecules such as DNA, which serves as an additional marker for identifying an individual. NIR light will not damage DNA, unlike the UV light used to excite traditional fluorescent NPs, such as QDs. Thus, the DNA collected from fingerprints after fingerprint development could still be analyzed and used for verifying the identity of individuals. Therefore, the use of NIR light for triggering the visible light emission from UCNP-stained fingerprints makes dry UCNP powders more attractive for forensic scientists.

4 Conclusions

In summary, NaY_{0.78}F₄:Yb_{0.20},Er_{0.02} UCNP with strong UC fluorescence induced by 980 nm NIR light, synthesized via a solvothermal approach, were successfully used as a novel fluorescent label for the development of latent fingerprints on various substrates, including glass, ceramic tiles, floor leathers, marble of different surface textures, metallic materials (aluminum alloy sheets, stainless steel sheets, and aluminum foils), polymeric materials (plastic cards), wood materials (wood floor and painted wood), and various papers (train tickets, printing papers, magazine covers, and note papers). The development procedure is facile and exhibits outstanding performance with high sensitivity, low background, high efficiency, and low toxicity. The work opens up a new avenue in the use of UCNP in developing whole latent fingerprints in forensic sciences.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Characterization of $\text{NaYF}_4:\text{Yb,Er}$ UCNPs synthesized at 180 °C for 24 h and their use in developing fingerprints along with other traditional developing materials. (a) TEM image, (b) powder XRD pattern, (c) photograph of the UCNPs powder excited with a 980 nm laser, and (d) UC fluorescence spectrum under 980 nm excitation.

Figure 2.

Latent fingerprints on the surface of marble stained by (a) magnetic iron oxide powder, (b) TiO_2 powder, (c) commercially available yellow fluorescent powder (Lot #D012, made by Beijing Fenge Science Ltd.), and (d) $\text{NaYF}_4\text{:Yb,Er}$ UCNPs. The bottles in (a)–(d) show the appearance of those materials used to stain the fingerprints. The scale bar corresponds to 8.0 mm.

Figure 3.

Magnified images of latent fingerprints stained by NaYF₄:Yb,Er UCNPs ((a), (b)) and micron-sized NaYF₄:Yb,Er UC powders ((c), (d)), and then imaged on the surface of glass: ((a), (c)) Images in bright field without 980 nm NIR excitation and ((b), (d)) UC fluorescent images formed owing to the excitation of UCNPs by a 980 nm NIR radiation. The scale bar corresponds to 2.5 mm.

Figure 4. Latent fingerprints aged on the surface of glass for various periods of time, stained by NaYF₄:Yb,Er UCNPs, and finally detected by 980 nm light irradiation: (a) 1 day, (b) 3 days, (c) 1 week, (d) 1 month, (e) 6 months, and (f) 1 year. The scale bar corresponds to 5.0 mm.

Figure 5. Latent fingerprints stained by $\text{NaYF}_4:\text{Yb,Er}$ UCNPs and imaged on the surface of glass ((a), (a')) and various types of marble with different textures ((b)–(f), (b')–(f')): ((a)–(f)) are images in bright field without 980 nm NIR excitation and ((a')–(f')) are UC fluorescent images formed owing to the excitation of UCNPs by a 980 nm NIR radiation. The scale bar corresponds to 5.0 mm.

Figure 6. Latent fingermarks stained by $\text{NaYF}_4\text{:Yb,Er}$ UCNP s and detected on the surface of various substrates after 980 nm light irradiation: (a) aluminum alloy sheets, (b) stainless steel sheets, (c) aluminum foils, (d)–(e) plastic cards, (f) floor leathers, (g) ceramic tiles, (h) wood floor, and (i) painted wood. The scale bar corresponds to 5.0 mm.

Figure 7. Latent fingerprints on the surface of various paper substrates, which were stained by NaYF₄:Yb,Er UCNPs and then detected by NIR-induced fluorescence imaging: (a) train ticket, (b) printing paper, (c) magazine cover, and (d) note paper. The scale bar corresponds to 5.0 mm.

Scheme 1.

Illustration of the development of latent fingerprints using a UCNP powder dusting process. A fingerprint was printed on a substrate such as glass, marble, alumina alloys, wood floor, or ceramic tiles. Then, $\text{NaYF}_4\text{:Yb,Er}$ UCNP powder was deposited onto the substrate to stain the fingerprint. A human-safe NIR light was then used to irradiate the fingerprint, leading to the excitation of UCNPs to emit green light and consequently revealing the fingerprint with high sensitivity and contrast.