Electronic Supplementary Information

Latent fingermarks light up: Facile development of latent fingermarks using NIR-responsive upconversion fluorescent nanocrystals

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S1. Experimental section

S1.1 Materials. Rare-earth oxides used in this work, including yttrium oxide (Y_2O_3), ytterbium oxide (Yb_2O_3), erbium oxide (Er_2O_3), thulium oxide (Tm_2O_3) and holmium oxide (Ho_2O_3) were all of 99.99% purity. Sodium fluoride (NaF), stearic acid ($C_{17}H_{35}COOH$), oleic acid ($C_{17}H_{33}COOH$), sodium hydroxide (NaOH), nitric acid (HNO_3), zinc oxide (ZnO), and ferric oxide (Fe_2O_3) were of analytical grade. Triple-distilled water was used throughout the experiments.

S1.2 Synthesis of $NaY_{0.78}F_4:Yb_{0.20},Er_{0.02}$ UCNCs. In this synthesis, rare-earth stearate was used as precursor. A mixture of 0.8807 g of Y_2O_3, 0.3941 g of Yb_2O_3, and 0.0383 g of Er_2O_3 was dissolved in nitric acid by heating to form rare-earth nitrates, and the nitrates powder was obtained after evaporation of solvent. In a flask, the as-prepared powder and 8.5344 g of stearic acid were dissolved in 150 ml ethanol 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 within 30 min. The resulting mixture was refluxed at 78 °C for another 40 min. Precipitates from the reaction mixture were filtrated under decompression, washed with ethanol for three times. 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 solvothermally treated at 175 °C for 36 h. After the autoclave was cooled to room temperature naturally, the UCNCs 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 UCNCs were purified by centrifugation, washed with a mixture of water and ethanol (1:2, v/v) for three times, and dried at 60 °C for 12 h. Finally, $NaY_{0.78}F_4:Yb_{0.20},Er_{0.02}$ UCNCs were thus formed.

S1.3 Synthesis of $NaYb_{0.98}F_4:RE_{0.02}$ (RE = Er, Tm, Ho) UCNCs. $NaYb_{0.98}F_4:RE_{0.02}$ (RE = Er, Tm, Ho) UCNCs were prepared in a similar manner by employing corresponding rare earth oxide (Yb_2O_3, Er_2O_3, Tm_2O_3, and Ho_2O_3), respectively.

S1.4 Preparation of UCNCs suspension. Firstly, 10.0000 g of UCNCs was dispersed in 100 ml of water by magnetic stirring under sonication for 15 min to form the mixture A. Then, 0.2000 g of sodium dodecyl sulfonate (SDS) was dissolved in 100 ml of water by magnetic stirring to form the mixture B. Finally, mixture B was added into mixture A, and the mixture was stirred for another 5 min to form

the UCNCs suspension.

S1.5 Preparation of conventional powder suspensions. Conventional powder suspensions were prepared in a similar manner by employing corresponding conventional powder (zinc oxide powder, ferric oxide powder, and green fluorescent powder), respectively.

S1.6 Development of latent fingermarks by using UCNCs suspension. Fingermarks were collected from the same donor by the following procedure: firstly, the hands were washed thoroughly with soap; then fingers were gently wiped across the forehead; finally, latent fingermarks were pressed onto the various substrates. To develop the fingermarks: firstly, the latent fingermarks were immersed into the UCNCs suspension for 30 s; then, the treated fingermarks were carefully washed by water to remove the excess UCNCs; finally, the developed fingermarks were dried naturally or by heating at 50 ^{o}C. The resultant fingermarks were excited and observed in a dark field by using a 980 nm NIR laser (Suzhou Xiaosong Science & Technology Co., China) equipped with a beam expander. The output power of the 980 nm laser was 15 W, the light spot was expanded to 9 cm^2, and the corresponding power density was 1.67 W/cm^2. The fingermark images were photographed in a dark field by using a Nikon D810 digital camera equipped with a Nikkor AF-S VR MICRO 105mm f/2.8G IF-ED lens. The camera was set to manual mode, the aperture was f/4, the exposure time was 2 s, and the ISO value was 200.

S1.7 Development of latent fingermarks by using conventional powder suspensions. Development of latent fingermarks by using conventional powder suspensions were carried out in a similar manner by employing corresponding conventional powder suspensions, respectively. The latent fingermarks developed by zinc oxide powder suspension and ferric oxide powder suspension were directly observed and captured in a bright field without any excitation. The latent fingermarks developed by green fluorescent powder suspension were excited and observed in a dark field by using a 254 nm UV lamp. The output power of the 254 nm UV lamp was 24 W. The fingermark images were photographed in a dark field by using a Nikon D810 digital camera equipped with a Nikkor AF-S VR MICRO 105mm f/2.8G IF-ED lens. The camera was set to manual mode, the aperture was f/4, the exposure time was 2 s, and the ISO value was 200.

S1.8 Characterization. Crystal structures of the samples were performed by using a Philips X' Pert Pro Super diffractometer (PANalytical Co., Holand) with Cu Kα radiation (λ=1.5406 Å). Morphology and size of the samples were observed by using a transmission electron microscope (TEM) using an accelerating voltage 200 kV. Fluorescent spectra of the samples were measured on a LS-55 fluorescence spectrophotometer (Perkin Elmer Co., USA), which were attached with an external 980 nm laser (Beijing Hi-Tech Optoelectronic Co., China) instead of internal excitation source. The maximum power of the laser was 1250 mW.

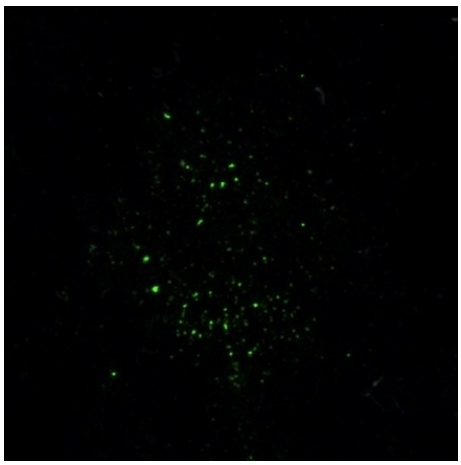

Figure S1. Latent fingermarks stained by $NaYF_4$:Yb,Er UCNCs suspensions without SDS added, and developed on the surface of glass after 980 nm NIR light irradiation.

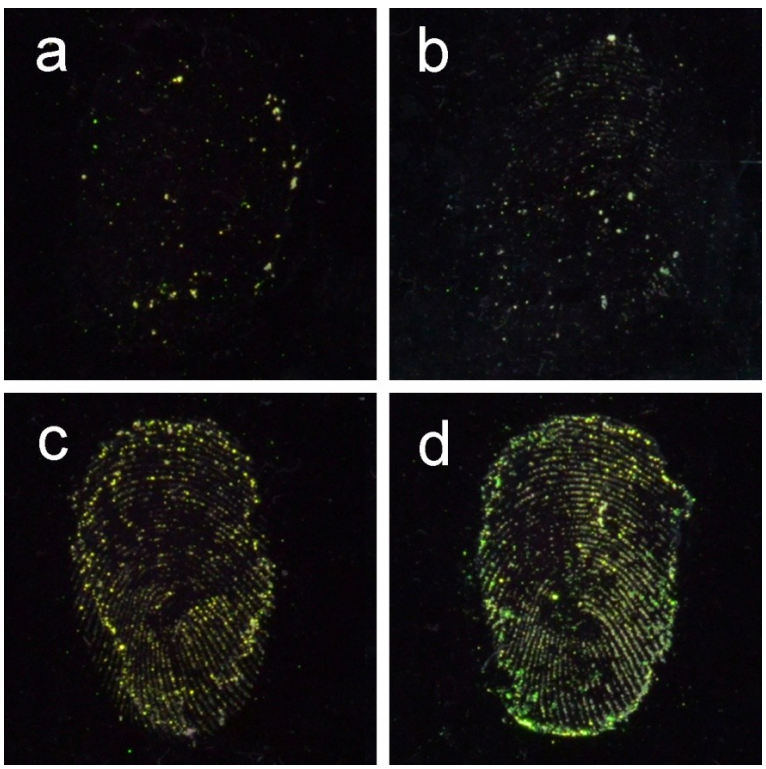

Figure S2. Latent fingermarks stained by $NaYF_4$:Yb,Er UCNCs suspensions for different time periods, keeping the SDS concentration of 0.05% unchanged, and developed on the surface of glass after 980 nm NIR light irradiation: (a) 10 s, (b) 30s, (c) 1 min, (d) 3 min.

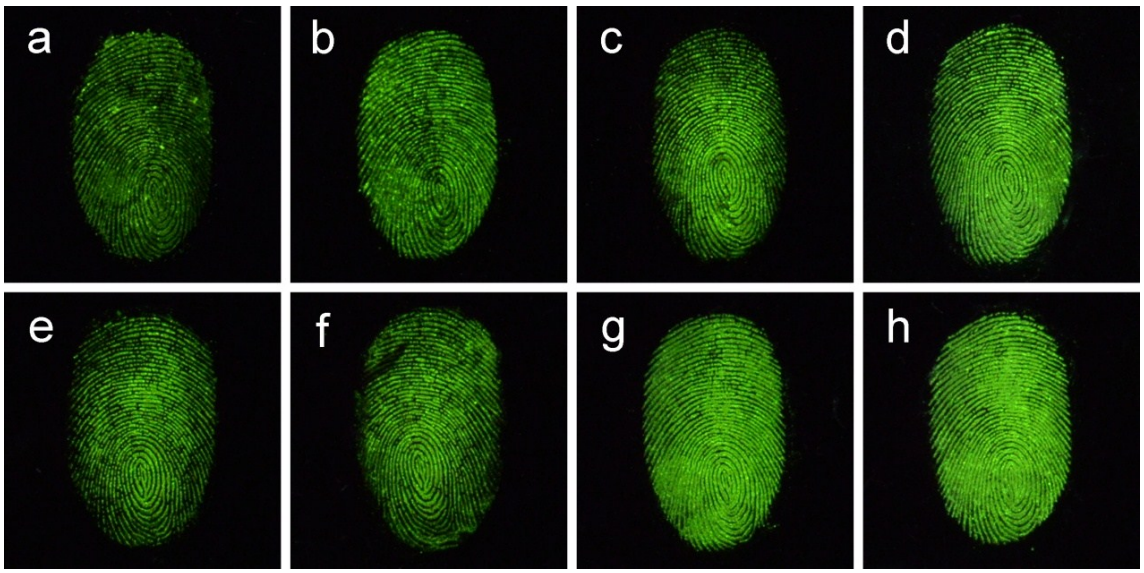

Figure S3. Latent fingermarks stained by $NaYF_4$:Yb,Er UCNCs suspensions for different time periods, keeping the SDS concentration of 0.1% unchanged, and developed on the surface of glass after 980 nm NIR light irradiation: (a) 10 s, (b) 20s, (c) 30 s, (d) 1 min, (e) 2 min, (f) 3 min, (g) 5 min, (h) 10 min.

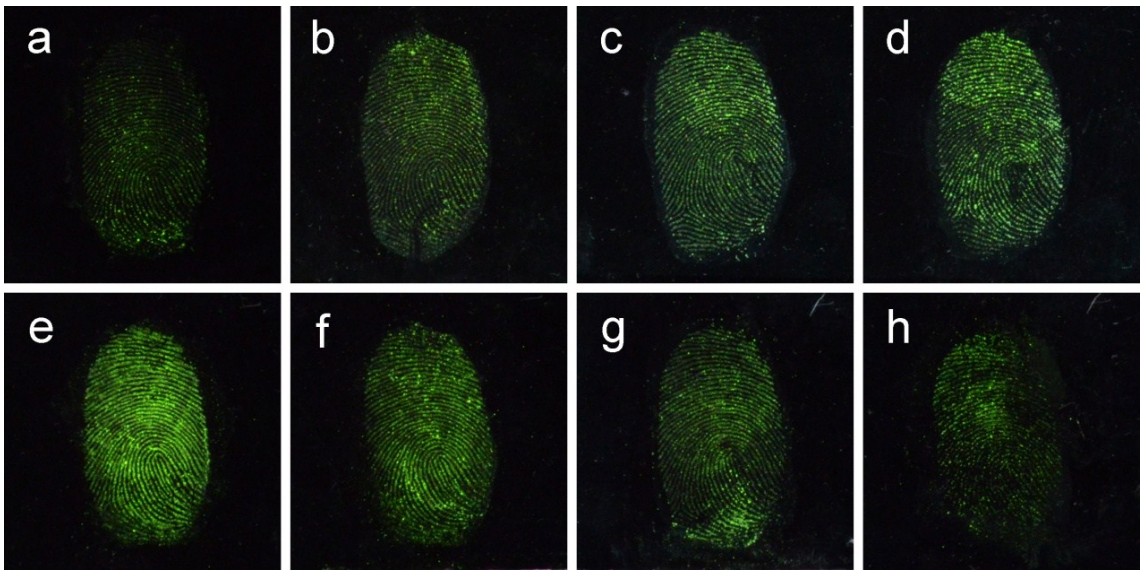

Figure S4. Latent fingermarks stained by $NaYF_4$:Yb,Er UCNCs suspensions for different time periods, keeping the SDS concentration of 0.2% unchanged, and developed on the surface of glass after 980 nm NIR light irradiation: (a) 10 s, (b) 20s, (c) 30 s, (d) 1 min, (e) 2 min, (f) 3 min, (g) 5 min, (h) 10 min.

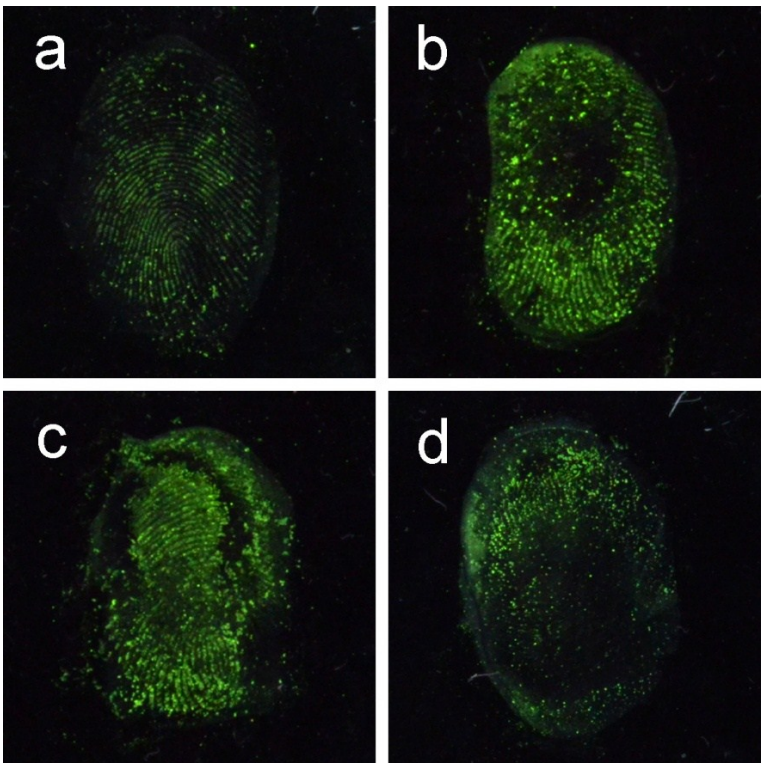

Figure S5. Latent fingermarks stained by $NaYF_4$:Yb,Er UCNCs suspensions for different time periods, keeping the SDS concentration of 0.3% unchanged, and developed on the surface of glass after 980 nm NIR light irradiation: (a) 10 s, (b) 30s, (c) 1 min, (d) 3 min.

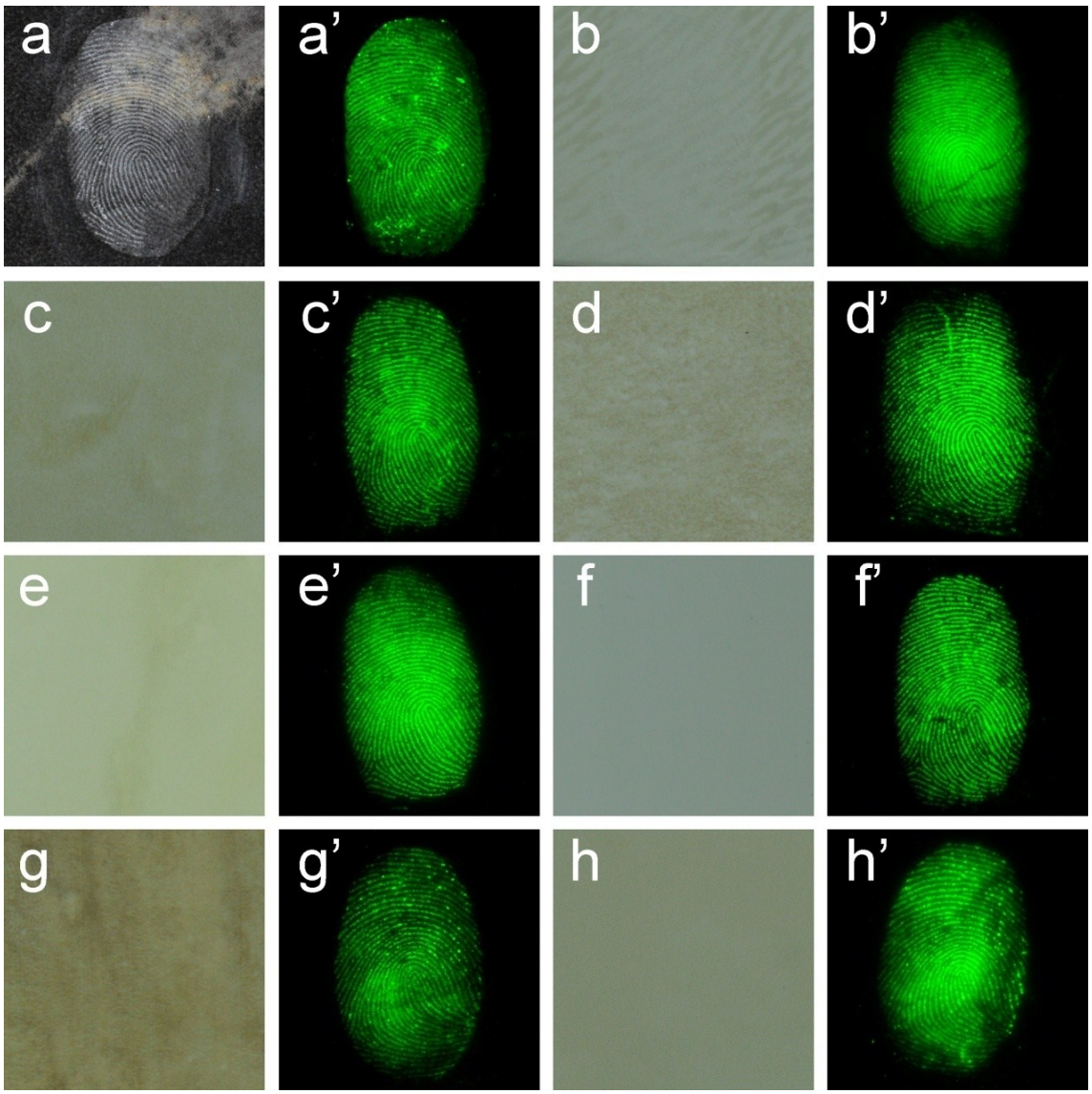

Figure S6. Latent fingermarks stained by $NaYF_4$:Yb,$Er_{0.02}$ UCNCs and developed on the surface of various marbles with different textures: (a-h) are images in a bright field without 980 nm NIR excitation, (a'-h') are fluorescent images in a dark field formed due to the excitation of UCNCs by 980 nm NIR radiation.

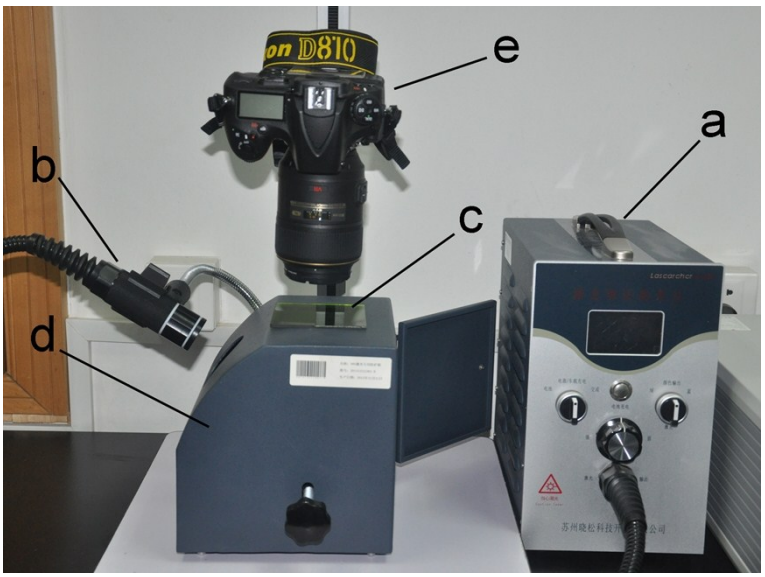

Figure S7. The imaging setup: (a) 980 nm NIR laser, (b) beam expander, (c) optical filter, (d) observation box, and (e) digital camera.

Figure S8. The image of $NaYF_4$:Yb,Er UCNCs excited by a 980 nm NIR laser in a dark field.