Supporting Information for

Fast Imaging of Eccrine Latent Fingerprints with Non-toxic Mn-doped ZnS QDs

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1. Preparation of Mn-doped ZnS QDs in organic phase

1.1 Preparation of $MnSt_2$, Zinc, and sulfur Stock Solutions:

$MnSt_2$ was obtained via the precipitation reaction between $MnCl_2$ and stearic acid (SA). Typically, 20 mmol of SA was dissolved in 35 mL of methanol and heated until all particles were dissolved to get a clear solution, and then a TMAH solution (dissolving 20 mmol TMAH in 15 mL methanol) was added. To this mixed solution, 10 mmol of $MnCl_2$ dissolved in 15 mL of methanol was added dropwise with vigorous stirring, and a white precipitate of $MnSt_2$ slowly flocculated. The precipitates were repeatedly washed with methanol for 3 times and dried under vacuum.

The zinc stock solution (0.5 M, for ZnS shell growth) was prepared by dissolving 1.0975 g of $Zn(OAc)_2$ in a mixed solvent system containing 3.0 mL of OAm and 7.0 mL of ODE at 160 ºC under nitrogen flow. The obtained Zn stock solution was stored at 50 ºC for the following use. The sulfur stock solution (0.6 M) was prepared by dissolving 0.0256 g of sulfur power in 1.33 mL of ODE at 120 ºC.

1.2 Synthesis of Mn-doped ZnS QDs in organic phase

Mn-doped ZnS QDs were synthesized via the "nucleation-doping" approach developed by Peng *et al.*[(S1-S3)] Typically, 0.3 mmol (186.6 mg) of $MnSt_2$, 9.0 mL of ODE were loaded into a 50 mL four-neck flask and degassed at 100 ºC for 15 min under vacuum. Then, the reaction system was filled with N_2, and the temperature was further raised to 250 ºC to get a colorless and clear solution. At this temperature, 1 mL of sulfur solution was injected into the reaction system. Immediately after the injection of sulfur solution, the color of the reaction solution turned to faint yellow, showing the formation of MnS nanoclusters. Two minutes after the injection of sulfur solution, 3 mL Zn stock solution was slowly added to the vigorously stirred solution at for 20 min. After finished the addition of Zn stock solution, the temperature cooled down to 230 ºC and again adding 3 mL Zn stock solution, the reaction mixture stayed at the temperature for another 20 min. Finally, the reaction was cooled down to room temperature, and the QDs were purified using acetone/$CHCl_3$ extraction for 3 times.

2. Ligand exchange of the as-prepared Mn-doped ZnS QDs[S4]

The as-synthesized Mn-doped ZnS QDs coated with OAm were dissolved in a minimum amount of chloroform and treated with excess ligand (MPA, TGA, MSA, N-Cys, Cys). The mixture was shaken for 10 min with sonication. The chloroform solution gradually became turbid as the original ligands with a long hydrocarbon chain were replaced by the above thiols. The thiol-coated QDs precipitate was isolated by centrifugation and decantation. Excess thiols were further removed by washing the precipitate with chloroform and centrifugation. Finally, water with NaOH was added to the precipitate, and the QDs were then dissolved in the water.

3. Synthesis of N-L-Cys-capped Mn-doped ZnS QDs with aqueous route

Highly-luminescent and water-soluble N-L-Cys-capped Mn-doped ZnS QDs were also directly prepared with an aqueous route.[S5] 3.5 mL of 0.1 M $ZnAc_2$, 0.2 mL of 0.05 M $MnCl_2$, and 20 mLof freshly prepared 0.07 M N-L-Cys were combined with 45.0 mL water in a three-neck round-bottomed flask. After the pH of the solution was adjusted to ~11 with 2.0 M NaOH, 4.5 mL of freshly prepared 0.1 M Na_2S was quickly injected with stirring. After stirred for 10 min, the mixture solution was refluxed at 100 ºC for one hour. Then, 3.8 mL of 0.1 M $ZnAc_2$ was injected into the reaction solution, and finally it was refluxed at 100 ºC for another hour. The obtained N-L-Cys-capped ZnS QDs were precipitated with ethanol, and separated by centrifugation. The resultant QDs were directly dissolved in water for further use.

4. Cyanoacrylate fuming of eccrine LFP

Cyanoacrylate fuming is a technique in which the latent fingerprint is exposed to vapors of cyanoacrylate monomer, a liquid adhesive sold commercially under numerous trade names. The cyanoacrylate monomer vapor polymerizes on the material comprising the latent fingerprint to form a layer of white polymer, which increases the contrast between the fingerprint and the background, thus enhancing its visibility.[S6]

Cyanoacrylate fuming of fingerprints was performed in a closed-vessel, in which cyanoacrylate monomer was placed at the bottom. Aluminum foil bearing the eccrine LFP was suspended in the fuming vessel at 24 ºC for 15 min. During fuming, the cyanoacrylate monomer vapor was vaporized and polymerized when captured by the LFP on the aluminum foil.

5. Staining sebaceous fingerprint with N-L-Cys-capped Mn-doped ZnS QDs

In real cases, secretion from sebaceous gland is also commonly found in LFPs. Thus, we also checked the applicability of N-L-Cys-capped Mn-doped ZnS QDs in staining sebaceous LFPs. As shown in Figure S11A, fresh sebaceous LFPs can be stained with N-L-Cys-capped Mn-doped ZnS QDs in 10 s, but the performance is slightly poorer than that of eccrine LFPs. However, after aging sebaceous LFPs for 5 days before staining with N-L-Cys-capped Mn-doped ZnS QDs, a perfect fluorescent fingerprint image can be obtained (Figure S11B). Probably, the larger contents of long-chain fatty acids in sebaceous gland prohibit quick adhesion of QDs. After aging, these long-chain fatty acids may be degraded into short-chain ones,(S17) which increases the subsequent interactions with QDs for better staining. Overall, the above information indicates that N-L-Cys-capped Mn-doped ZnS QDs can also be explored for imaging of sebaceous LFPs.

Table S1 Required time for staining of the fingerprints in literature reports.

Imaging moiety	LFP origin	Incubation time	Ref.
MPA-capped $Zn_xCd_{1-x}Se$ QDs	sebaceous	30 min	(S7)
MSA-capped CdTe QDs	sebaceous	10 s	(S8)
MSA-capped CdTe QDs	sebaceous	3 s	(S9)
AuNPs	sebaceous	Become visible: 1h; total time: 4 h	(S10)
Plasmonic scattering AuNPs	sebaceous	30 min	(S11)
Dye-doped silica NPs	Not clear	5-10 min	(S12)
Electrochemiluminescence-active $Ru(bpy)_2(dcbpy)NHS$	Sebaceous and eccrine	1-2 min	(S13)
$Fe_3O_4@SiO_2$-Au	sebaceous	40 min	(S14)
Aptamer-based reagent	sebaceous	1-4 h	(S15)
Antibody-functionalized magnetic NPs	Not clear	30 min	(S16)
cyanoacrylate fuming (Superglue®)	eccrine	About 10 min	This work
N-L-Cys-capped Mn-doped ZnS QDs	eccrine	5 s	This work

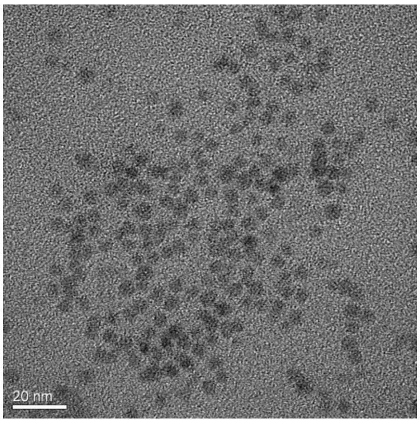

Figure S1 TEM image of the as-prepared Mn-doped ZnS QDs.

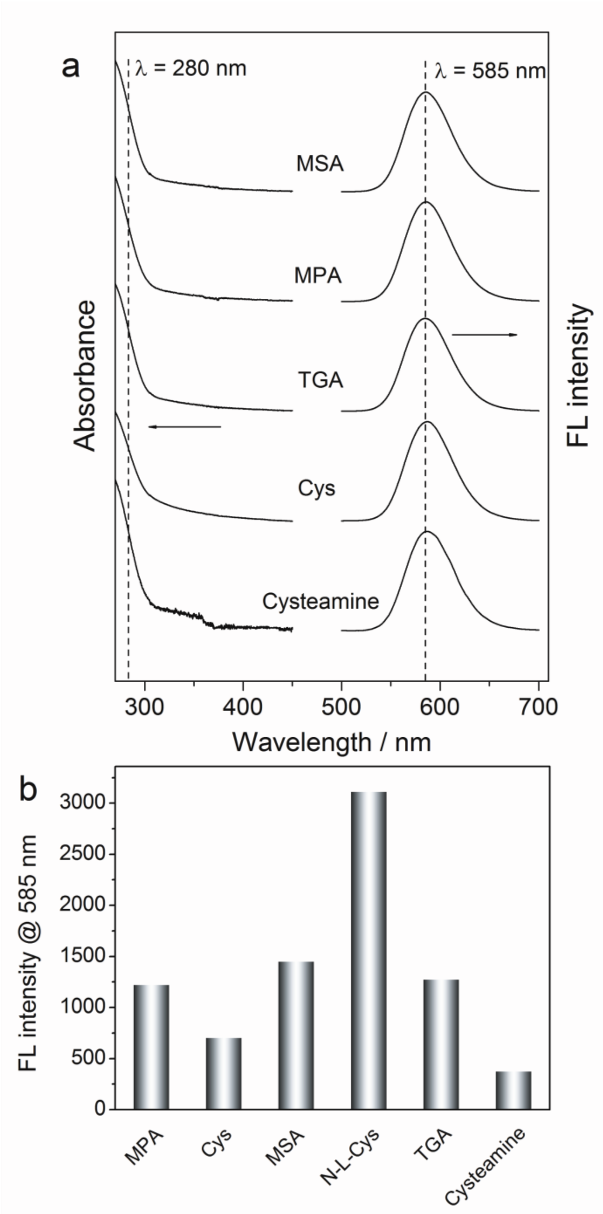

Figure S2 (a) UV-vis absorption and fluorescence emission spectra of various ligands capped Mn-doped ZnS QDs. All QDs possess the characteristic orange emission (centered @585 nm) originated from the Mn^{2+} $^4T_1 \rightarrow {}^6A_1$ transition. (b) The emission intensity (@585 nm) of various ligands-capped Mn-doped ZnS QDs. The concentrations of vairous ligands capped Mn-doped ZnS QDs were set at the same (0.078 × 50) based on their absorbance @280 nm, and the concentration of the QDs is about 2 mg/mL.

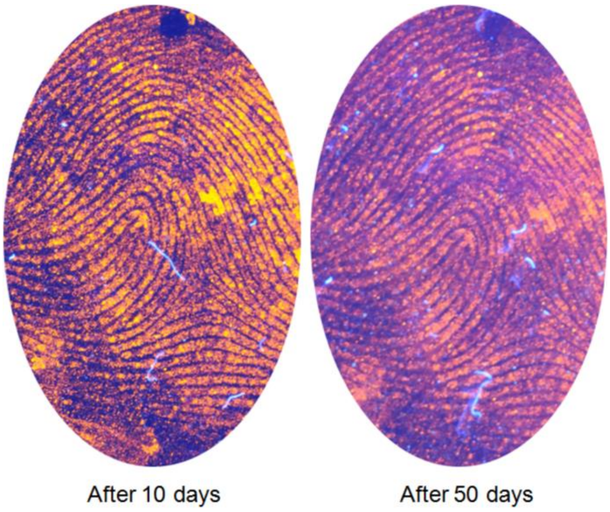

Figure S3 Fluorescent image of the eccrine LFP stained with N-L-Cys-capped Mn-doped ZnS QDs after 10 and 50 days.

Figure S4 Eccrine LFP obtained with cyanoacrylate fuming for 15 min.

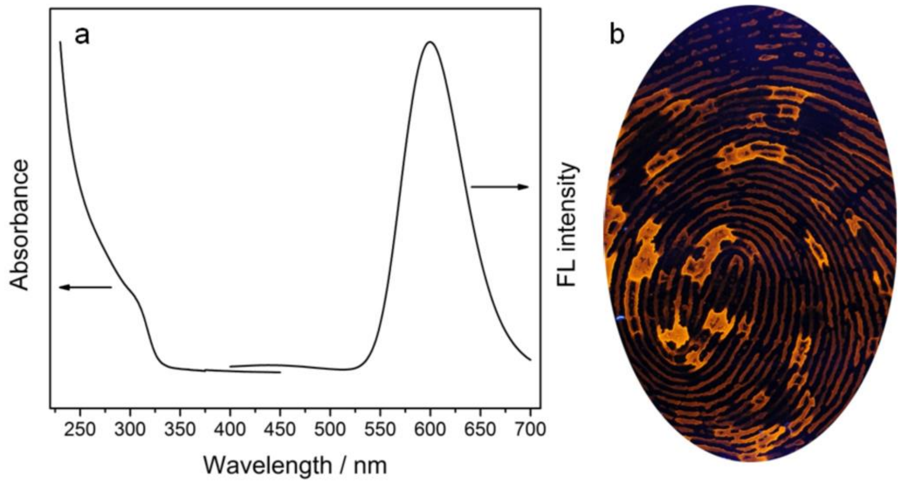

Figure S5 (a) UV-vis absorption and fluorescence emission spectra of N-L-Cys-capped Mn-doped ZnS QDs synthesized with the aqueous route; and (b) eccrine fingerprint image stained (5 s) with the aqueous-synthesized Mn-doped ZnS QDs.

Figure S6 Fluorescent image of aluminum foil with eccrine fingerprint without QDs.

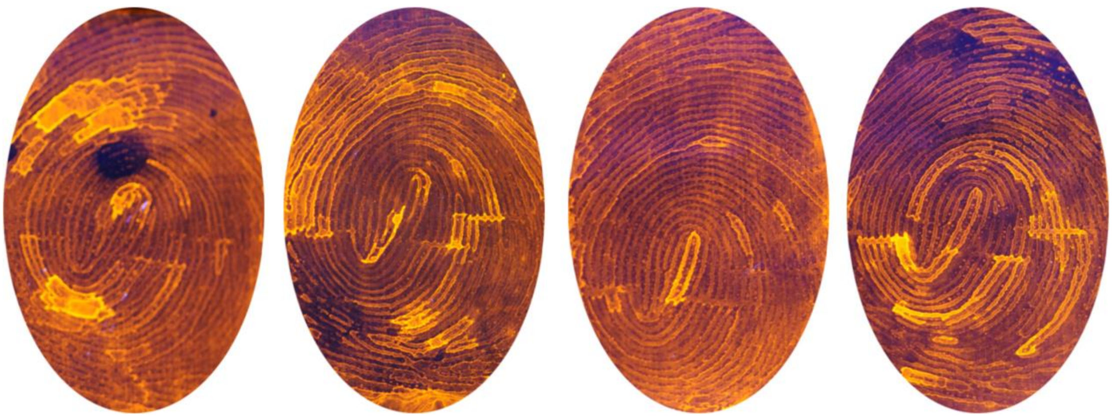

Figure S7 Good reproducibility of the fast (5 s) imaging of eccrine LFPs with N-L-Cys-capped Mn: ZnS QDs.

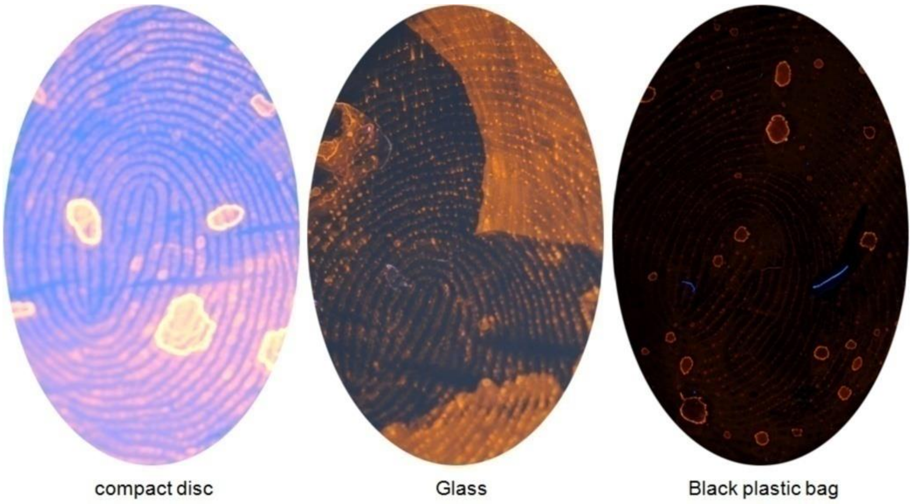

Figure S8 Fast imaging of eccrine LFPs on various substrates with N-L-Cys-capped Mn: ZnS QDs.

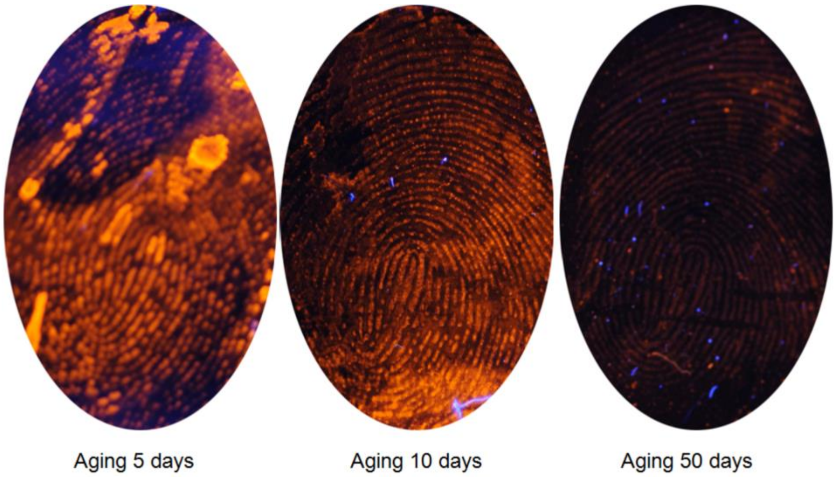

Figure S9 Fast imaging of aged eccrine LFPs with N-L-Cys-capped Mn-doped ZnS QDs.

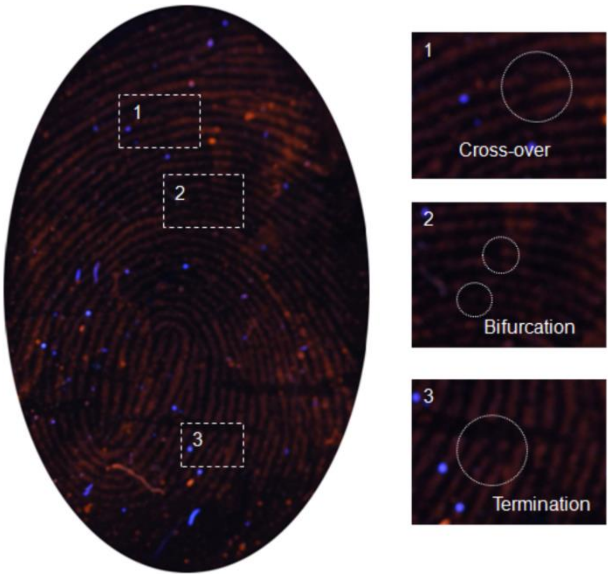

Figure S10 The sub-structures of aged eccrine LFP (50 days) imaged with N-L-Cys-capped Mn-doped ZnS QDs. 1, cross-over; 2, bifurcation; and 3, termination.

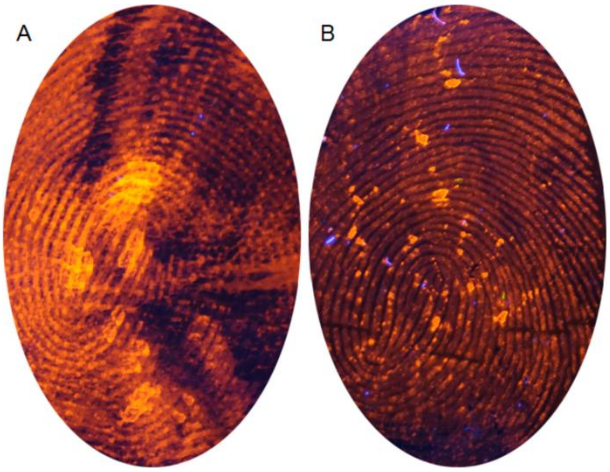

Figure S11 Fluorescent images of fresh (A) and aged (B, for 5 days) sebaceous fingerprint stained with N-L-Cys-capped Mn-doped ZnS QDs in 10 s.

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