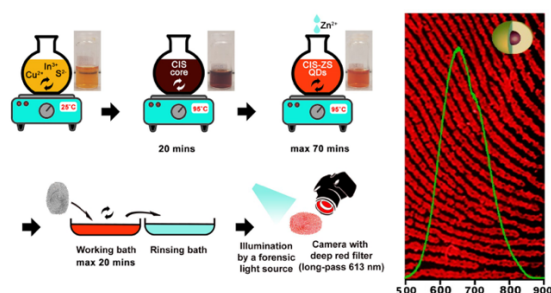


Luminescence Detection of Latent Fingermarks with Heavy-Metal-Free Quantum Dots

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Here we demonstrate the development of latent fingermarks on non-porous surfaces using water dispersed luminescent Cu-In-S/ZnS core-shell quantum dots. A simple synthesis afforded these heavy-metal-free quantum dots in large volumes, which were subsequently used to detect latent fingermarks on a range of challenging surfaces.

The detection of latent (not visible to the naked eye) fingermarks has been carried out for more than a century to enable associations between individuals and objects found at crime scenes to be evaluated.^{1,2} In more recent years innovative methods and materials based on nanotechnology have been applied to the visualisation of latent fingermarks with noticeable progress from specifically targeting fingermark components.³⁻⁵ Luminescent quantum dots (QDs) manifesting large cross sections of the UV/visible spectral range, narrow and size-dependent emission wavelengths, high quantum efficiencies, and enhanced photostabilities, have been applied to the development of latent fingermarks over the last two decades.^{6,7} However, even though cadmium-based QDs such as CdS,⁶ CdSe⁸ and CdTe^{9,10} have successfully visualised latent fingermarks, issues relating to the toxicity associated with heavy metals remain a concern.¹¹ In order to increase their biocompatibility some reported methods have included covering the QDs with a surfactant or over coating them with a non-toxic inorganic shell,¹² however, even with these techniques, the underlying issue of toxicity is still not resolved. Heavy-metal-free QDs such as carbon,¹³ Cu- and Mn-doped ZnS^{14,15} quantum dots have been proposed as alternatives, however, the latent fingermarks visualised by these QDs, which luminesce in the visible part of the spectrum, exhibit reduced sensitivity of the detection due to background noise.¹³⁻¹⁵ Luminescence increases the contrast between latent fingermark ridges and the underlying substrate by moving the means of detection outside of the ambient illumination.^{16,17}

Materials luminescing at a longer wavelength, (red to near infrared (NIR) region), have the potential to improve detectability of fingermarks since there is less interference in this region. However, only a limited number of NIR-based techniques have been reported for the detection of fingermarks and these techniques suffered drawbacks including toxicity, being a post-treatment rather than a standalone process and lack of contrast.¹⁸⁻²⁰ To fill this technology gap, three main objectives for this work were identified: first, preparation of a red-NIR luminescent heavy-metal-free QDs water-based solution; second, modification of the QDs to boost their affinity to interact with the fingermark residue and third, making the procedure simple and practical for operational use.

Ternary metal complex chalcogenide, Cu-In-S/ZnS (CIS-ZS) core-shell quantum dots are of low toxicity and exhibit strong and broad absorption of ultraviolet and visible light, intense photoemission and reasonable stability under photoexcitation.^{21,22} CIS QDs have been used in a variety of light-emitting applications such as solar cells,²³ electroluminescence,²⁴ photocatalysts²⁵ and bio-imaging.²⁶⁻²⁸ However, to the best of our knowledge, ternary core-shell QDs with photoluminescence (PL) in red/NIR range have not been used for fingermark visualisation.

A preliminary investigation was carried out using CIS-ZS QDs synthesised in organic solvent which were then transferred to the aqueous phase by ligand exchange (see ESI for experimental details). The aqueous solution of QDs gave promising results demonstrating that it is possible to develop fingermarks with CIS-ZS QDs on non-porous surfaces (see Figures S1 and S2 in ESI). Synthesis of QDs in an organic phase produces uniform and brightly luminescent products. However, an organic synthesis method is complicated, time-consuming and expensive due to the tedious preparation steps, requirement of inert atmosphere and high reaction temperature (>200°C).^{26,29} Also, the yield of QDs is very low (~tens of mg) and the required organic substances raise significant safety issues.^{30,31} Furthermore, as a post-synthesis treatment, QDs must be transferred from organic to aqueous phase by ligand exchange to render them biocompatible and applicable to fingermark development,

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which is a long process and may result in agglomeration and loss of luminescence.⁹ We experienced all the aforementioned issues during the organic-synthesis and ligand exchange of the CIS-ZS QDs as well as their application to fingerprints development (See ESI, Figure S1 and Figure S2 for more experimental details and results). These drawbacks limit the usage of this method for application in an operational environment.

Preparation of QDs in water has the potential to be more rapid, simpler, more biocompatible and inexpensive. However, the surfaces of the as-prepared QDs have dangling bonds which are tentatively passivated by organic surfactants. Subsequent exposure of the synthesised QDs to an aqueous environment results in surface oxidation and a decrease in luminescence efficiency.²⁹ Previous studies have used nitrogen gas purging to attempt solving this problem but this method cannot completely suppress the quenching effect.^{14, 30} A more effective strategy, namely passivation of QDs with an inorganic shell made of other semiconductor materials, noticeably minimises the trap-state defects and increases the luminescent quantum yield and stability.^{32, 33} Aqueous-synthesis of CIS-ZS QDs has been achieved using microwave-assisted²⁶ and hydrothermal methods, however these approaches suffer drawbacks including the necessity of special facilities and being a time consuming procedure. Most recently, a convenient, fast and inexpensive water-based synthesis method with a possibility of upscaling has been established to produce CIS-ZS QDs in safer way. In this approach, a mixture of copper, indium and sulfur precursors in water is heated at low temperatures (<100°C) to produce the Cu-In-S core, and then a zinc precursor is added to form the shell around the cores. We used this approach with modifications to produce CIS-ZS working solutions that could be used directly for the effective visualisation of latent fingerprints on different non-porous substrates without any further changes such as purification or pH and temperature adjustments.

Colloidal CIS-ZS core-shell QDs were synthesised in water in a simple one-step technique. First, aqueous solutions of CuCl₂, InCl₃, Na₂S were mixed in water in presence of a surfactant and ammonium solution. The reaction mixture was heated and kept at 90-95°C (see ESI† for experimental details). Cu and In salts participate in a precipitation reaction with sodium sulfide and produce the Cu-In-S spherical nanoparticles.²⁹ Zn (II) precursor was added to the reaction mixture without any purification and the ZnS layers epitaxially grew on the cores as a shell producing a luminescent CIS-ZS QDs solution (Figures 1a-1c). This QD solution can be prepared within 90 min on a large scale (at least 400 mL of 0.96 M solution per batch). Figure 1d and Figures S3a-S3d show the TEM images of the synthesised CIS-ZS core-shell QDs. The size of the QDs was less than 5 nm. Absorption (Ab) and PL spectra of the CIS core and CIS-ZS core-shell QDs are illustrated in Figure 1e.

The synthesised QDs fluoresced at deep red to NIR (emission maximum at 660 nm) when excited in a wide range of wavelengths from UV to red region. The growth of ZnS shells around the CIS cores noticeably increased the PL intensity (approximately 15 times). Increasing the amount of Zn (II) precursor resulted in significant enhancement of the

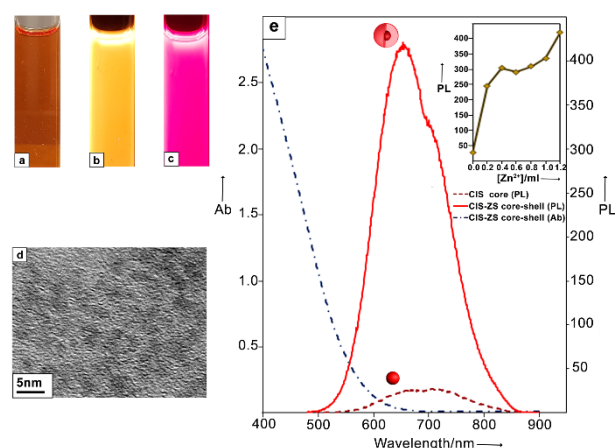


Figure 1. (a-c) CIS-ZS QDs solution photographed under (a) no illumination and (b and c) 350 nm illumination and through (a and b) no filter and (c) deep red filter (long-pass 613 nm). (d) TEM image of CIS-ZS QDs. (e) PL (excited at 350 nm) and Ab spectra of CIS core and CIS-ZS core-shell QDs. Inset in (e): maximum (excited at 350 nm) PL of CIS-ZS QDs with different amounts of Zn²⁺ precursor ([Zn²⁺]).

luminosity due to an increase of the thickness of the shell (Inset in Figure 1e); however, it led to a slight blue-shift from 680 nm for the core to 660 nm for the final product. This is most probably related to the surface reconstruction rather than the diffusion of Zn into the CIS core taking into account the relatively low temperature of 90-95°C.²⁷ Aging the prepared QDs solution under light for about one month, noticeably boosted the PL intensity (Figure S3e) due to the photodegradation of the surfactant leading to thickening of the shell, increasing the crystallinity and reducing the surface defects, as reported previously.^{30, 34}

Addition of more than 0.6 mL of Zn (II) precursor led to the formation of a cloudy solution due to agglomeration and precipitation of the QDs (Figures S4). This unstable solution was undesirable as it hindered fingerprint development, developing less ridge detail. Initially, 3-Mercaptopropionic acid (MPA) surfactant (the same surfactant used during the synthesis) was added to the prepared solution to stabilise the quantum dots as a post-synthesis step to prevent sedimentation by providing an electrostatic shield against inter-particle interactions. The long carbon chain and carboxylic acid group in the chemical structure of MPA was also proposed to increase both polar and non-polar interaction affinity with the components within the fingerprint residue. Although only used in small amounts, MPA is a toxic and malodorous chemical. To increase the safety of the working solution alternative molecules were explored as capping ligands, including L-cysteine and N-acetyl-cysteine (NAC), to replace MPA in the post-synthesis step. Both are non-hazardous chemicals with NAC used for medical purposes such treatment of paracetamol poisoning.³⁵ Xu et al. has previously demonstrated that NAC-capped QDs developed more ridge details of latent fingerprints compared to other ligands including MPA,¹⁵ fingerprints developed on transparent tape in our studies with NAC as the endcapping ligand consistently produced defined ridge detail and contrast (See Figure S5). This is proposed to be due to the variety of functional groups present in NAC, such as thiols, carbonyl and amide groups which enable

interactions with lipids and amino acids present in fingerprint secretions.

A typical procedure for the treatment of latent fingerprints with CIS-ZS QDs solution involved immersing the sample in the solution and agitating for varying durations, with most substrates requiring no longer than 20 minutes. International Fingerprint Research Group (IFRG) guidelines relating to initial proof of concept (Phase 1) studies were followed to conduct the experiment (see ESI for experimental details).³⁶ A range of substrates including transparent, black and blue adhesive tapes, glass slides, aluminium foil, aluminium drink cans and zip-lock bags were tested and developed fingerprint ridge detail (see Figure 2). The sticky side of adhesive tapes demonstrated particularly promising results, Figure 2g shows excellent ridge detail including the sweat pores of a natural latent fingerprint on a transparent sticky tape developed with the NAC-coated CIS-ZS core-shell QDs. To further investigate potential of the technique, the natural split fingerprints of 6 donors on transparent tape, aluminium foil and glass slides were developed. The results demonstrated full or partial development of the latent fingerprints from all 6 donors (Figure S6).

As a proof of concept, several charged latent fingerprints on new Australian polymer banknotes and aluminium drink cans as nonporous multi-coloured substrates were treated with MPA capped CIS-ZS QDs. Development produced marks well enough to distinguish high levels of ridge detail (Figure 3a,b). Being luminescent in deep red to NIR region facilitated visualising the latent fingerprints on these multi-coloured and multi-patterned substrates. The CIS-ZS QDs can be excited with a broad range of wavelengths. This is advantageous when working with inherently luminescent surfaces. Figure 3f shows that the security feature on the banknote of a UV-fluorescent bird interfered with the fingerprint on top of it.

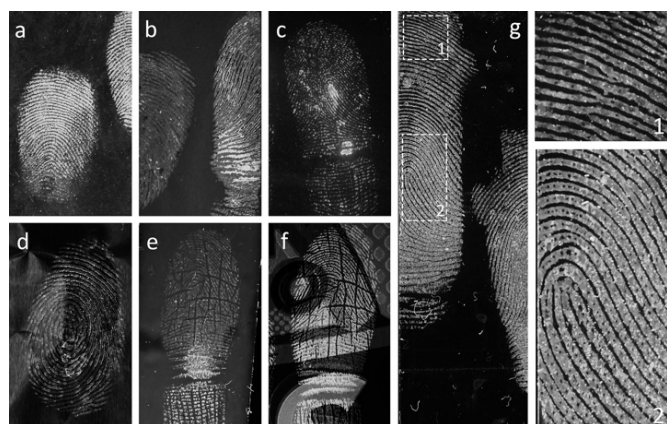


Figure 2. Developed (a-d,g) natural and (e,f) charged latent fingerprints on (a) glass slide, (b) black adhesive insulating tape, (c) zip lock bag, (d) aluminium foil, (e) blue adhesive insulating tape, (f) aluminium drink can and (g) transparent adhesive tape. The marks were illuminated at 350 nm and pictured through the deep red filter. The marks were shaken at ((a-d and f-g) 20 rpm for (b) 10 min, (a,c) 20 min, (d) 15 min, (f) 2 hrs and (g) 5 min in CIS-ZS QDs solution, (e) the mark was treated with no shaking for 20 min. The marks were illuminated at 350 nm and imaged through the deep red filter. See Table S1 for the photography conditions.

To visualise the hidden part of the fingerprint, it was illuminated at 450 nm instead of 350 nm leading to the elimination of fluorescence caused by the dye used for the bird printed on the note (Figure 3g). Subsequent testing explored natural fingerprints on these substrates with NAC capped CIS-ZS QDs. (Figure S7) demonstrates the level of ridge detail developed from 8 day old natural fingerprints. Whilst a larger number of donors showed poor development, the use of aged, natural marks gives a more realistic representation of fingerprint evidence. Further investigation will continue to explore the use of CIS-ZS QDs on these surfaces, particularly on the role of the surfactant.

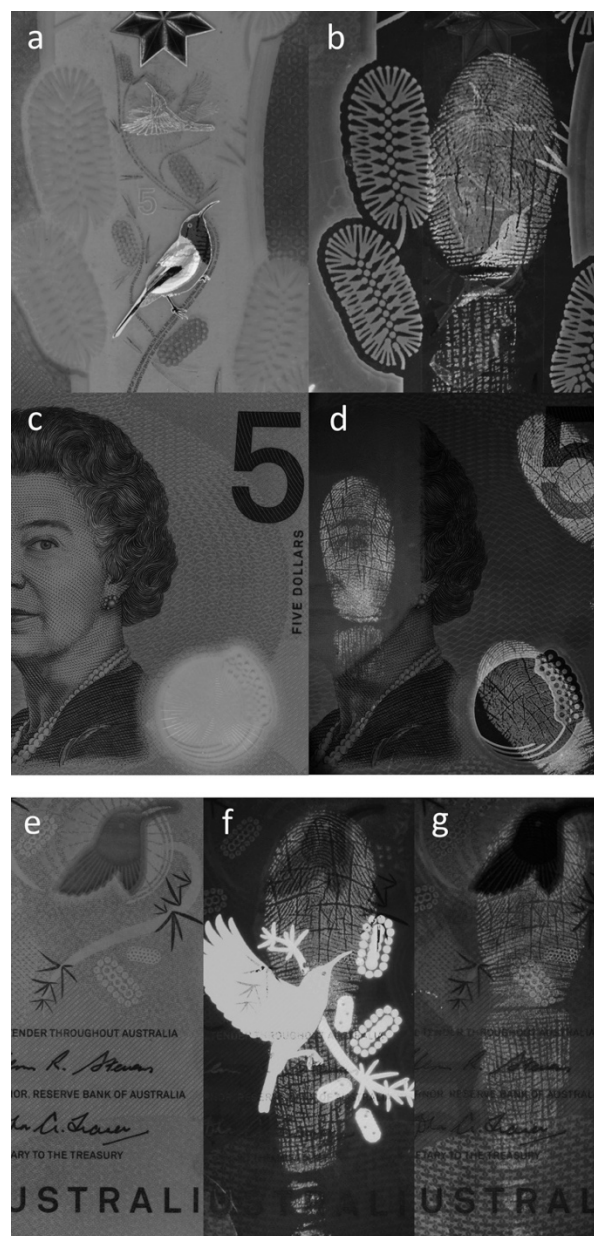


Figure 3. (a,c,e) Unilluminated and (b,d,f) illuminated at 350 nm and (g) 450 nm charged latent fingerprints (one female donor) deposited on Australian polymer banknote. The illuminated marks were imaged through a deep red filter. The samples were shaken at 20 rpm for 20 min in a MPA-coated CIS-ZS QDs solution. See ESI† and Table S1 for the photography details.

In conclusion, a safe innovative and straightforward procedure was developed for preparation and application of an aqueous working solution containing surface modified CIS-ZS core-shell QDs for visualisation of latent fingermarks. Latent fingermarks on various non-porous substrates were rapidly developed with high levels of ridge detail being observed. Being luminescent at wavelengths from deep red to NIR allowed elimination of the problem of dark, multi-coloured and multi-patterned backgrounds. However, issues remain in application to natural fingermarks on some challenging substrates such as polymer banknotes and cans. Further studies with a wider range of donors and substrates are required, as well as optimisation of the technique, including factors such as additional surface modification of the QDs, pH adjustment of the working solution and combination with other methods (such as cyanoacrylate fuming).

Acknowledgments

The authors thank all fingerprint donors for their cooperation. This research has been conducted in accordance with the Curtin University Human Research Ethics Committee (approval number: HRE2016-0252 and HRE2018-0476). S.S. was supported by an Australian Postgraduate Award (APA) and Research Training Scheme (RTS) and RB is funded by an Australian Government Research Training Program Scholarship. G.J. acknowledged ARC for funding support through the DECRA scheme (Project ID: DE160100589). There are no conflicts to declare.

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