**Title:**

Cadmium-free Quantum Dots in Aqueous Solution: Potential for Fingermark Detection, Synthesis and an Application to the Detection of Fingermarks in Blood on Non-porous Surfaces

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**Abstract**

The use of quantum dots (QDs) in the area of fingermark detection is currently receiving a lot of attention in the forensic literature. Most of the research efforts have been devoted to cadmium telluride (CdTe) quantum dots often applied as powders to the surfaces of interests. Both the use of cadmium and the nano size of these particles raise important issues in terms of health and safety. This paper proposes to replace CdTe QDs by zinc sulphide QDs doped with copper (ZnS:Cu) to address these issues. Zinc sulphide-copper doped QDs were successfully synthesized, characterized in terms of size and optical properties and optimized to be applied for the detection of impressions left in blood, where CdTe QDs proved to be efficient. Effectiveness of detection was assessed in comparison with CdTe QDs and Acid Yellow 7 (AY7, an effective blood reagent), using two series of depletive blood fingermarks from four donors prepared on four non-porous substrates, i.e. glass, transparent polypropylene, black polyethylene and aluminium foil. The marks were cut in half and processed separately with both reagents, leading to two comparison series (ZnS:Cu vs. CdTe, and ZnS:Cu vs. AY7). ZnS:Cu proved to be better than AY7 and at least as efficient as CdTe on most substrates. Consequently, copper-doped ZnS QDs constitute a valid substitute for cadmium-based QDs to detect blood marks on non-porous substrates and offer a safer alternative for routine use.

**Keywords**

Fingermark detection; fingerprint; blood; forensic science; nanoparticles; quantum dot; zinc sulphide; cadmium telluride; toxicity; luminescence; Acid Yellow 7.

## Introduction

Like many other scientific areas, forensic science is now beginning to embrace nanotechnology. This is particularly true for fingermark detection for which nanoparticles have been a subject of intensive research efforts for more than a decade. Instances of this trend can be found in the evolution of fingermark detection with gold nanoparticles, the first use of which being reported by Saunders in the late 1980s under the name of multimetal deposition (MMD) [1,2]. The exact mechanism leading to the detection of fingermarks remains not fully understood but it is commonly accepted that, at low pH range, the gold nanoparticles are negatively charged and are consequently attracted onto papillary secretions which are positively charged. Because treated marks are only faintly visible, a modified physical developer is then used to grow metallic silver on the deposited gold nanoparticles, leading to dark ridges on a light coloured background. The technique was optimized by Schnetz and Margot in 2001 [3], and further modified by Stauffer *et al.* [4,5], and Bécue *et al.* [6,7].

In addition to the use of gold colloids, numerous different nanoparticle types are being studied for fingermark detection and have already been the subject of different reviews [8-10]. Choi *et al.* used metal-containing nanoparticles, such as gold, silver and some metal oxides that can be powder dusted [11]. As reported by Sodhi and Kaur [12], fine particles adhere more easily to the fingermark residue than larger ones; therefore, it is suggested that nanopowders may lead to improved results. However, nanopowders raise some serious health and safety issues, as we will discuss below.

The strong interest in nanoparticles stems from a simple fact: at a nanometric scale, stable and inert materials with well established properties as a bulk may acquire new ones, unsuspected until then. Even their physical and electronic behaviour may change when nanoparticle size is reduced, a good example being the ruby-red colour of a colloidal gold solution (compared to

the golden colour of macroscopic gold). Another very attractive and promising property for fingermark detection is the ability to customize the surface of nanoparticles by grafting various molecules or chemical functions onto it. This provides the ability to tune the solubility in different solvents, but also and especially to tailor the affinity with papillary secretion compounds. For example, the molecular grafting – also called functionalization – has already led to the detection of metabolites in secretions [13-16]. In Leggett's work [13], gold nanoparticles were functionalized with antibodies targeting the cotinine (i.e., the metabolite of nicotine), that can be found in the sweat of smokers. By doing so, fingermarks from smokers can be specifically targeted. In another study, aliphatic chains ($C_{18}$) were grafted onto gold nanoparticles that were then used to detect fingermarks [10]. It has been shown that the length of the chain has an influence on the detection quality: the longer the grafted chain, the better the results. These functionalization capabilities, combined with tunable optical properties, offer nanoparticles great potential for fingermark detection [17].

Since 2000, a new kind of nanoparticles with increased possibilities of grafting and uncommon optical properties has been studied for fingermark detection: the quantum dots (QDs) [18-20]. QDs are nanocrystals of a size varying from 1 to 10 nm composed of semiconductor material [21]. Among the different existing types, cadmium sulphide (CdS), cadmium selenide (CdSe) and cadmium telluride (CdTe) are the most studied. These are strongly luminescent under UV radiation, with an emission wavelength varying according to the particle size. Indeed, small-sized particles emit in the blue part of the spectrum, whereas bigger ones emit in the red part [22]. This phenomenon can be explained through quantum theories (for a detailed explanation see [23-25]).

QDs have been studied with regards to fingermark detection mainly because of their optical properties and their extensive grafting potential (for a review, see [9]). They have not been used in casework yet, but numerous papers are showing promising results. Uses of different

QD types, such as cadmium sulphide (CdS) built into nanocomposites [18,20,26-30], cadmium selenide (CdSe) with or without a protective shell [10,19,20,31,32] and cadmium telluride (CdTe) [33-36], have already been reported.

However, aside from the results obtained, health and safety issues in relation to these particles constitute a major drawback regarding their application in a casework environment. This is rarely mentioned in the forensic literature, but nanoparticle inhalation (while power dusting) represents a danger for lungs, and consequently for the practitioner's entire respiratory tract, especially when nanosize particles are concerned [37]. Despite the fact that nanoparticle powder dusting has shown superior capabilities compared to conventional powders, its use, in our opinion, should be avoided, as the long-term effects of prolonged exposition have yet to be determined. The suspected hazard is mainly due to the small particle size, which facilitates penetration into body cells, and to a stronger reactivity than their non-nanometric counterparts. In our view, research attention should rather be drawn onto quantum dots that are applied in solution (aqueous, in particular), so as to reduce inhalation risks. In addition, and more specifically for cadmium-based QDs, the main concern is the carcinogenicity of the heavy metal contained in the core. Aside from risks derived from cadmium precursor manipulation during synthesis, toxic cadmium ions might leak from the core if the particles are damaged [38,39]. As we have already stated in a previous paper about CdTe quantum dots applied to the detection of blood fingermarks [33], it is crucial to find alternative materials to properly address this particular health and safety issue. To reach this goal, the toxic core can be coated with a protective layer of zinc sulphide (ZnS). This approach prevents cadmium leakage and therefore decreases cytotoxicity [39,40]. Nevertheless, coating procedures are tedious and a good quality protective layer is not easily achieved, leaving the toxicity problems unsolved. Another approach consists in using non-heavy metals for the core: QDs made of indium phosphide (InP) are relatively new and promising [41]. Their synthesis is,

however, laborious as it involves high temperatures and organic solvents. Moreover, production costs are high, as indium is a rare metal. This makes their use difficult in a forensic context.

Another option lies in the use of zinc sulphide (ZnS), not as a protective layer but as the main component of the core itself [42]. These ZnS QDs can be obtained easily at a low cost and are proven to be non-toxic [43]. They can be functionalized in the same way as CdTe, but do not possess the same optical properties: ZnS QDs exhibit a blue luminescence under UV illumination, but their emission wavelength does not vary with the particle size, contrary to conventional cadmium-based QDs. It is, however, possible to change the optical behaviour by doping the crystal structure with metallic ions during synthesis [43]. When copper ions ($Cu^{2+}$) are added, the luminescence becomes green, while manganese ions ($Mn^{2+}$) shift the emission peak towards the red region of the spectrum (longer wavelengths). By varying the nature of the ions and their concentration, the entire visible spectrum can be covered. ZnS QDs are thus characterized by interesting properties (i.e. non-toxic components, easy synthesis and functionalization, optical behaviour) that may allow them to replace the toxic cadmium-based QDs. Such ZnS:Mn QDs (manganese-doped) have already been used to detect latent fingermarks on glass, aluminium foil and polymethylpentene plastic, with encouraging results for the two latter substrates [44].

As a follow-up to our previous publication describing the use of CdTe QDs on blood fingermarks, this paper offers to replace CdTe QDs by doped ZnS QDs, to address health and safety issues. This study aimed to assess if doped ZnS represents a suitable alternative to CdTe to detect blood fingermarks using QDs. It involved the synthesis and characterization of QDs and their subsequent application to fingermarks in blood. Its efficiency was tested against that of Acid Yellow 7 (AY7, an effective blood reagent) and CdTe QDs.

## Material and methods

*Synthesis of quantum dots, optimisation and characterization*

All chemicals were reagent grade and were purchased from Sigma-Aldrich. No further purification was required before use.

The synthesis of copper-doped zinc sulphide quantum dots (ZnS:Cu) stabilized with 3-mercaptopropionic acid (MPA) was based on a published protocol [45]. This protocol was optimized by varying several parameters in order to get the best results in terms of luminescence intensity, solution stability and narrowness of the size distribution. In the original synthesis, zinc nitrate ($Zn(NO_3)_2 \cdot 6\ H_2O$) was used as the zinc source. According to various authors [46-48], other zinc precursors can be used. Therefore, zinc acetate ($Zn(CH_3CO_2)_2 \cdot 2\ H_2O$), zinc chloride ($ZnCl_2$) and zinc sulphate ($ZnSO_4 \cdot 7\ H_2O$) were tested and the obtained solutions were further characterized to determine the best zinc source. The amount of doping ions was also investigated for copper concentrations of 1% and 3%. To study the influence of copper as a doping agent, a synthesis without a doping ion was performed. The effect of the MPA was explored using three different molar ratios of Zn:MPA (1:4, 1:2, 1:1). The molar ratio of Zn:S was also varied (1:2, 1:0.9, 1:0.5).

In a typical synthesis of ZnS doped with 1% copper, 2 mL of 0.5 M zinc chloride ($ZnCl_2$), 100 µL of 0.1 M copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$) and 350 µL of 3-mercaptopropionic acid (MPA) were mixed together in a three-neck round-bottom flask, leading to a 1:0.01:4 molar ratio of Zn:Cu:MPA. After diluting that volume to 45.5 mL with reverse osmosis deionised (RO/DI) water (18.2 Ω·cm), the pH was adjusted to ~11 by the addition of 2 M sodium hydroxide (NaOH). The mixture was then degassed by bubbling nitrogen ($N_2$) through the

solution for half an hour. In another flask, sodium sulphide nonahydrate ($Na_2S{\cdot}9H_2O$) was dissolved in RO/DI water to obtain a concentration of 0.2 M. This solution was kept under an inert atmosphere ($N_2$) and stirred for 15 minutes. Afterwards, 4.5 mL of the sodium sulphide solution was quickly injected into the first mixture under strong stirring, which was maintained for 15 minutes (i.e. a molar ratio of 1:0.9 for Zn:S). No changes occurred in the solution. It was then refluxed under open-air conditions at 100 °C. After one hour, 1520 µL of 0.5 M $ZnCl_2$ was added to the solution and refluxing continued for an additional hour.

The CdTe quantum dots were synthesised according to a previous published protocol without any modifications [33].

The absorption spectra of both the ZnS:Cu and CdTe solutions were measured with a Biotek Epoch Micro-Volume spectrophotometer. These measurements were made directly on the obtained solution or on diluted aliquots, if required. For the ZnS:Cu QDs solutions, the measurements were made right after the $Na_2S$ injection, and then after two hours of refluxing.
The photoluminescence excitation and emission spectra were measured at room temperature on a Hitachi F-2500 fluorescence spectrophotometer, following the same procedure as described for the absorption spectra.
Particle size and zeta potential (ζ) were determined by dynamic light scattering (DLS), on a Zetasizer Nano ZS (Malvern Instrument Ltd.). For each sample, the hydrodynamic diameter was measured five times while the ζ potential was measured three times. In both cases, average data were used.

*Blood fingermark deposition*

The fingermark deposition procedure was similar to the one used previously [33]: blood

fingermarks (i.e. marks left after the papillary surface was covered with the donor's fresh blood) of four donors (two females and two males) were deposited on four substrates (i.e. glass, transparent polypropylene sleeves, black polyethylene bags and aluminium foil). Each donor was asked to prick his/her left index with a blood lancet and to deposit and spread out a drop of blood on their right index. The volume of blood deposited on the finger was not measured, neither was the deposition pressure. Immediately afterwards, 20 successive appositions of the blood-contaminated finger were made on the same surface, without adding more blood on the finger so as to obtain a series of marks presenting a decreasing quantity of blood. The same procedure was followed for each donor and surface. When the marks appeared to be dry (after approximately one hour), the substrates were stored in the dark at room temperature for one month. Temperature and relative humidity were not controlled nor measured.

*Staining solutions and detection protocol*

In order to optimize the detection process, several parameters of the ZnS:Cu staining solution were studied. The concentration was varied from the initial concentration obtained after the synthesis to a 40-times dilution. Five different pH values were tested (3, 3.5, 4, 7 and 11), using MPA to adjust the pH when necessary. To reach pH 11, NaOH was used. Finally, immersion times ranging from 5 to 60 minutes were tested.

In order to compare and evaluate the efficiency of the ZnS:Cu QDs, the series of marks were cut in half before treatment. For practical reasons, the glass substrates were cut in half and rejoined before blood fingermark deposition. That way, one half could be processed with the technique to be tested and the other with a reference technique. This procedure was done twice: "ZnS:Cu versus Acid Yellow 7" and "ZnS:Cu versus CdTe". Acid Yellow 7 was chosen for reasons already detailed elsewhere [33]. For the first set of comparison, the

ZnS:Cu QD solution was applied on the left half, whilst, for the second, it was applied on the right half.

Similarly to CdTe, the ZnS:Cu QD working solution must be prepared just before use. It is done by diluting the solution with RO/DI water and by adjusting its pH using MPA (undiluted), according to the values determined during optimisation.

The CdTe working solution was prepared following the protocol described by Bécue *et al.* [33].

The Acid Yellow 7 staining solution was prepared by following the procedure recommended by the product supplier BVDA (http://www.bvda.com/EN/prdctinf/en_acid_yellow_7.html). One gram of Acid Yellow 7 was dissolved in 50 mL of acetic acid, 250 mL of ethanol and 700 mL of demineralised water.

The detection procedure is illustrated in Figure 1. Firstly, both sides of the samples were immersed together in a fixing bath consisting of 5-sulfosalicylic acid solution (2.3% w/v) for ten minutes [49]. Following that step, each side underwent its own detection procedure. For both QD solutions, the samples were briefly rinsed in water to remove excess 5-sulfosalicylic acid and then immersed in the QD staining solution under gentle orbital shaking (i.e. 50 rpm). The samples were finally rinsed with water to remove excess unattached QDs. For Acid Yellow 7, the samples were immersed in the staining solution straight after the fixing bath, for 15 minutes, and were then rinsed in two subsequent baths. The first one consisted of the same solvent mixture used for the dye solution while the second was a simple water bath. This procedure was also as recommended by BVDA. All treated samples were hung to dry for one hour.

*Method efficiency and quality evaluation*

The efficiency and sensitivity of the methods were compared by rejoining the corresponding halves of the depletion series. Each fingermark was then photographed under UV illumination using a Mini-Crimescope® 400. The excitation source was set to the UV position, corresponding to a large bandwidth from 300 nm to 400 nm. No observation filter was required. The quality of the detected marks was assessed on two sets of images: the as-obtained images without any digital enhancement and the images converted into greyscale and inverted to get dark ridges on a light background. No other specific digital enhancement was performed to avoid favouring one side of the samples compared to the other.

Following the guidelines offered by Kent [50], results were classified across four quality levels, ranging from zero (0) to three (3). Zero (0) meant that there was no sign of development or only faint dots without any possibility of stating if a fingermark was present or not. One (1) was for marks with a low contrast and where some areas were not visible. Two (2) was used when the mark was visible and luminescent but with missing areas. Three (3) stood for strongly luminescent and clearly visible marks without any missing areas.

Both series (i.e. comparison of ZnS:Cu vs. AY7 and ZnS:Cu vs. CdTe) were assessed separately and each half mark was evaluated independently of its opposite half. The assessor was not aware of which reagent was under evaluation.

## Results

### *Optimisation of the ZnS:Cu quantum dot synthesis*

Figure 2 illustrates the emission spectra of the ZnS:Cu QD solutions made with the chosen zinc precursors. For the measurements, the excitation wavelength was set at 330 nm, corresponding to the absorption maximum common to the four solutions. All zinc salts lead to the formation of luminescent quantum dots. The emission spectra share the same characteristics, except for the luminescence intensity. Since zinc chloride ($ZnCl_2$) leads to the

solution with the most intense luminescence, it was selected for the subsequent syntheses.

Figure 3 illustrates the influence of the copper ion doping on the luminescence properties. As can be seen, the addition of 1% copper to the zinc solution during the synthesis leads to a shift of about 50 nm towards longer wavelengths. The position of the maximum emission intensity shifts from 423 to 470 nm, changing the colour of the luminescence from blue to green-blue. For a 3% doping, the shift is even more pronounced since the maximum intensity is then located around 489 nm. However, the doping causes a decrease in the intensity of the luminescence (-7 and -38% for doping of respectively 1 and 3%). A copper doping of 1% has been chosen for the following syntheses, since it led to a Stokes shift of 120 nm (calculated from the middle of the excitation window, i.e. 350 nm) sufficient to get rid of background interference, and its luminescence intensity remained high. Moreover, solutions doped with 3% copper presented a loss of stability after a few days, which was not the case with the 1% doping.

The effect of MPA was also studied by varying the Zn:MPA molar ratio. An equimolar ratio (1:1) leads to a rapid flocculation of the solution. This indicates that the amount of MPA is not sufficient to stabilize the QDs. For the other ratios, both 1:2 and 1:4 lead to luminescent ZnS:Cu nanoparticles. However, although the ratio of 1:2 produces stronger luminescence, the solution precipitates more quickly and the size distribution of nanoparticles is wider. It therefore appears that the 1:4 ratio is a good compromise between luminescence intensity and solution stability.

The study of the Zn:S molar ratio shows that a 1:2 ratio leads to a turbid and non-luminescent solution, with a nanoparticle size much larger than those obtained with ratios of 1:0.9 or 1:0.5. Syntheses with 1:0.9 and 1:0.5 Zn:S ratios result in luminescent solutions of almost the same intensities and maxima positions, and with a nanoparticles size of around 6 nm for both solutions. As confirmed by Suyver *et al*. [51], an excess of sulphide ions (beyond the

stoichiometric ratio) results in a decrease in luminescence. The ideal ratio seems to be around 1:1. Since Corrado *et al*. [45] used a ratio of 1:0.9, this value was chosen for the following syntheses.

From the above results, we recommend the use of $ZnCl_2$ as a zinc precursor, a copper doping of 1% and a Zn:S:MPA molar ratio of 1:0.9:4. As already mentioned by Corrado *et al.* [45], zinc and copper solutions can be used for several syntheses as they are stable over time. It is not the case with $Na_2S{\cdot}9H_2O$, which must be freshly prepared for each synthesis. MPA was used concentrated to avoid preparing the 0.1 M solution. This did not affect subsequent results.

With the above-mentioned optimum parameters, the reactant solution remained clear throughout the entire process, except during pH adjustments with NaOH. Indeed, for a pH between 4 and 7, the solution becomes cloudy and turns clear again at alkaline pH. No changes were noticed during the $Na_2S{\cdot}9H_2O$ injection or during refluxing. After the second injection of $ZnCl_2$, a white precipitate appears, but is readily dissolved a few seconds later.
The resulting solution is colourless and is characterized by a blue-green luminescence under UV illumination. As QDs are stabilized in solution by the MPA present on their surface, they remain stable for months when stored in the dark at 4 °C.

*Characterization of the optimised ZnS:Cu and the CdTe quantum dot solutions*

Figure 4 illustrates the UV-vis absorption spectra obtained from the 1% copper-doped ZnS QDs solution right after $Na_2S{\cdot}9H_2O$ injection and after two hours reflux. As Corrado *et al.* indicated [45], the solution before the reflux is characterized by an UV absorption excitonic peak around 290 nm. After the reflux, this peak is broadened and red-shifted to around 310

nm.

Photoluminescence measurements of both the ZnS:Cu and CdTe QDs solutions are shown in Figure 5. Both samples are luminescent under UV, but their respective excitation and emission spectra differ. The ZnS:Cu excitation spectrum is narrow and located between 300 and 400 nm, while the CdTe excitation spectrum is wider, ranging from 350 to 470 nm. The emission of the CdTe QDs is narrow and centred at 550 nm, while ZnS:Cu is characterized by a wider emission peak, ranging from 425 to 550 nm, centred at around 470 nm. The ZnS:Cu solution exhibits a strong blue-green luminescence, whereas the CdTe solution is green-yellow.

As the samples do not show to the naked eye any sedimenting particles, they are suitable for DLS measuring. The results show the presence of some aggregates in both solutions, respectively around 260 nm for ZnS:Cu and 200 nm for CdTe. The presence of 6.4 ± 1.0 nm ZnS:Cu nanoparticles and of 3.3 ± 0.8 nm CdTe particles was confirmed by the measurements, as depicted on Figure 6. Size distribution was narrow, showing a low polydispersity. The zeta potential was measured on samples that were respectively diluted 20 times with water for the ZnS:Cu particles and 10 times for the CdTe ones – this dilution being necessary for the data to be accurate. The resulting ZnS:Cu and CdTe average zeta potentials were respectively of -45.5 ± 4.1 mV and -46.5 ± 3.7 mV (not illustrated) guaranteeing a high stability of both solutions. Indeed, according to DeLuca *et al.* [52], a solution is considered stable when the zeta potential value is greater than +30 mV or lower than -30 mV.

*Blood fingermark deposition*

An observation under ambient light of the deposited blood fingermarks showed some differences between donors, as well as between surface types. There was a clear variation in the blood amount within and between donors. For some of the fingermark depletion sets, the

first appositions (up to the second or even the third ones) showed no legible ridges, due to an excessive initial amount of blood, which obscured the ridge details. After successive appositions, ridges began to be distinguishable from the valleys, and finer detail became legible (i.e. sweat pores and ridge edges). This implies that more (or less) marks may be visible to the naked eye for a depletion series, according to the donor, the surface and the initial amount of blood. As an example, for donor #4 on aluminium foil, the 13$^{th}$ depletion was still visible to the naked eye, while for donor #2 on the same surface, the 7$^{th}$ depletion was no longer visible. Therefore, caution should be exerted when comparing the quality and sensitivity between donors after the application of the detection techniques. Another point is the aspect of the marks, which changes depending on the surface. As can be seen on Figure 7, on some surfaces like glass or aluminium foil, blood tends to spread to such an extent that some fingermark ridges merge, hindering the detail. On transparent polypropylene and black polyethylene, blood gathered in droplets. As a consequence, the general ridge patterns remained consistent, but no minutiae could be distinguished.

All of these qualitative differences can be explained by numerous factors as described by Langenburg [53]. The deposition pressure, the interval between blood deposition on the finger and the deposition of the mark itself, the amount of blood and the temperature (ambient air or skin) could influence the appearance of ridge detail. However, the final appearance of the blood mark was not of paramount importance in this study since we compared the sensitivity and selectivity of different enhancement methods on half fingermarks.

*Optimisation of the QDs staining solution*

Different parameters were varied to optimize the detection of blood fingermarks using the ZnS:Cu QD solution. The reference conditions were the ones recommended for the use of CdTe QDs [33]: a dilution by 10 of the initial QDs solution, a pH set at 3.5 and an immersion

of 20 minutes in the staining solution. A 5-times dilution was shown to give the best results. Similarly to the CdTe staining solution, the optimum pH was determined to be in the acidic range, around 3.5. Finally, regarding the immersion times, treatments of 60 minutes lead to the most intense luminescence of the detected mark, but there was small quality difference between marks immersed for 20, 30 and 60 minutes. Such a small gain in luminescence intensities did not justify such a long immersion time. Since the biggest difference appears between 10 and 20 minutes, a 20-minutes immersion time was chosen. Finally, the optimum parameters for the ZnS:Cu staining solution were determined to be: a dilution by 5 of the as-synthesized solution, a pH value of 3.5 and an immersion time of 20 minutes in the staining solution.

*Staining of blood fingermarks*

Fingermarks processed with ZnS:Cu and CdTe QDs appear colourless in white light, while those treated with AY7 appear yellowish. Observation under UV radiation provided by a Mini-Crimescope® 400 (300 to 400 nm) showed a luminescence for all the samples (at least for the first marks of the depletion series). As expected, the marks immersed in the copper-doped ZnS QDs showed a blue-green luminescence, those immersed in the CdTe QDs presented a yellow-green luminescence, and finally the marks stained with AY7 exhibited a yellow luminescence, close to the one obtained with CdTe QDs. On all substrates and for all donors, good results were obtained with the three reagents, with clear ridge detail and 3$^{rd}$ level characteristics (sweat pores and ridge shape). An absence of background staining was observed for all three reagents, which indicates good selectivity for blood (Figures 8 and 9). In terms of luminescence intensity, ZnS:Cu QDs appeared less visible on surfaces like transparent polypropylene, due to background luminescence.

*Evaluation of the results*

As stated in the Material and Methods section, both depletion series (i.e. comparison of ZnS:Cu vs. AY7 and ZnS:Cu vs. CdTe) were assessed separately and each half mark was evaluated independently of its opposite half. Grey-scale images provided conjointly were also used to assess the quality of the detected marks.

Each half mark obtained a score ranging from 3 to 0. The first mark was generally of quality 3, while the last one, with no visible fingermark, received a score of 0. A sum for each combination of substrate and detection technique was obtained by adding the score of each half mark of each depletion series for the same substrate. This was undertaken separately for each donor. However, for several series, the first marks presented an overload of blood. In order to minimize the differences between each donor, these overloaded marks were ignored during the evaluation.

The scores obtained for each donor were then added to compare the efficiency of the techniques for each substrate (Figure 10). The comparative examination between ZnS:Cu and CdTe showed an almost equivalent efficiency on both aluminium foil and black polyethylene. For transparent polypropylene and glass, CdTe performed slightly better than ZnS:Cu.

AY7 was judged to give almost equivalent results to ZnS:Cu on transparent polypropylene, but it was always less effective on the other substrates.

Figure 11 illustrates the sensitivity of the methods by plotting the average number of marks detected in a depletive series (regardless of their quality). It can be concluded from this graph that ZnS:Cu and CdTe were more sensitive than AY7 on all substrates. On average, the QD solutions can detect one more mark in the depletion series than AY7. When compared to CdTe, ZnS:Cu showed almost the same sensitivity for all the substrates.

**Discussion**

*Synthetic protocols*

The choice for a particular synthetic protocol was mostly driven by the possibility of implementation and by the intensity of luminescence obtained from the synthesized nanoparticles as measured with the spectrofluorometer. Various protocols were tested according to these two parameters. Eventually, the synthetic protocol of Corrado *et al.* [45] was found to give the best results in terms of luminescence intensity, solution stability and narrowness of the size distribution. This protocol was further optimized.

Contrary to the original synthesis using zinc nitrate as the zinc source, zinc chloride was chosen since it gave the most intense luminescence. This effect was not further investigated, but according to Manzoor and co-workers [46], halide ions such as chloride ($Cl^-$) might have an influence on the luminescence properties.

Copper ions are known to modify the position of the maximum intensity. Without doping ions, the position is located around 420 nm, whereas with 1% copper, the maximum is shifted to 470 nm. Adding more copper is possible, but a decrease in the solution stability has been observed for the higher concentration. The 1% doping was thus chosen, following the recommendations of Corrado *et al.* [45].

The choice of a ligand molar ratio of 1:4 (Zn:MPA) is a compromise between luminescence intensity and solution stability. With a lower amount of MPA, the solution is unstable, due to an insufficient number of ligand molecules. For the molar ratio of zinc and sulphur, the value recommended by Corrado *et al.* [45] has been kept unchanged and this choice is further justified by the work of Suyver *et al.* [51].

*Characterization of the obtained ZnS:Cu QDs*

For the copper-doped ZnS solution, the results obtained by spectrophotometry were consistent with those obtained by Corrado *et al.* [45]. Prior to the reflux, the excitonic peak of the UV

absorption was not as narrow, which can be seen as a consequence of a broader size distribution. After the reflux, the peak was broader, as a result of the particle growth. Consistency with the above publication was also observed for the excitation and emission spectra, with a shift of the maximum emission to longer wavelengths upon the addition of copper. Both CdTe and ZnS:Cu solutions show an excitation peak in the UV region. The emission peak of ZnS:Cu is more than twice as wide as that of CdTe.

No transmitted electron miscroscopy (TEM) observations were performed in this study, but the DLS measurements gave a diameter value of 6.4 nm for the ZnS:Cu QDs, which is consistent with the value reported by Corrado *et al.* [45] using TEM (i.e., 6 nm). The slight difference can be explained by the very nature of a DLS value, which does not report the particle diameter but its hydrodynamic diameter, known to be slightly larger. For CdTe, the smaller size is also consistent with the literature and does not seem to have a great influence on the resulting quality of the detected marks.

Overall, the characterization results were satisfactory and in line with the formation of both copper-doped ZnS and CdTe quantum dots. The solutions were stable for months when stored in the dark at 4 °C. The solutions remained clear without formation of cloudy precipitate, and DLS measurements performed on aged samples showed a constant nanoparticle size.

*Outer Functionalization of the quantum dots*

3-Mercaptopropionic acid (MPA) is present at the surface of the quantum dots and plays a major role in the stabilization of the ZnS:Cu nanoparticles in solution. The absence of MPA during the synthesis still leads to the formation of ZnS:Cu nanoparticles, but the resulting solution is cloudy and unstable. From a molecular point of view, the thiol extremity of the MPA molecule is bound to the surface of the quantum dots while the other end (i.e. the carboxylic acid) ensures their solubility in water. Consequently, the molar ratio between zinc and MPA plays a major part in the stability of the QDs in solution, but also in their resulting

luminescence. It has been shown that an equimolar ratio gave a poorly luminescent solution, which precipitated within a few hours. A ratio of 1:2 led to stronger luminescence intensity (i.e. 1.5 times more intense) than the recommended 1:4 ratio. However, the 1:2 ratio solution was characterized by a weaker stability and a wider size distribution. The ratio of 1:4 was thus a good compromise between luminescence intensity, size homogeneity and stability.

In order to compare the efficiency of ZnS:Cu and CdTe, it was first envisaged to coat the surface of both QDs with the same ligand, i.e. thioglycolic acid (TGA) as used for the CdTe synthesis. ZnS:Cu was thus synthesized with TGA and this led to a stable and luminescent solution. However, the luminescence intensity was weak, compared to the MPA-capped nanoparticles. TGA-capped ZnS:Cu can detect blood fingermarks but, as they were less luminescent, their sensitivity threshold diminished. Hence, it was decided to compare MPA-capped ZnS:Cu QDs with TGA-capped CdTe QDs. It is not expected, however, that the presence of either MPA or TGA has a great influence on the detection process, since MPA and TGA are quite similar. Indeed, they share the same terminal groups (i.e. a carboxylic acid and a thiol) and differ only by an additional $–CH_2–$ group in the inner aliphatic chain for MPA.

*Blood fingermark detection using ZnS:Cu, CdTe and Acid Yellow 7*

The biggest difference between the ZnS:Cu QDs, the CdTe QDs and AY7 was the colour of the obtained luminescence. The human eye is well adapted to see the yellow emission of CdTe and AY7, but not the pale green-blue emission of copper-doped ZnS QDs. As a consequence and to avoid biasing the observer, the quality assessment was performed on grey-scales images with inverted contrast so as to get black ridges on light backgrounds. Under these conditions, ZnS:Cu showed a better efficiency compared to AY7 on most substrate and proved to be almost equivalent to CdTe QDs on both aluminium foil and black

polyethylene.

*Costs related to the use of nanoparticles*

The cost analysis made by Bécue *et al.* [33] also applies to the ZnS:Cu QDs. Since the nanoparticles are directly synthesised in the lab, the costs are low. One litre of working solution obtained by diluting 200 mL of concentrated solution costs approximately US$0.65. By comparison, the same volume of AY7 costs more than US$5. Given the low prices of these two solutions, the cost parameter does not have a great influence on the choice of one technique or the other.

*Health and Safety Issues*

In this study, no toxicity assessment of the synthesized nanoparticles was performed. The presumed non-toxicity of ZnS was only based on studies found in the literature [39,43]. It is shown that ZnS exhibits no increased risk, unlike the cadmium-based QDs, which could release free toxic cadmium ions. Despite these encouraging statements, large-scale studies are yet to be conducted and the actual risks inherent to the use of nanoparticles remain difficult to ascertain. Therefore, it is recommended to work under a fume hood, wearing adequate personal protective equipment.

**Conclusions**

Nanoparticles – and more specifically quantum dots (QDs) – are subject to intensive research for their application in the field of fingermark detection. Promising results have been obtained so far with cadmium-based QDs used as dusting powder [26,28] or in solution [10,18-20,27,29-36]. Despite their unusual optical properties and their various functionalization possibilities – which allow specific targeting of latent fingermark compounds – the issue of

their toxicity is seldom mentioned in forensic publications. Indeed, the particles' degradation implies the release of free toxic cadmium ions. Coating the toxic CdSe or CdTe core with a passivating layer is feasible but this does not solve the problem entirely. Cadmium can still leak if the coating is not complete or if the layer deteriorates. An option would simply be to stop using cadmium. As an attempt to address this issue, this paper proposes the use of non-toxic QDs based on a zinc sulphide core (ZnS). ZnS QDs are luminescent under UV illumination as other QDs, but their emission spectra do not vary with particle size. The optical properties can be tuned by doping the structure with metallic ions, such as copper or manganese. In this study, copper has been chosen as the doping element. As such, ZnS:Cu QDs represent a valid candidate for fingermark detection.

Cu-doped ZnS QDs with a blue-green luminescence emission were synthesized in water, using 3-mercaptopropionic acid as a ligand. The solution was stable for months when stored in the dark at a temperature of 4 °C.

After having checked that ZnS:Cu QDs were able to detect blood fingermarks, they were compared to CdTe QDs and Acid Yellow 7 on depletive series of blood fingermarks left by four donors on four non-porous substrates. As a result, ZnS:Cu was demonstrated to be better than AY7 and at least as efficient as CdTe on most substrates. Consequently, ZnS:Cu quantum dots constitute a valid substitute for cadmium-based QDs in the context of blood fingermark detection. Given that ZnS:Cu QDs contain no heavy metal in their composition, they are less dangerous for routine use compared to cadmium-based QDs.

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**Figure captions**

**Figure 1**

Illustration of the staining protocol followed to compare ZnS quantum dots and Acid Yellow 7, by using depletive blood fingermark series cut in half.

**Figure 2**

Effect of the zinc precursor on the luminescence emission properties, with respectively zinc chloride ($ZnCl_2$), zinc acetate ($Zn(OAc)_2$), zinc sulphate ($ZnSO_4$) and zinc nitrate ($Zn(NO_3)_2$), measured at an excitation wavelength of 330 nm.

**Figure 3**

Effect of the copper doping on the position of the maximum emission intensity, with respectively no copper, 1 and 3 %, added during the synthesis of the ZnS quantum dots, measured at an excitation wavelength of 330 nm.

**Figure 4**

UV – visible absorption spectra of the copper-doped ZnS quantum dot solution, before and after two hours reflux.

**Figure 5**

Excitation and emission spectra of the copper-doped ZnS quantum dots (QDs) and the CdTe QD solutions. The CdTe solution was obtained by stopping the reflux after 90 minutes (synthetic protocol described in [33]). The ZnS solution was obtained after two hours reflux. In the upper right box are CdTe (a) and ZnS (b) samples, photographed under UV illumination.

**Figure 6**

Size distributions obtained by dynamic light scattering (DLS), for ZnS and CdTe quantum dot solutions.

**Figure 7**

Untreated blood fingermarks on different substrates: a) glass, b) transparent polypropylene, c) black polyethylene, and d) aluminium foil. Images taken under white light, before any enhancement treatment.

**Figure 8**

Blood fingermarks processed with copper-doped ZnS quantum dots (left halves) and Acid Yellow 7 (right halves) on different substrates: a) glass, b) transparent polypropylene, c) black polyethylene, and d) aluminium foil. The samples were excited in the UV range (300–400 nm) using a Mini-Crimescope 400, and observed without an emission filter. Images a'), b'), c') and d') are the corresponding grey-scale images.

**Figure 9**

Blood fingermarks processed with copper-doped ZnS quantum dots (right halves) and CdTe quantum dots (left halves) on different substrates: a) glass, b) transparent polypropylene, c) black polyethylene, and d) aluminium foil. The samples were excited in the UV range (300–400 nm) using a Mini-Crimescope 400, and observed without an emission filter. Images a'), b'), c') and d') are the corresponding grey-scale images.

**Figure 10**

Efficiency of the three techniques, in terms of average quality scores for each tested substrate.

**Figure 11**

Sensitivity of the three techniques, in terms of average numbers of detected marks in a depletive series for each tested substrate.

Figure 1
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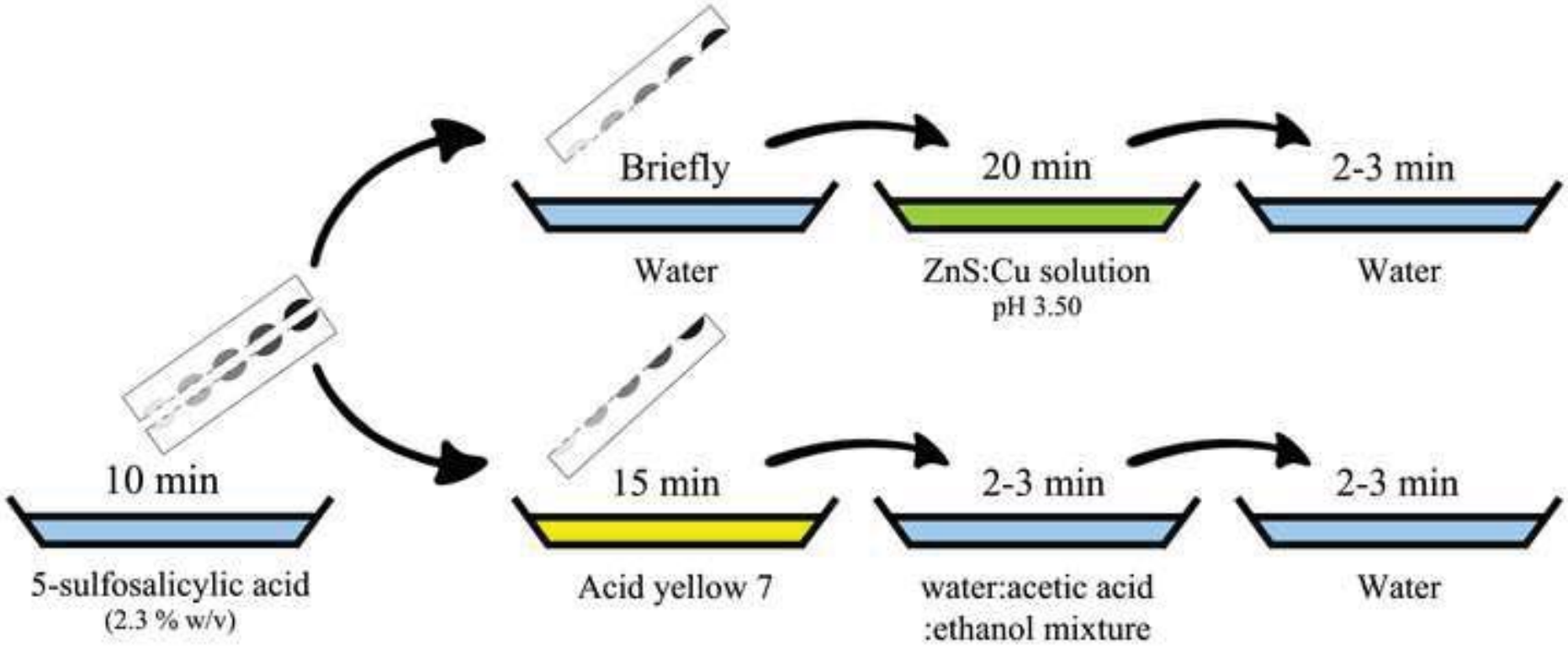

**Figure 2**

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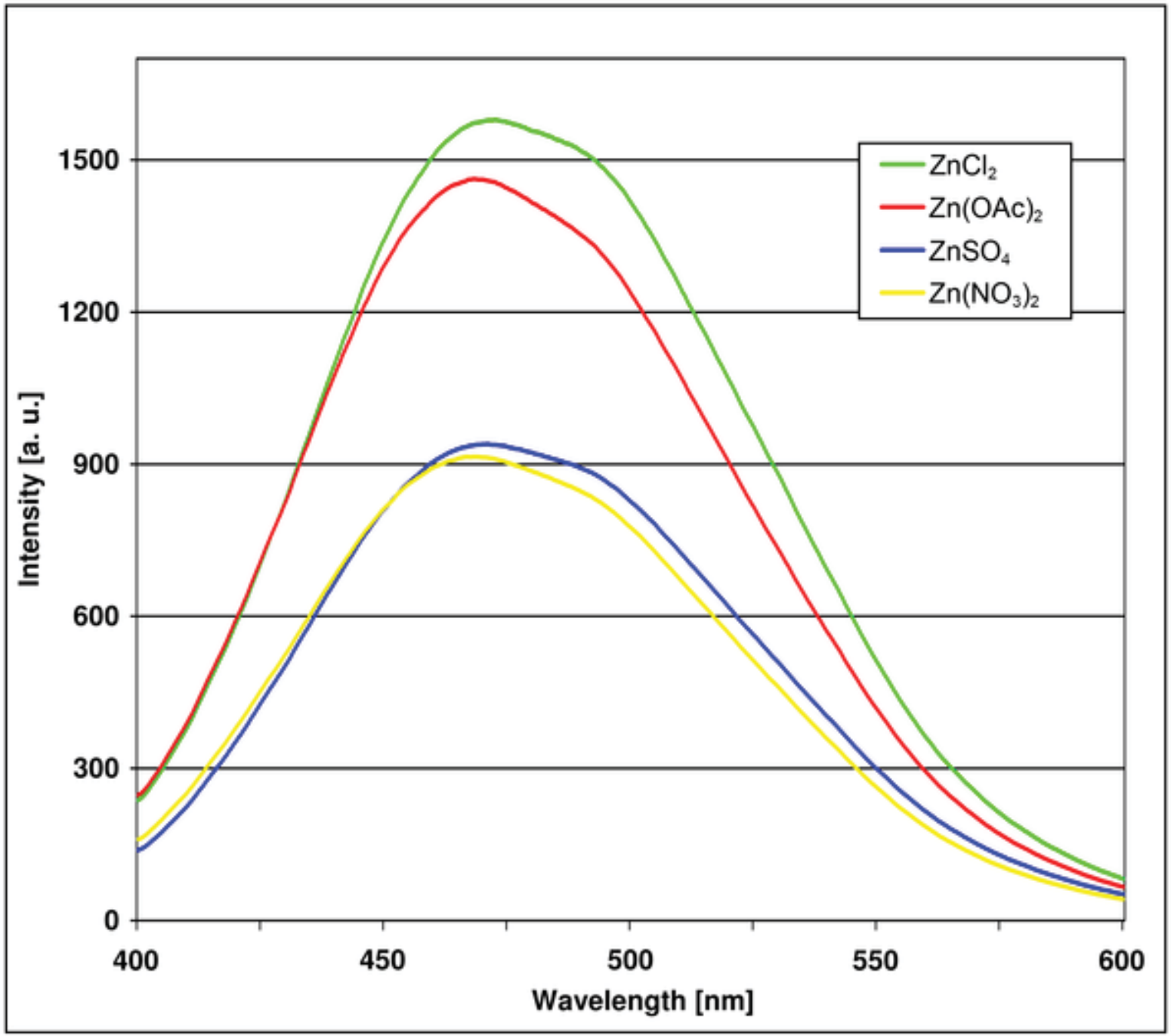

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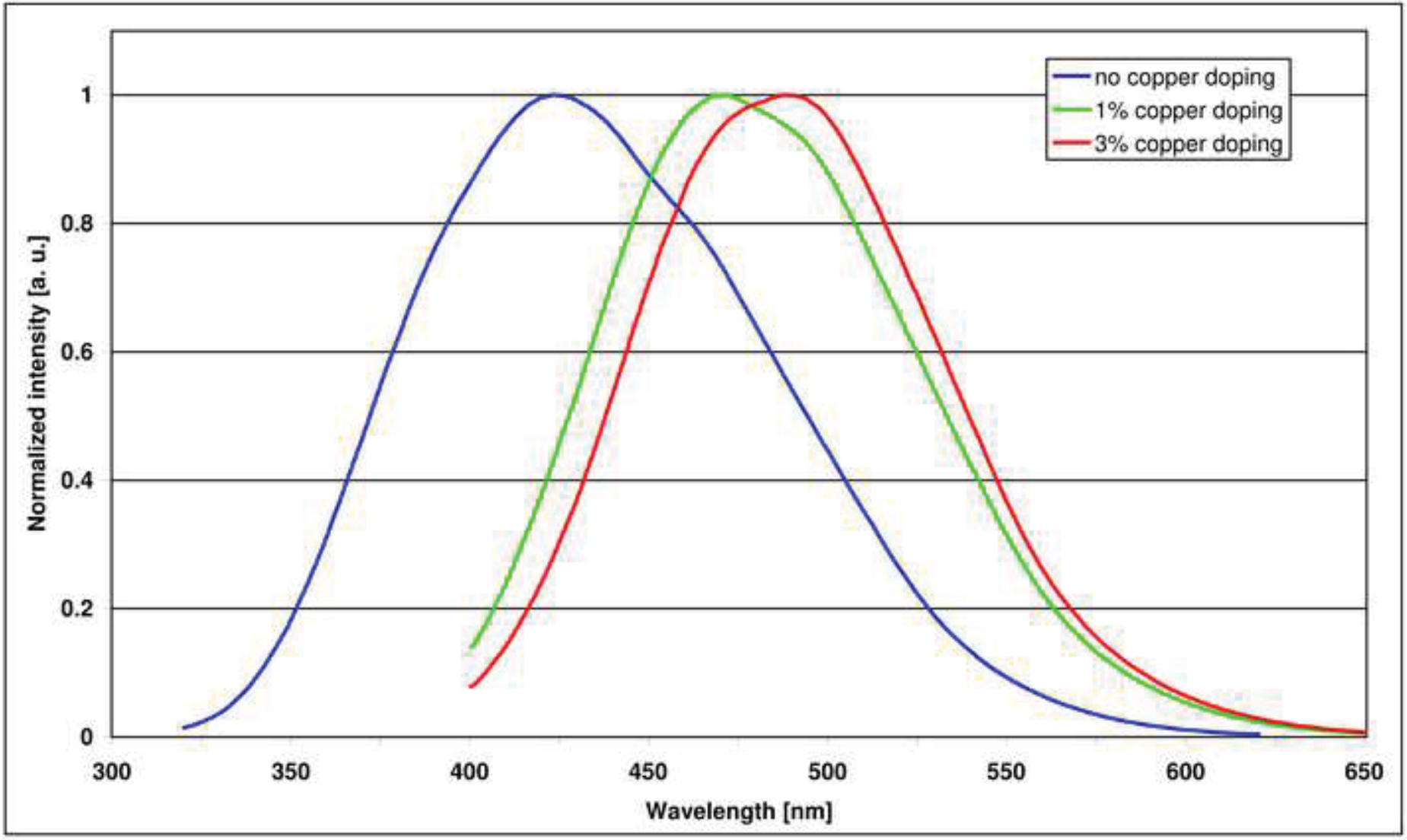

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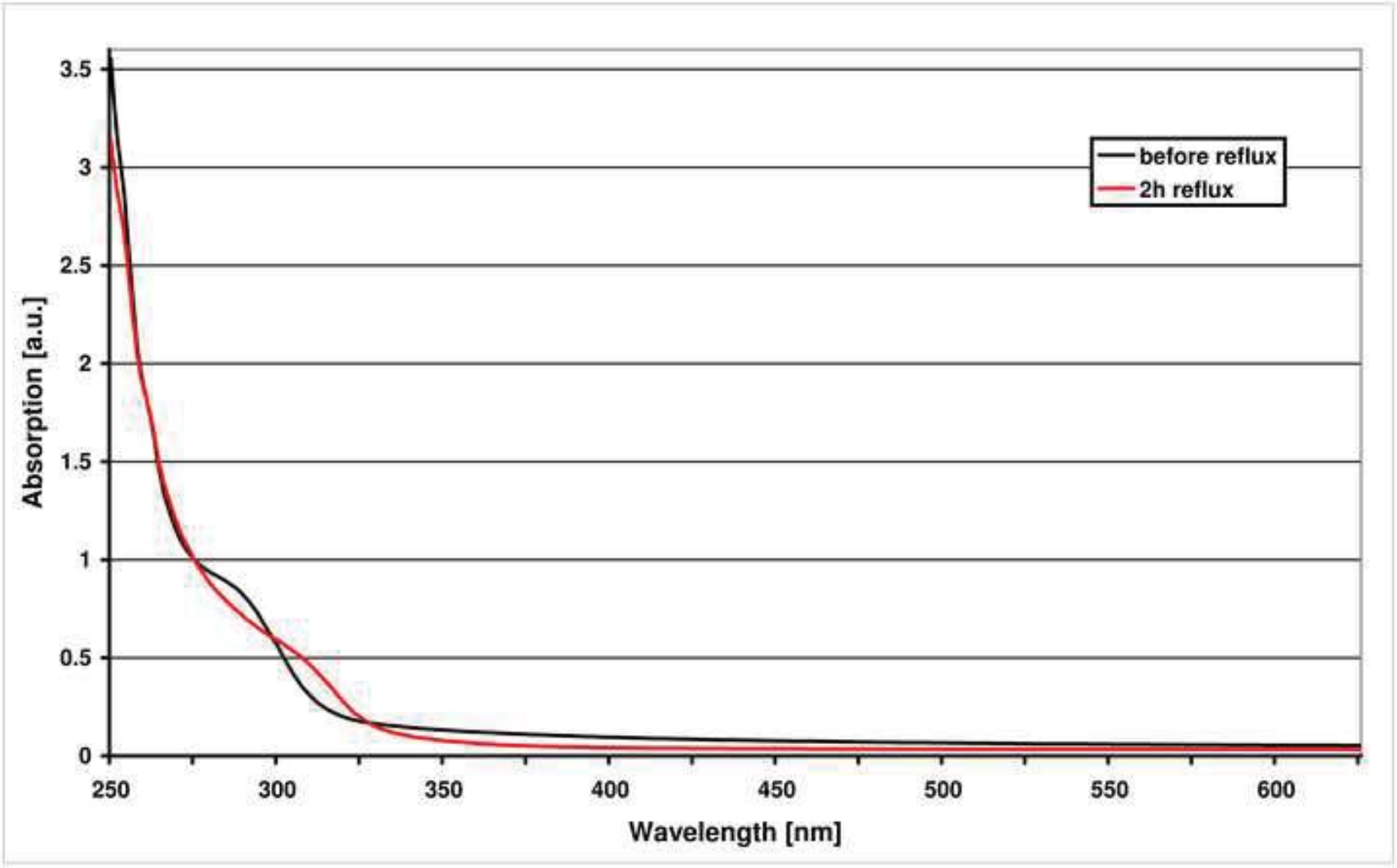

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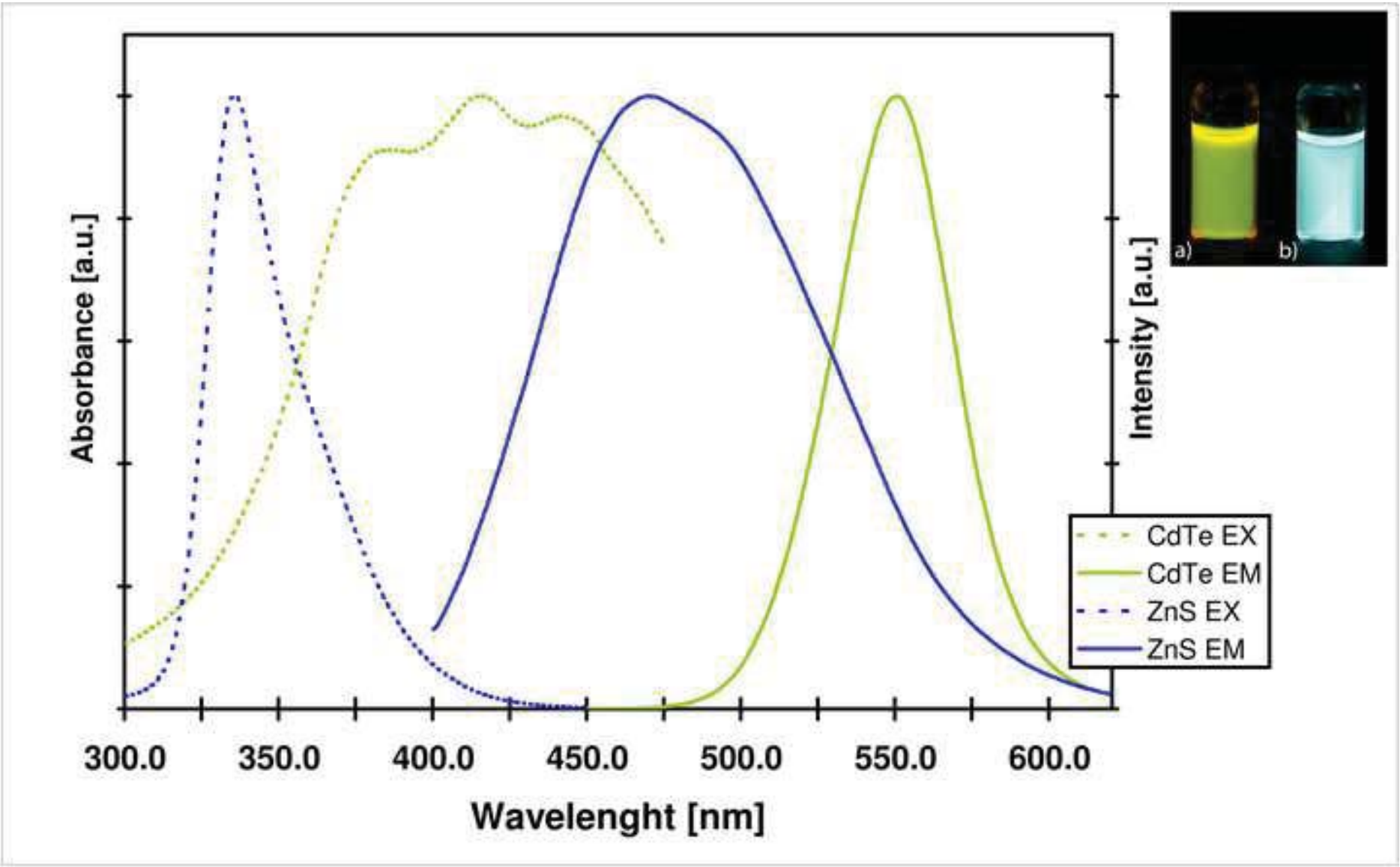

**Figure 6**

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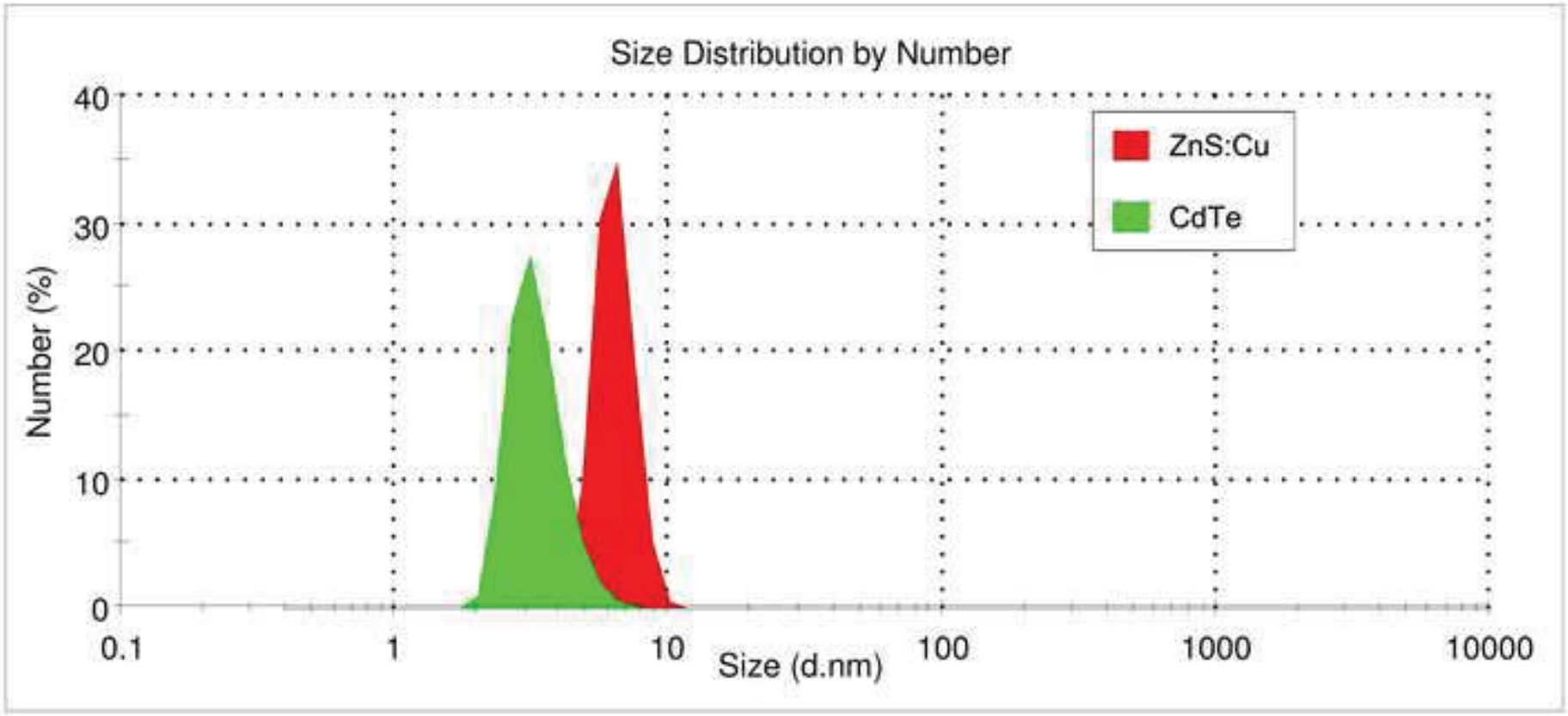

**Figure 7**
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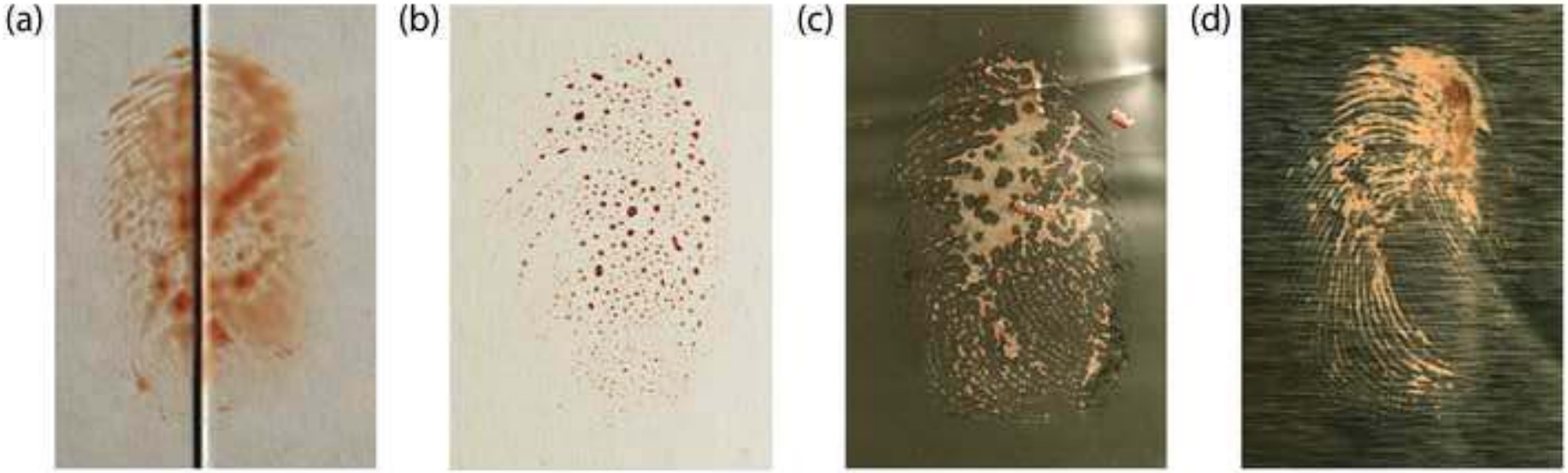

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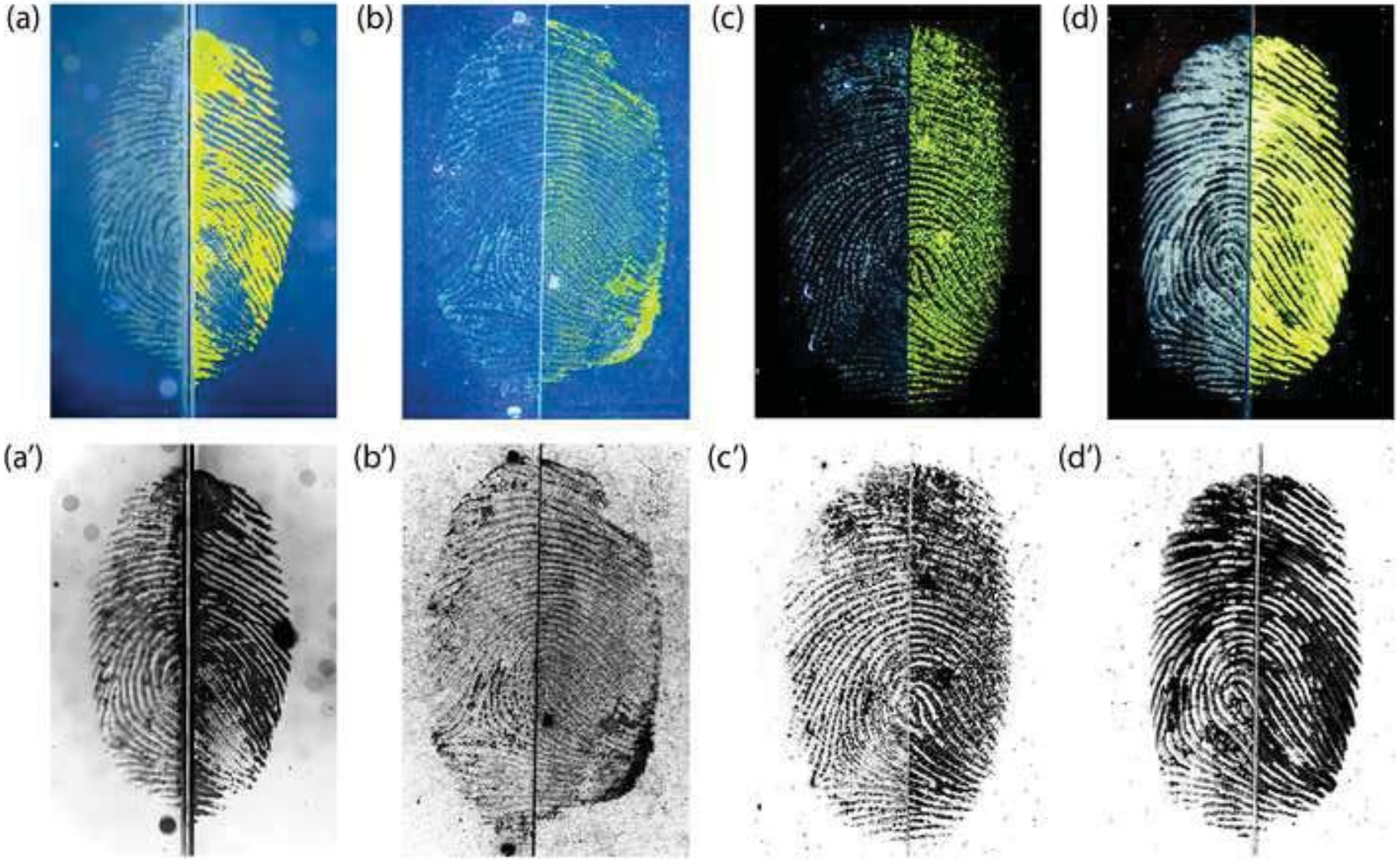

Figure 9
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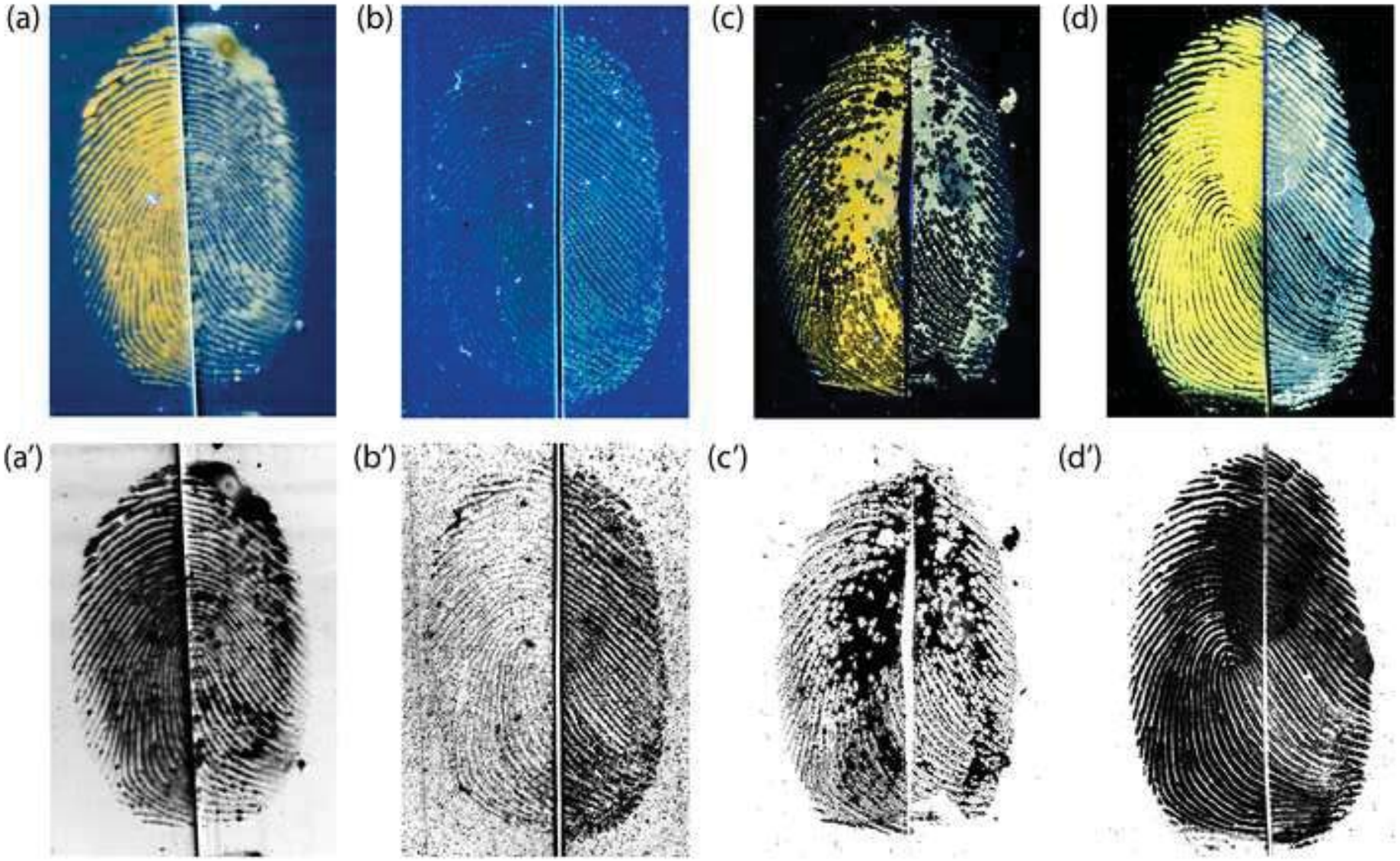

Figure 10
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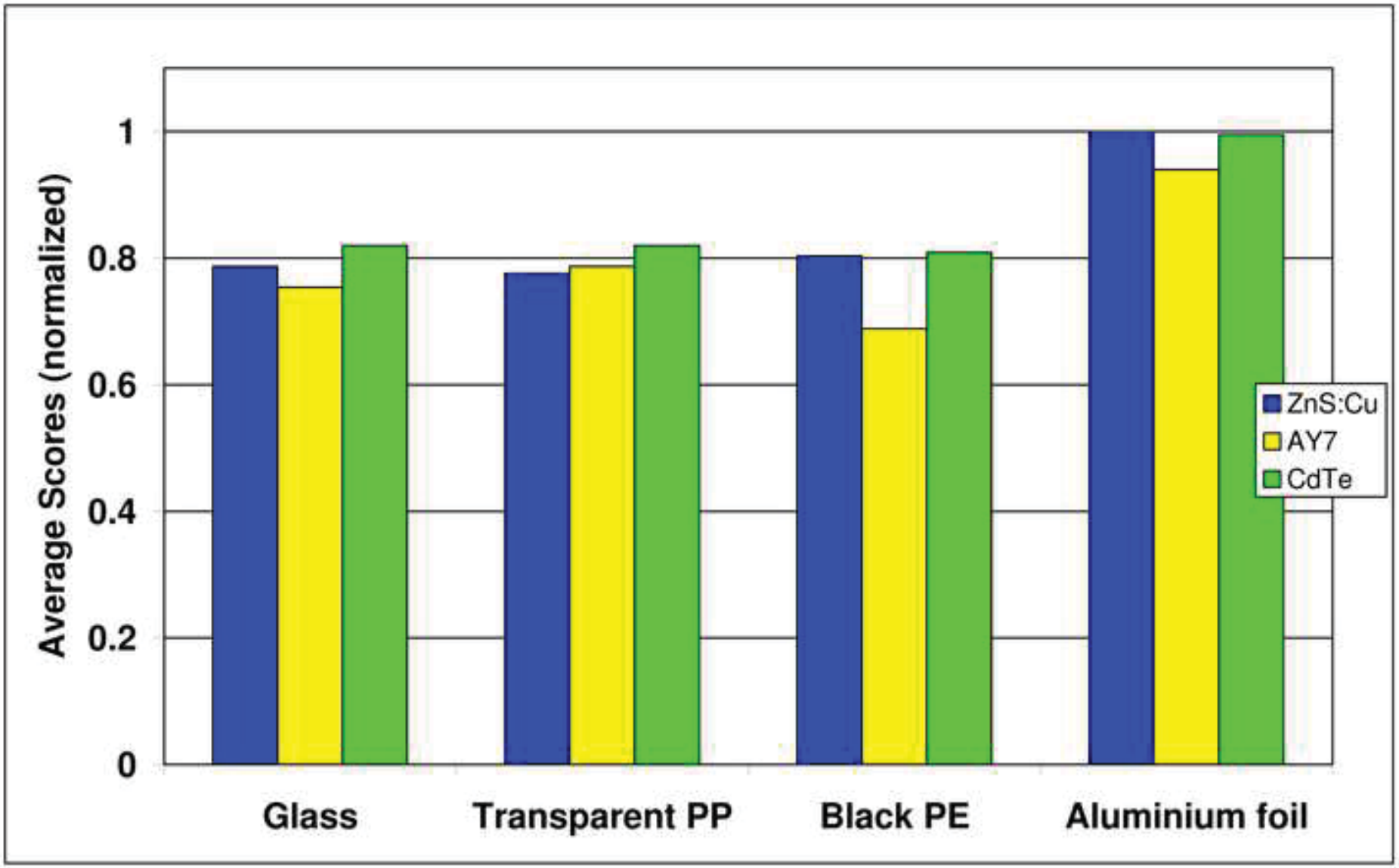

Figure 11
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