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COMMUNICATION

Carbon dots based nanopowders and their application for fingerprint recovery

Cite this: DOI: 10.1039/x0xx00000x D. Fernandes,^a M. J. Krysmann^b and A. Kellarakis^aReceived 00th January 2015,
Accepted 00th January 2015

DOI: 10.1039/x0xx00000x

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Incorporation of a minor amount of carbogenic nanoparticles to powder compositions imparts remarkable colour-tuneability, without compromising flowability. In a proof-of-concept demonstration we report the use of the hybrid nanopowders for the visual enhancement of latent fingerprints where they effectively resolve issues arising from poor contrast against multi-coloured or patterned backgrounds.

Carbogenic nanoparticles (otherwise known as C-dots) represent a rapidly emerging class of high performance photoluminescent (PL) nanoemitters carrying great promise for multicolour printing, bioimaging, selective sensors and catalysis¹⁻⁶. Unlike conventional polyaromatic dyes and heavy metals based quantum dots, C-dots are biocompatible and non-toxic for the humans and the environment⁷. In addition, C-dots can be synthesized following cost-efficient and, to a certain extent, green protocols. With respect to the starting materials and the synthetic route, the structure of C-dots, their graphitization degree and their elemental content (in carbon, oxygen and heteroatoms) significantly varies, giving rise to an expanding gallery of photoactive materials⁸. To that end, graphitic C-dots are facilely produced by oxidation or electro-oxidation of carbon nanotubes or graphite, while amorphous C-dots are conveniently derived via thermal or hydrothermal treatments of carbon rich precursors such as polymers⁹, carbohydrates¹⁰, grass¹¹, hair fibers¹², fruit juice¹³ and soy milk¹⁴. Likewise, C-dots based nanocomposites are formed, for example a nanomaterial that exhibits supreme magnetic and fluorescent properties is derived by thermal treatment of carbon precursors in the presence of iron oxide¹⁵.

A large body of the literature emphasises on the exceptional PL properties of aqueous dispersions of C-dots. Systematic studies indicate that surface passivation of C-dots (for example via amine¹⁶ or sodium borohydrate¹⁷ treatment) not only enhances the colloidal stability, but also improves the fluorescence intensity. Despite intensive efforts, the origin of their intriguing photophysical behaviour

is still not well understood and contributions stemming from either the carbogenic core¹⁸ or the surface functionalities¹⁹ have been identified. It has been demonstrated that isolated sp² centres placed in a sp³ network show inherent PL characteristics and those defects structurally resemble the carbon atoms placed on the surface of C-dots²⁰.

By comparison, much less information is available regarding the solid-state physics and the PL performance of anhydrous C-dots. In this study we report for the first time the preparation of hybrid nanopowders containing low concentration levels of C-dots (typically below 1 wt%) homogeneously dispersed within the major phase (silica, titania, laponite, white fingerprint powder). Those materials combine distinct advantages arising from the supreme flowability of the major powder component and the unique PL of C-dots.

In particular, we demonstrate the use of the nanopowders for the recovery of latent fingerprints, e.g. poorly visible impressions unintentionally deposited in crime scenes. Fingerprint dusting visually enhances those marks so that they can be photographed and processed for identification purposes. Forensic analysis compares the recovered fingerprints with those available in national and international databases populated by a large set of exemplar fingerprints recorded via digital imaging or ink fingerprinting.

It is interesting to note that water-based formulations based on C-dots have been shown to be highly effective for ink fingerprinting²¹⁻²³. This process refers to the intentional recording of fingerprints by pressing the ink covered fingertips against a suitable substrate.

Our work however centres on dusting (using a brush) chance impressions found in crime scenes, as opposed to previous reports that focus on creating exemplar ink fingerprints. In other words, we demonstrate for the first time the use of C-dots based powders for latent fingerprint enhancement. Significantly, this report expands the application spectrum of C-dots beyond the liquid phase dispersions and polymer composites, by introducing

a novel class of non-toxic, yet colour tuneable and highly fluorescent hybrid nanopowders.

We have previously reported that controlled thermal annealing of a mixture of citric acid and ethanolamine leads to a series of photoactive materials with dual PL emission²⁴. At the early stages of pyrolysis intermolecular condensation generates amide rich functionalities that are progressively consumed to generate carbogenic nanocores. As a result, the C-dots prepared at 230 °C have an average diameter of 19 ± 2 nm (S.I. Figure 1) and show an excitation wavelength independent emissive contribution stemming from amide groups (note the vertical line in Figure 1a for excitation wavelengths 350 and 380 nm) and an excitation wavelength dependent emissive mode characteristic of their carbogenic nature (note the peaks in Figure 1a corresponding to excitation wavelengths 410, 440, 470 nm). Self-passivation is an important feature for this type of materials given that surface polar groups formed *in situ* during pyrolysis enhance both the colloidal stability and the PL properties of the aqueous dispersions.

Figure 1 compares the fluorescence spectra of an aqueous dispersion containing 13 $\mu\text{g/ml}$ C-dots in the presence of a large excess of silica nanoparticles (Figure 1b) with the silica-free dispersion (Figure 1a). It is clear that PL is not significantly quenched by the silica nanoparticles and both emissive modes are active. This effect points to the lack of specific particle-particle interactions that could alter the charge distribution on the surface of C-dots. (The fluorescence spectra of C-dots/fingerprint powder and C-dots/laponite aqueous dispersions are shown in S.I. Figure 2a and 2b, respectively).

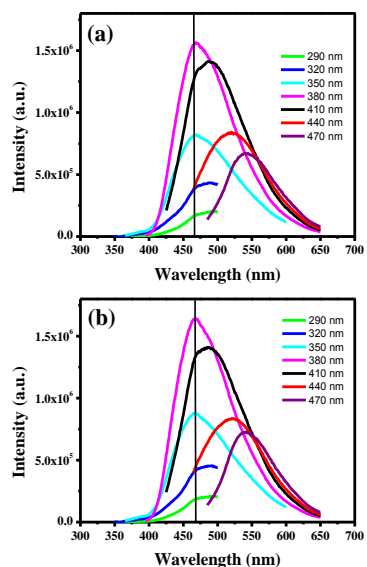


Fig. 1 Photoluminescence spectra (under different excitation wavelengths) of aqueous dispersions containing (a) 13 $\mu\text{g/ml}$ C-dots and (b) 13 $\mu\text{g/ml}$ C-dots in the presence of (150 times higher concentration) silica nanoparticles.

The C-dots/SiO₂/water system was freeze-dried, yielding a fine nanopowder having 0.7 wt% carbogenic content. Figure 2

suggests that the hybrid nanopowder adopts different colours when exposed to different types of incident radiation. For reference, we note that preparation of fine powder purely from C-dots is rather challenging due to the strong tendency of carbogenic nanoparticles to aggregate. It has been supported that solid powder of C-dots is not photoactive possibly due to extensive clustering and self-quenching effects²⁵.

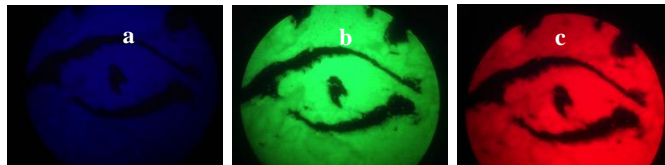


Fig. 2 Fluorescence microscopy images of 0.7 wt% C-dot/silica nanopowder obtained under (a) UV violet, (b) blue and (c) green excitation wavelength.

The remarkable photophysical behaviour of the hybrid nanopowders carries great promise for a versatile range of technologically important applications. In a proof-of-concept demonstration, we explore here the use of the hybrid nanopowders for latent fingerprint detection. Suffice to say that fingerprint analysis remains the corner stone in forensic investigation providing reliable evidence for more than a century. Recent approaches on fingerprint development capitalise on the ability of nanoparticles not only to visually enhance fingerprints, but also to detect certain analytes within them²⁶⁻²⁸. Many types of fingerprint powders²⁹ have been suggested throughout the years including aluminium flake, magnetic powders, luminescent powders and more recently formulations containing gold nanoparticles, or semiconductor quantum dots (which are generally considered toxic³⁰). However, there is a persisting need for the development of an environmentally benign, low cost and universal fingerprint powder suitable to be used in the crime scene that ideally will provide strong contrast against a variety of radically different backgrounds.

Owing to their minor C-dot content, the hybrid nanopowders retain the supreme flowability of the silica nanoparticles and can be easily applied with a brush to a fresh fingerprint deposited on a glass microscope slide. As seen in Figure 3, the hybrid nanopowder revealed high quality images that show well-resolved ridge patterns that meet the requirements for individual identification for forensic purposes.

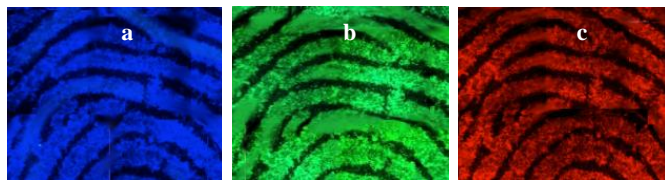


Fig. 3 Fluorescence microscopy images of fingerprints developed with hybrid nanopowder (0.7 wt% C-dot/silica) on a glass slide under (a) violet, (b) blue and (c) green excitation wavelength. A number of fluorescence images (captured at 100x magnification) have been merged via Photoshop software to create the larger images displayed.

Significantly, the developed fingerprints exhibit colour-tuneability in response to the wavelength of the incident beam. In Figure 3 it

can be clearly seen that the fingerprints appear to be blue, green or red when they are excited under violet, blue and green wavelength, respectively. Likewise, color-tuneable patterns were obtained using 0.7 wt% C-dots/ laponite for fingerprints deposited on glass and metal surfaces (S.I. Figure 3 and 4, respectively). In contrast, no signal is detected in the absence of C-dots in an otherwise identical experiment (S.I. Figure 5).

This remarkable optical behaviour offers significant advantages to forensic investigation by circumventing issues related to strong background interference arising from textured or multi-coloured surfaces. To that end, the fingerprint deposited in a soft drink bottle foil (Figure 4a) shows a poor contrast under bright field illumination (Figure 4b), while only weak ridge patterns are detected under green light (Figure 4e). At the same time, well resolved features are discerned under violet and blue radiation (Figures 4c and d, respectively).

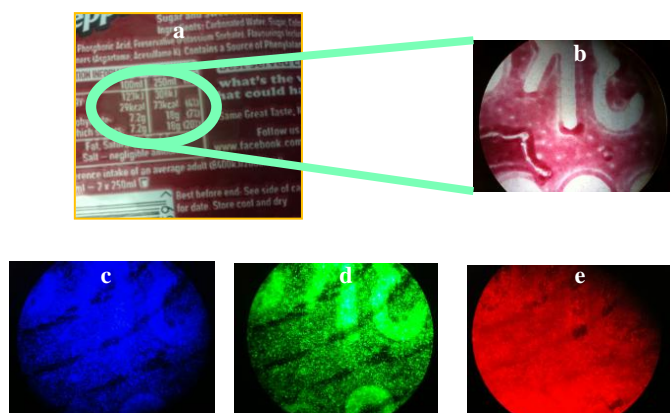


Fig. 4 (a) Fingermarks in a soft drink bottle foil developed with 0.7 wt% C-dot/silica hybrid nanopowder, (b) their bright field image and (c, d, e) their fluorescence microscopy images under violet, blue and green excitation wavelength, respectively.

In other words, the hybrid nanopowders presented here can facilitate optimal visualization for fingerprints found in radically different substrates. In that sense, the forensic investigator can be released from the need to carry and use in the crime scene a number of different powders to accommodate a variety of backgrounds. Recall that C-dots are non-toxic^{7,31} and thus can be readily used in the crime scene, following standard forensic procedures.

Automated Fingerprint Identification System (AFIS) analysis is the standard method to evaluate the quality of the fingerprint images. AFIS analysis for a fresh fingerprint developed by a commercial white fingerprint powder reveals 65 minutiae detail as shown in Figure 5a. Under identical conditions the C-dots based hybrid nanopowder yields an improved image quality displaying 71 minutiae (Figure 5b).

To further test the generality of the effects described above we have prepared hybrid nanopowders by using a different type of C-dots that are derived via pyrolysis of biomass. The corresponding hybrid powders (based on titania or laponite) show similar effects, albeit their PL intensity is substantially weaker (S.I. Figure 6 and 7, respectively).

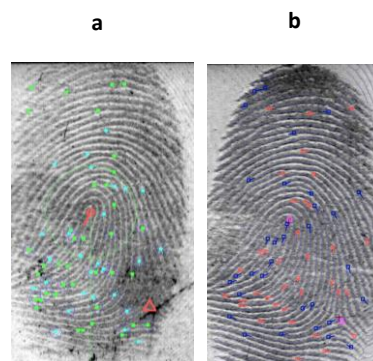


Fig. 5 AFIS analysis for fresh fingerprints developed using (a) a commercial white fingerprint powder and (b) a C-dot based hybrid nanopowder.

In conclusion, we describe the synthesis of hybrid nanopowders containing minor amounts of C-dots that exhibit colour-tuneability without any adverse effect on the flowability of the diluent. While this behavior carries great promise in a variety of applications, we have focused on their use for fingerprint enhancement. We demonstrate here that the non-toxic hybrid nanopowders can be readily applied for fingerprint development, affording improved image quality and optimal contrast against colored backgrounds.

Notes and references

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Electronic Supplementary Information (ESI) available: [Detailed experimental section, TEM images of C-dots, photoluminescence spectra of aqueous dispersions and fluorescence images of fingerprints in various surfaces]. See DOI: 10.1039/c000000x/

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