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Dual-encryption based on facilely synthesized supra-(carbon nanodots) with water-induced enhanced luminescence†

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A series of low cost and easily prepared supra-(carbon nanodots (CNDs)) were developed by injecting CND ethanol solutions into toluene under vigorous stirring to induce nano-sized aggregates. Water-jet printing of luminescent patterns and mapping of human sweat pore patterns can be realized on the supra-CND-coated paper. With the application of two kinds of supra-CNDs, dual-encrypted luminescence information was constructed through water-jet printing and hand writing. We found that the low-cost and easily prepared supra-CNDs can be expected to show considerable potential to achieve multi-level encryption in anti-counterfeiting and information security.

Introduction

Anti-counterfeiting and information encryption are significant issues in economic and military fields as well as in our daily lives. The development of the issues depends on exploring new anti-counterfeiting/encryption materials and methods.[1–4] A photoluminescent material is suitable to construct single level encryption, because its luminescence information is invisible under room light but perceptible under UV irradiation.[5–7] With increasing demands for information security, it is highly desired to exploit new luminescent materials and methods for constructing dual-encryption with more confidentiality and reliability.

Up to now, plentiful photoluminescent materials, including organic dyes[8,9] and inorganic semiconductor quantum dots,[10,11] have been explored as fluorescent ink for data storage and encryption. However, the investigated materials show undesirable properties. Organic dyes show inferior resistance to photobleaching and most inorganic semiconductor quantum dots contain toxic heavy metal elements, which pose potential environmental hazards and produce toxicity in the long term. Therefore, it is of great interest to develop new stable, low toxic and environmentally friendly luminescence encryption materials and methods.

Carbon nanodots (CNDs) are riveting luminescent materials, which have been widely investigated as innovative fluorescent ink in data encryption and storage due to their excellent biocompatibility, environmental friendliness, low cost and superb resistance to photobleaching.[12–17] CNDs were applied to achieve single-level encryption.[18–21] However, dual-encryption based on CNDs is rarely investigated. Water-induced enhanced photoluminescence, as a green and riskless fluorescent imaging method, is an attractive technique in recent years, because water is an ideal medium for its non-toxicity and ubiquity on earth. Thus, water-induced enhanced photoluminescence should be better utilized for practical applications in security fields.[22–25]

In our previous work, we developed a single encryption of water-triggered luminescent enhanced supra-CNDs.[18] These supra-CNDs, with weak emission in toluene, are assembly of partially alkyl-chain-functionalized CNDs, and can be readily decomposed upon water triggering, resulting in strong photoluminescence. With these supra-CNDs, water-jet printing luminescence patterns and mapping human sweat pore patterns were realized in the supra-CND-coated paper. However, further chemical synthesis somehow increased the production cost.

In this work, we simplify the preparation of supra-CNDs from our reported microwave-synthesized CNDs in an accessible, low cost and one-step method without further chemical synthesis. Two kinds of supra-CNDs were simply prepared by respectively injecting blue and green emissive CNDs ethanol solutions into toluene under vigorously stirring. The process induced nano-sized aggregates and formed the supra-CNDs. Water-jet printing luminescence patterns and mapping human sweat pore patterns can be realized in the supra-CND-coated paper. With the application of two kinds of supra-CNDs, dual-encrypted luminescent information was constructed through water-jet printing and hand writing. This

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method is universal to prepare water-induced multicolour luminescent supra-CNDs from different luminescent CNDs. The low cost, easy preparation and environmental friendliness of as-prepared supra-CNDs will demonstrate considerable potential to achieve multi-level encrypted information in anti-counterfeiting and information encryption.

Experimental

Chemicals and materials

Citric acid (99.5%) were purchased from Aladdin, urea (99%) from Macklin, toluene from Beijing Shiji and ethanol from Tianjin Fuyu Chemical Co., Limited. The commercial fluorescent dye ink were directly purchased from the supermarket. All chemicals were used without further purification. The water used in all experiments was purified with a Millipore system.

Synthesis of green luminescent CNDs (CND-g)

The CND-g were prepared according to our previous work,[20,26,27] involving citric acid (3 g) and urea (6 g) as starting materials. Subsequently, these agents were added to 25 ml deionized water, forming a transparent solution. Then the mixed solution was heated in a domestic 750 W microwave oven for about 5 minutes, during which the solution turned from colourless liquid to light brown and finally dark brown clustered solid, indicating the formation of CND-g. The solid was then dissolved in ethanol and centrifuged to remove agglomerated particles at RCF (relative centrifugal force) of 22 610 g for 10 minutes.

Synthesis of blue luminescent CNDs (CND-b)

The CND-b were prepared according to our previous work.[28] 3 g citric acid was added to 20 ml ammonia water to form a transparent solution. The mixed solution was heated in a domestic 750 W microwave oven for about 5 minutes, during which the solution converted from colourless liquid to light brown and ultimately dark brown clustered solid, signifying the formation of CND-b. The solid was then dissolved in ethanol and centrifuged to remove agglomerated particles at RCF of 22 610 g for 10 minutes.

Preparation of supra-CND-g and supra-CND-b

As-prepared CND-g and CND-b ethanol solutions were injected into toluene solution under 400 rpm of magnetic stirring to form a transparent solution with large-scale aggregative nanoparticles, since CND-g and CND-b perform unsatisfactory solubility in toluene solution. The concentration of CND-g and CND-b ethanol solutions is 0.8 mg ml^{-1}. Moreover, the CNDs may have aggregated in the poor solvent mixtures with high toluene content. Visible to the unaided eye, the solution was transparent with no precipitate, signifying that the CNDs aggregates are of nano dimension.

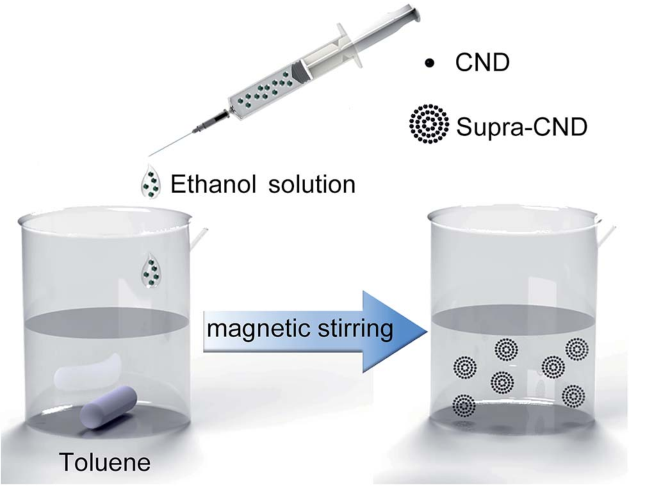
Fabrication of supra-CND-paper composite

Commercial filter paper (diameter = 12 cm) was immerged in supra-CNDs solution uniformly at room temperature to form the supra-CND-paper composite through the interaction between supra-CNDs and cellulose. Furthermore, the supra-CND-coated paper composites were transferred to a naturally-dried cupboard. Then the supra-CND-coated paper had been fabricated and the obtained composite was ready to water-jet printing, which exhibited water induced enhancement of photoluminescence.

Results and discussion

Scheme 1 shows the schematic illustration of the supra-CNDs preparation process. The as-prepared CNDs were water soluble. For the CNDs, ethanol is a benign solvent while toluene is a poor solvent *i.e.* CNDs could be monodisperse in ethanol solution but be aggregated in toluene solution. Thus, toluene could induce CNDs to aggregate upon adding CNDs ethanol solution into toluene.[29,30] Bearing this in mind, 2 ml CNDs ethanol solution was injected into 100 ml toluene under magnetic stirring at 400 rpm to induce aggregates of CNDs. It should be noted that the mixed solution was transparent with very weak luminescence, indicating the formation of supra-CNDs. CND-g exhibits strong green emission under UV excitation, while supra-CND-g toluene solution is nearly non-luminescent, as shown in Fig. 1. The inset of Fig. 1 shows the optical images of supra-CND-g and CND-g under room light and UV excitation. The obvious luminescence changes endue supra-CND-g potential application in encryption. The UV-vis absorption spectra of CND-g ethanol solution and supra-CND-g toluene solution are shown in Fig. 1. The obvious broadened, weakened absorption band centred around 415 nm with enhanced level-off tails in the visible spectral region, which is due to increased scattering intensity, indicates that the supra-CND-g were nano-size aggregates of CND-g.

The morphologies of CND-g and supra-CND-g were characterized using atomic force microscopy (AFM) and scanning electronic microscopy (SEM). Fig. 2a shows the heights of the CND-g, which are distributed in the range of 2 to 15 nm. AFM



Scheme 1 The schematic illustration of supra-CND-g preparation process.

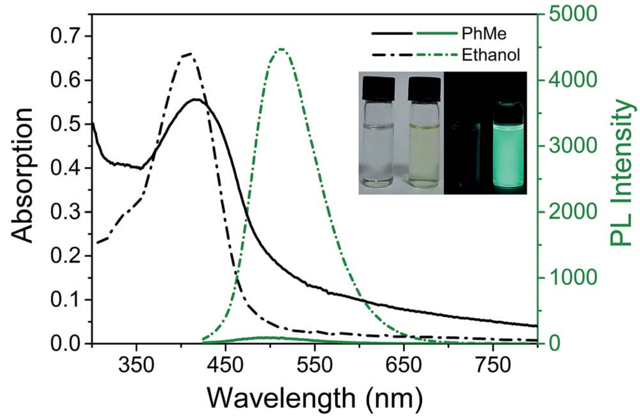


Fig. 1 UV-vis absorption (black line) and photoluminescence spectra (olive line) of supra-CND-g in toluene (PhMe) and CND-g in ethanol. Inset: photographs of CND-g ethanol solution and supra-CND-g toluene solution under room light (left) and UV illumination (right).

(Fig. 2b) and SEM (Fig. 2c) images show that supra-CND-g are spherical particles ranging in the size from 100 to 250 nm, indicating supra-CND-g are aggregates of numerous CND-g. Photoluminescent property is irrelevant to range distribution and solubility decreases as the size increases.

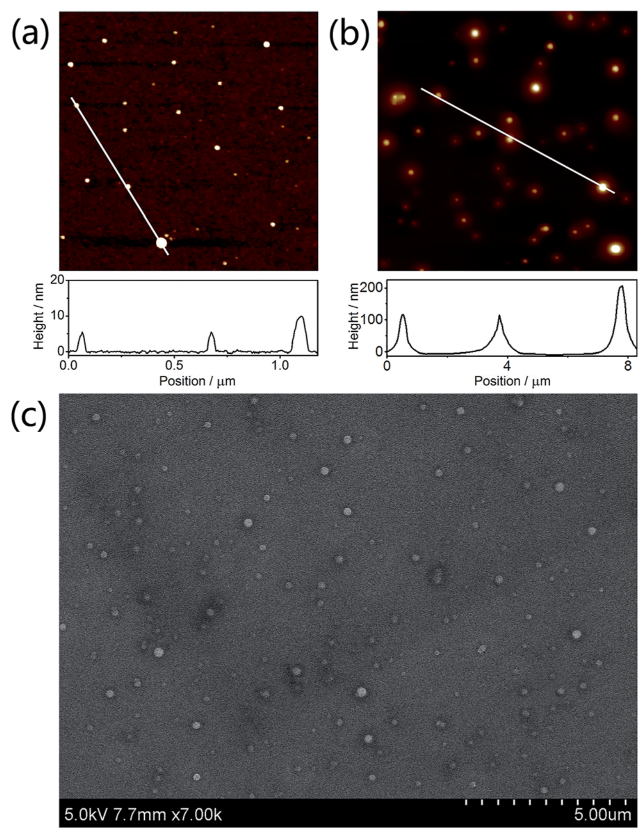


Fig. 2 AFM images of (a) CND-g and (b) supra-CND-g on silicon substrates, respectively. (c) SEM image of supra-CND-g on a silicon substrate.

Upon coating supra-CND-g toluene solution on paper, the supra-CND-g-coated paper also exhibits weak luminescence, indicating supra-CND-g remains in the paper after coating, providing an opportunity for water-induced enhanced photoluminescence. It is interesting to find that PL of the supra-CND-g-coated paper can be significantly enhanced after water-spraying treatment as our previous reported supra-CND-coated paper prepared from partially alkyl-chain-functionalized CNDs, as shown in Fig. 3a. The enhanced PL of the water-spraying treated supra-CND-g-coated paper retained after air drying. This phenomenon indicates that water induces supra-CND-g to decompose into separated CND-g, which could be absorbed in paper fibres to realize irreversible enhanced PL. Thus, the supra-CND-g-coated paper can be used for water-jet luminescent printing and human sweat pore luminescent mapping. With a water filled cartridge, commercial ink-jet printer can easily print luminescent encryption patterns using the supra-CND-g-coated paper, as shown in Fig. 3b. Water-jet printed encryption image can only be identified under UV illumination, indicating that information encryption has been achieved. It can be found that the supra-CND-g-coated paper has distinct advantage in the cost of production than our previous reported supra-CND-coated paper, which is more suitable for mass practical applications in anti-counterfeiting and information encryption.

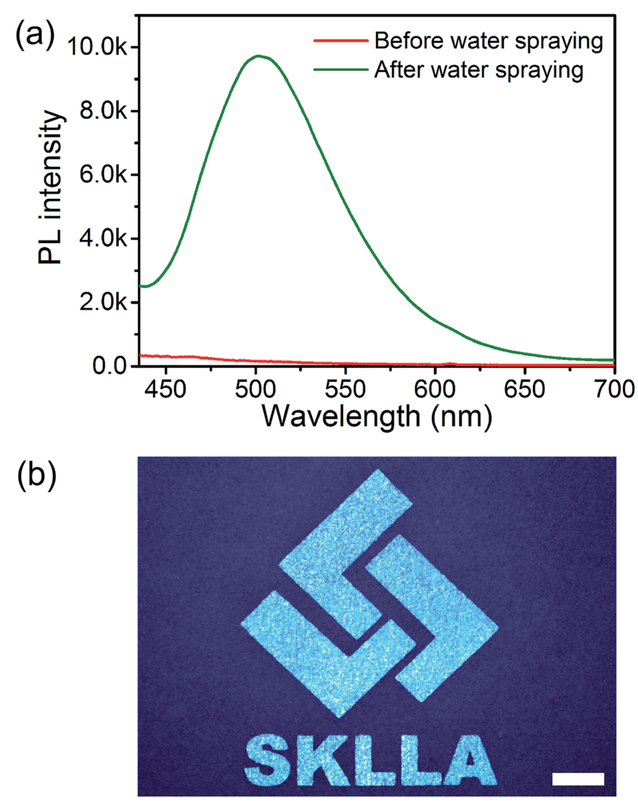


Fig. 3 (a) PL spectra of supra-CND-g-coated paper before and after water-spraying treatment. (b) Photograph of printed image of supra-CND-g-coated paper using only purely water-filled cartridge under UV excitation (scale bar = 1 cm).

Moreover, this method of preparing supra-CNDs can also be suitable for other CNDs. By utilizing CND-b, water-induced enhanced blue luminescence could also be achieved from supra-CND-b in the same route, which provides more possibilities in constructing dual-luminescence encrypted information. It is shown in Fig. 4 that the luminescent encrypted institute logo could be water-jet printed on supra-CND-b-coated paper where the characters of "CIOMP" was handwritten with supra-CND-g toluene solution.[31] Under day light, all the water jet printed and handwritten patterns were invisible. Under UV excitation, the water-jet printed blue luminescent patterns can only be observed, while the characters written in supra-CND-g toluene solution are invisible, which could be a first level of encrypted information, as shown in Fig. 4a and b. Upon full area water-spraying on the paper, the patterns are undistinguishable as they merged into the same background, while the characters can be observed in strong green luminescence under UV excitation, which could be a secondary level of encrypted information, as shown in Fig. 4b and c. Thus, dual-encryption based on the facile synthesized supra-CNDs with water-induced enhanced luminescence was constructed. It should be noted that if the secondary level of encrypted information be read, the first level of encrypted information was vanished. The irreversible deciphering process endows the supra-CND-based dual-encryption a distinct feature. These interesting phenomena indicated that the as-prepared supra-CNDs with multicolour water enhanced luminescent property could be useful in constructing multi-level encrypted information in anti-counterfeiting and information encryption.

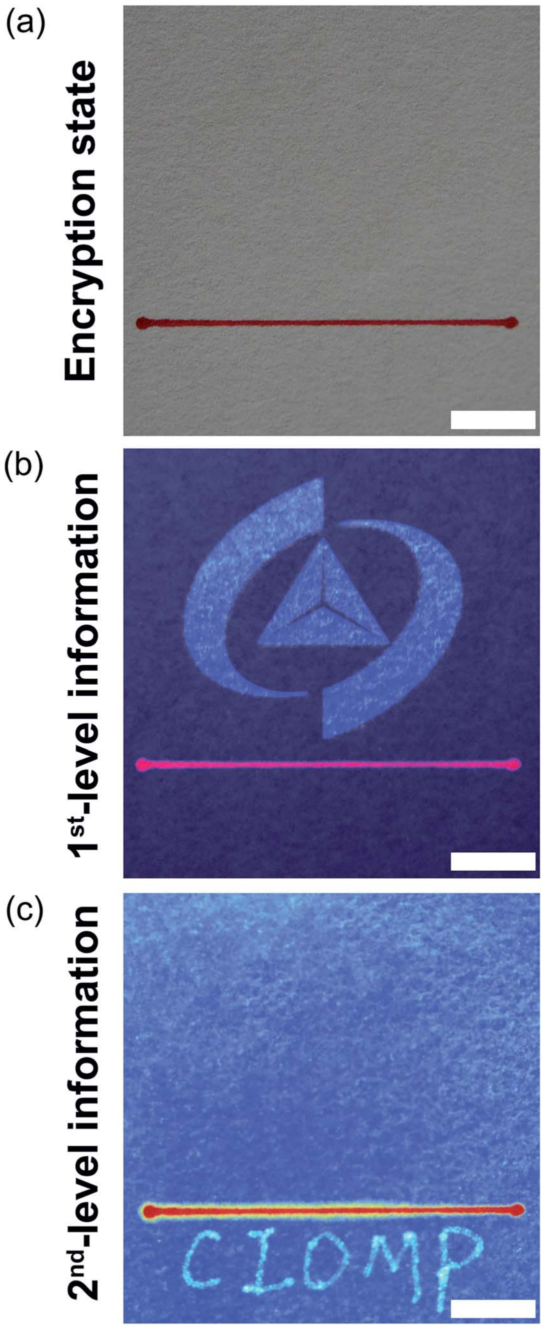


Fig. 4 Photographs of water-jet printed image of supra-CND-b-coated paper and handwrite characters of "CIOMP" with supra-CND-g in toluene before water-spraying treatment under (a) room light and (b) UV excitation and (c) after water-spraying treatment under UV excitation (the red line is hand written in commercial red luminescent marker pen and scale bar = 1 cm).

Conclusions

In summary, we introduce a simplified synthesis of supra-CNDs from our reported microwave-synthesized CNDs in an accessible, low cost and one-step method without further chemical synthesis. Two kinds of supra-CNDs were simply prepared by separately injecting blue and green emissive CNDs ethanol solution into toluene solution under vigorously stirring. Water-jet printing luminescence patterns and mapping human sweat pore patterns were realized in the supra-CND-coated paper. Using the two kinds of supra-CNDs, dual-encrypted luminescent information was constructed through water-jet printing and hand writing. This method is universal to prepare water-induced multicolour luminescent supra-CNDs from different luminescent CNDs. We prospect that the low cost, easy preparation and environmental friendly supra-CNDs will find substantial potential in constructing multi-level encrypted information in anti-counterfeiting and information encryption.

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