

# **An Innovative Microwave-Assisted One-Step Green Synthetic Approach of Biowaste Derived Fluorescent Carbon-Dot Invisible Ink for Currency Anti-Counterfeiting Applications**

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The quest for the design and synthesis of carbon dots with anti-counterfeit properties that are derived via green, environmentally friendly and economical procedures is a continuous process. Carbon dots (C-dots) derived from biowaste are cheap to synthesize, possess good photo-stability

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and high synthetic yield, making them applicable in the anti-counterfeiting of currency. Herein, we report a novel eco-friendly, cheaper, and faster method for the synthesis of carbon dots with strong photoluminescence properties from monkey orange fruit (*Strychnos spinosa*) biowaste. The presence of the hydroxyl and carbonyl functional groups of the carbon dots were determined by the Fourier transform infrared spectroscopy (FTIR). The carbon dots showed strong blue emission fluorescence (emission wavelength of 452 nm) when excited at 330 nm. The morphology and size were determined by the atomic force microscopy (AFM) which indicated amorphous and spherical nanoparticles with an average size of less than 2 nm. The no-crystallinity of the as-prepared carbon dots was confirmed using X-ray diffraction which showed the graphite-like structure. The carbon dots were produced and demonstrated good photo and chemical stability as well as high covert properties. The anti-counterfeiting of currency application by the synthesized carbon dots was demonstrated when the subsequent gel ink printed on the currency showed excellent chemical stability when exposed to washing with water, ethanol, and acetone. It also showed superior photostability when exposed to UV light at 365 nm and daylight for an extended period of up to 6 h. This work provides a facile, economical, and green approach for large scale production of carbon dots from the abundant biowaste.

**Keywords:** Anti-counterfeiting; carbon-dot gel ink; green synthesis; photoluminescence; monkey orange fruit.

## 1. Introduction

Counterfeiting is an issue bedeviling governments, organizations, private companies, and consumers the world over.<sup>1</sup> Fabrication and sale of counterfeit merchandise and commodities is increasing at an alarming rate around the world resulting in huge financial losses, pose serious risk to human life and threat to national security.<sup>2–4</sup> Forgery of high value products such as currency notes, pharmaceuticals, jewelry, electronic components, invoices, and legal documents such as passports and national identity cards is a growing concern worldwide that needs to be fully addressed.<sup>5,6</sup> The magnitude and threat posed by production and sale of fraudulent goods include loss of trillion US dollars by governments and industries resulting in loss of many jobs.<sup>7,8</sup> To be specific, the effects of counterfeiting have been increasing annually and the economic losses due to this unscrupulous act reached highs of 1.7 trillion US dollars in the year 2015.<sup>9</sup> In addition, production of counterfeit goods infringes on the rights of copyright owners and economic losses. As a result, there is need for anti-counterfeiting and security technology measures that are highly effective.

Various methods and techniques have been employed in the fight against counterfeiting. The use of anti-counterfeiting strategies such as the physical anti-counterfeiting tags including radio frequency identification tags (RFIDs),<sup>10</sup> holograms,<sup>11</sup> deoxy ribonucleic acid (DNA) chemical

tags,<sup>12</sup> inkjet-printed security labels,<sup>13,14</sup> magnetic security tags,<sup>15,16</sup> plasmonic security prints,<sup>17</sup> barcoding,<sup>18</sup> water marking<sup>19</sup> and luminescence printing<sup>14</sup> have all been used in the fight against counterfeiting. Unfortunately, most of these methods are familiar to the counterfeiters and do not provide an effective means to stop illegal duplication and cloning of authentic products. These common anti-counterfeiting strategies depend on laid down processes which are less complex and more obvious which imply that these tags can be easily duplicated by counterfeiters. For example, some of the old-fashioned methods such as barcoding, and water marking can be easily recreated and reproduced.<sup>20</sup> Consequently, this has motivated scientists and researchers to develop advanced, sophisticated, and innovative anti-counterfeit technologies such as triple-mode emission,<sup>21</sup> atomic force microscopy (AFM) nanoxerography,<sup>22</sup> laser holography,<sup>11</sup> nuclear track technology<sup>23</sup> and photoluminescence (PL) printing.<sup>24</sup> However, some of these complicated techniques are too expensive for application in a large array of consumer goods.<sup>10</sup> In recent years, photoluminescence-nanoparticle based printing has attracted the attention of many researchers and scientists due to their ease of handling, superficial design and have accordingly been found suitable in the fight against counterfeiting.<sup>21,22,24–27</sup> Photoluminescent nano-particle inks have been designed and applied towards the fight against forgery such

as semiconductor nanocrystals,<sup>28,29</sup> nano-rods,<sup>30</sup> metal nanoclusters,<sup>31</sup> polymer nanoparticles.<sup>32</sup> These photoluminescent materials present determinate luminescent characteristics upon irradiation with specific electromagnetic energy.<sup>24,33</sup> The luminescent ink from these nanomaterials is used to fabricate diverse coded patterns resulting in high level concealment luminescent print and the advanced and sophisticated coded patterns which are difficult to replicate.<sup>27</sup> Klajn *et al.* have developed an azobenzene gold doped nanoparticles and successfully applied them as self-erasable security inks which change color from red to purple upon irradiation with ultraviolet light and invisible in under visible light.<sup>34</sup> Reactive pattern prints involving the use of insoluble salts such as the bright yellow patterns from lead (II) iodide obtained from application of aqueous lead (II) acetate on a dried substrate containing potassium iodide have been studied for possible application in the fight against counterfeiting.<sup>35</sup> Lu *et al.* synthesized and applied the CdTe photoluminescent semiconductor quantum dots (QDs) based on polyethyleneimine (BPEI) polymer as a possible anti-counterfeit security.<sup>36</sup> Although these photoluminescent materials are highly effective and show promise in the fight against counterfeiting, they do have undesirable attributes such as high cost of precursors, tedious preparation, toxicity and use of harmful solvents in their preparation.<sup>19,37</sup> Therefore, there is a need to develop anti-counterfeit materials that are simple, of low cost yet very sensitive and difficult to reproduce.

The discovery of a new class of carbon material in 2004 has attracted much attention from scientists and researchers.<sup>38</sup> Carbon-dots (C-dots) as they are commonly called, have stimulated interest, and are seen as the best substitute for the semiconductor quantum dots because of their low cost, less labor for their preparation, green synthesis approach, superior and tunable luminescence, low cytotoxicity, excellent water solubility, plasticity, high fluorescent quantum yields, superb chemical and photostability and exceptional biocompatibility.<sup>39–41</sup> The inherent properties of C-dots have made them suitable for application in many fields such as biosensing,<sup>42,43</sup> bioimaging,<sup>44</sup> drug delivery,<sup>45</sup> photocatalysis,<sup>46</sup> photovoltaic devices,<sup>47</sup> medical diagnostic tools,<sup>48</sup> forensic applications such as latent fingerprint enhancement<sup>49</sup> and anti-counterfeiting.<sup>9,19,50</sup> C-dots can be synthesized via the top-down and bottom-up approaches.<sup>19,51</sup> The

top-down approach involves peeling off nanomaterials from bulky parent carbon substances such as carbon nanotubes,<sup>52</sup> carbon fibres,<sup>53</sup> graphite,<sup>54</sup> activated carbon<sup>55</sup> using techniques like arc discharge, laser ablation, oxidation, and electro-oxidation of the carbon sources.<sup>56</sup> Alternatively, C-dots can be prepared using the bottom-up approach that entails the inexpensive carbonization of abundant natural carbon sources such as biomass,<sup>57</sup> fruit juice,<sup>58</sup> grass,<sup>59</sup> banana<sup>60</sup> and hair fibre<sup>61</sup> by means of pyrolysis and hydrothermal treatment of the molecular precursors. Most of the previous studies carried out on application of C-dots in anti-counterfeiting have used mainly commercially available carbon materials for preparation of C-dots.<sup>19,51</sup> Commercially available carbon sources such as xylose and m-phenylenediamine,<sup>62</sup> polyvinyl alcohol (PVA),<sup>21</sup> citric acid and ethylenediamine,<sup>42,50</sup> melamine and dithiosalicylic acid.<sup>63</sup> Therefore, the cost implications associated with preparation of these C-dots cannot be ignored.

Present work reveals an extremely simple, less time consuming and environmentally benign approach for the preparation of highly luminescent C-dots using natural and locally available carbon source material as the precursor — the monkey orange (*Strychnos spinosa*). The preparation of these photoluminescent C-dots follows a green synthetic route using a home microwave and water as the solvent. To the best of our knowledge, no study has been carried out involving the use of natural and locally available carbon precursor products and used them as a tool for anti-counterfeiting. The as-prepared C-dots were found to be chemically and photo stable as well as applicable in the fight against counterfeit currency notes.

## 2. Experimental

### 2.1. Chemicals and raw materials

The monkey orange fruit (*S. spinosa*) shells were collected from the hawkers selling the fruits by the roadside in Palapye (Makoro fields), Botswana. The edible part of the fruit had been consumed and the shells ready for disposal by the hawkers. Double deionized water was produced in the laboratory using Milli-Q system and was used throughout this study. Ethanol (99.99%) and glacial acetic acid (99.8%) were all purchased from Sigma Aldrich (St. Louis, USA). Chitosan was supplied by Rochelle chemicals company (Johannesburg, South Africa).

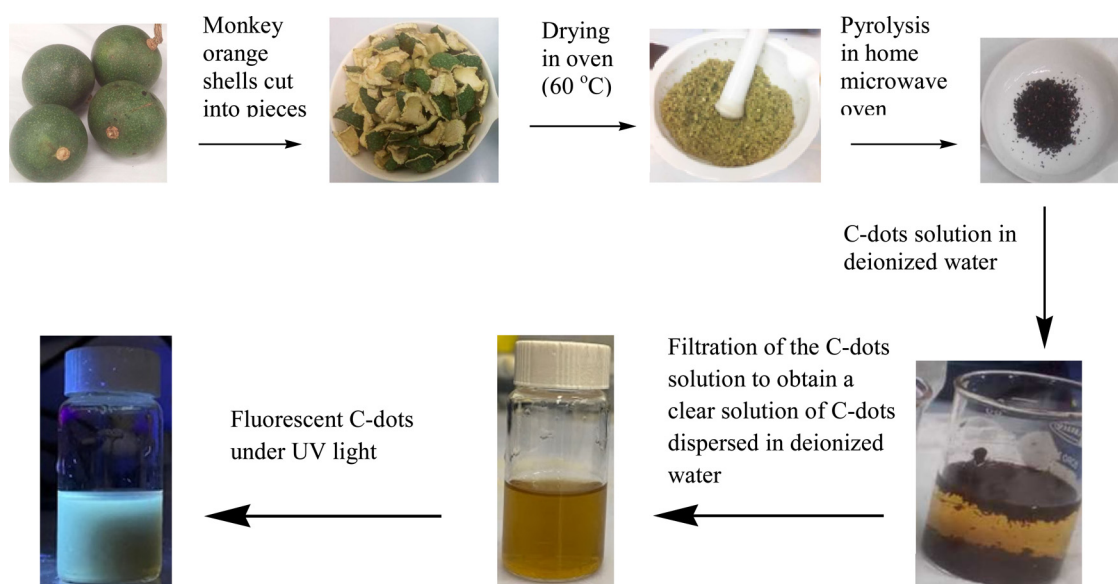


Fig. 1. Schematic representation of the microwave-assisted fabrication of C-dots.

All chemicals used were of analytical grade and used as received. Specimen bank notes were obtained from Central Bank of Botswana, Gaborone, Botswana.

## 2.2. Synthesis of carbon dots

The C-dots were synthesized via a microwave assisted synthesis procedure as reported in the literature.<sup>39</sup> Briefly, monkey orange fruit shells were washed with plenty of de-ionized water, cut into small pieces and then dried for 36 h in an oven at 60 °C. The dried material was then ground using pestle and mortar and the ground biowaste was placed in a crucible and taken into a home microwave (Russell Hobbs, 700 W). The ground matter was then subjected to microwave irradiation for a period of 20 min. Once the microwave assisted pyrolysis process is complete, the obtained product was allowed to cool to room temperature in a desiccator in a dark place. An exact mass 2.0 g of the pyrolytic product was weighed into a volumetric flask and 50 mL of double deionized water was added to disperse the C-dots. The resulting solution was then homogenized under sonication (Sonic-Clean, Labotec) for 15 min and centrifuged (Thermo Scientific, Heraeus, Megafuge 40 Centrifuge) at 8000 rpm for 15 min to remove large particles. The solution was then filtered using a 0.45  $\mu$ m syringe filter. The resulting supernatant solution was dialyzed (retained molecular weight: 1000 Da) against

double deionized water and this was done in the dark for 24 h. The final light-yellow solution containing C-dots was stored at 4 °C for further characterization and application. The schematic flow chart of the synthesis procedure is shown in Fig. 1.

## 2.3. Optimization of synthesis conditions

Synthesis conditions such as synthesis time were experimentally determined. The monkey orange shell precursor was subjected to varying microwave irradiation set at 10–40 min and time increments of 5 min. This was followed by photoluminescence studies of the product after sonication, centrifugation, and dialysis. The as-prepared C-dot nanomaterial synthesized at a time revealing the highest fluorescence intensity was taken as the optimum synthesis time.

## 2.4. Synthesis equipment and characterization of the as-prepared C-dots

A household microwave oven (Russell Hobbs, 700 W) used in the synthesis of C-dots was purchased from a local Furniture and Home Appliances store. An atomic force microscopy (AFM), (Bruker AFM dimension edge in Scan Asyst Peak Force), was used to determine the size and distribution in the tapping mode. The AFM specimen was

prepared by depositing a drop of the purified C-dots solution on a clean AFM mica slide and dried at room temperature in a desiccator for 2 h. The fluorescence measurements were taken using a Perkin–Elmer LS 55 spectrofluorometer. The Fourier transform infrared (FTIR) spectra were recorded using Thermo Scientific Nicolet iS10 FTIR spectrometer operated at 32 scans and resolution of  $0.50\text{ cm}^{-1}$ . The FTIR spectra of the pure C-Dots were obtained after dissolving in aqueous solution. UV–Vis spectra were obtained using a Thermo Scientific Evolution 201 spectrophotometer.

### 2.5. Determination of fluorescence quantum yield

The fluorescence quantum yield (FQY) of the as-prepared C-dots was determined following a procedure reported in the literature.<sup>64</sup> Anthracene in ethanol (literature FQY is 0.27 at 350 nm) was selected as the standard fluorescent molecule because its emission occurs in the same region as that of the as-prepared C-dots (360–480 nm).<sup>65</sup> The absorbance and fluorescence intensities of anthracene and that of the as-prepared C-dots were determined and substituted in equation (1) and the fluorescence quantum yield of the C-dots was calculated.<sup>65</sup>

$$\phi_{\text{C-dot}} = \phi_{\text{anthracene}}$$

$$\times \frac{I_{\text{C-dot}} A_{\text{anthracene}} \eta_{\text{C-dot}}^2}{A_{\text{C-dot}} I_{\text{anthracene}} \eta_{\text{anthracene}}^2}, \quad (1)^{65}$$

where  $\phi_{\text{C-dot}}$  and  $\phi_{\text{std}}$  are the fluorescence quantum yields of the as-prepared C-dots and anthracene, respectively.  $I_{\text{C-dot}}$ ,  $A_{\text{C-dot}}$  and  $I_{\text{anthracene}}$ ,  $A_{\text{anthracene}}$  are the respective fluorescence intensities and absorbance of the C-dots and anthracene standard material. On the other hand,  $\eta_{\text{C-dot}}$  and  $\eta_{\text{anthracene}}$  are the refractive indices of solvents in which C-dot and anthracene are dissolved. Absorbance of all solutions in the 1 cm cuvette were kept under 0.1 at excitation wavelength of 340 nm and 350 nm to suppress re-absorption effects inside the sample on the established emission spectrum.

### 2.6. Chemical and photostability tests of C-dots

Chemical stability tests were carried out by immersing the C-dot gel ink printed banknotes in water, ethanol, and acetone for 2 h. The solvent-soaked banknotes

were then allowed to air dry after which irradiation with a 365 nm UV lamp was carried out. The photostability test was carried out by continuous irradiation of the C-dot gel ink to daylight and UV lamp (365 nm). The fluorescence intensities of the C-dot gel ink were determined at intervals of 1 h for an extended period of 6 h.

### 2.7. Preparation of C-dot gel ink and anti-counterfeit applications

The C-dot gel ink was prepared using a procedure adopted from.<sup>66</sup> In brief, 0.5 g of chitosan was mixed with 50 mL of deionized water followed by 0.5 mL of glacial acetic acid. The solution was continuously stirred until a clear solution was obtained indicating complete dissolution of chitosan. To this solution was added 1 mL of 0.04 g/mL C-dot and stirring was continued for 5 min resulting in the formation of a viscous light-yellow C-dot gel ink. The resultant solution was placed in an amber glass vial and stored at 4°C for further characterization and application. For application studies, the gel ink was drawn into a bulb glass dropper and used to write the word “PULA” on different Botswana currency specimen notes. The ink was left to air dry for 2 h before examining under ultraviolet light. The results revealed a blue fluorescent “PULA” word on each currency specimen note.

## 3. Results and Discussion

### 3.1. Characterization of the as-prepared C-dots

The morphology and size distribution of the as-prepared C-dots were investigated using the atomic force microscope. The results obtained [Figs. 2(a)–2(c)] revealed that the synthesized C-dots nanoparticles were irregularly shaped and monodispersed with a broad particle size distribution of 0.7–1.0 nm (average size = 0.8 nm). Their three-dimensional presentation [Fig. 2(c)] shows an amorphous structure with no crystal lattice. Structural and morphological characterizations of the C-dots were further performed using XRD technique [Fig. 2(d)]. The strong peak at  $2\theta = 21^\circ$  characterizes the intergranular accumulation of carbon atoms in the carbon amorphous phase. This has also been reported in the literature.<sup>67</sup> It also confirms the highly flaking graphitic nature of the as-prepared C-dots which conveys the graphenic character of the

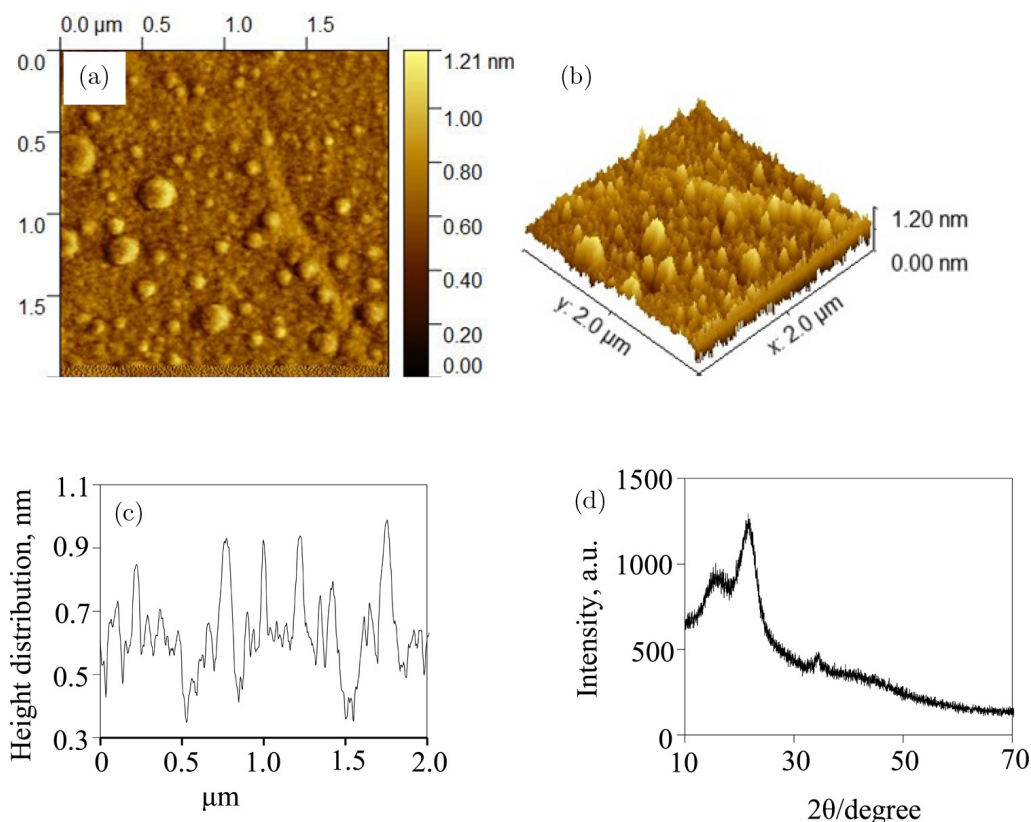


Fig. 2. AFM characterization of the as-prepared C-dots. (a) A 2-D image of the well dispersed C-dots; (b) A 3-D image of the C-dots revealing their amorphous structure; (c) the height distribution of the as-prepared C-dots and (d) XRD pattern of the as-prepared C-dots.

material.<sup>39</sup> The peak at  $2\theta = 15^\circ$  implies the structures of the as-prepared C-dots contain small crystalline cores with disordered surfaces.<sup>68</sup>

The FTIR shown in Fig. 3 reveals characteristic peaks at  $3385.96$  and  $1645.09\text{ cm}^{-1}$  which are representative of the stretching vibrations of hydroxyl (O–H) and carbonyl (C=O) respectively. The peak at  $3831.16\text{ cm}^{-1}$  represents the stretching vibration

of the –N–H. The stretching vibrations of the –C–H and –C=C–H–H are indicated by the peak at  $2090.89\text{ cm}^{-1}$ . The bending vibration of the –C–H surface of the as prepared C-dots is shown at  $648\text{ cm}^{-1}$ . In addition the –C–H of aromatic benzene are represented by the peak at  $559.01\text{ cm}^{-1}$ . The hydrophilic hydroxyl groups on the surface of the C-dots are responsible for the water solubility of the as-prepared C-dots.

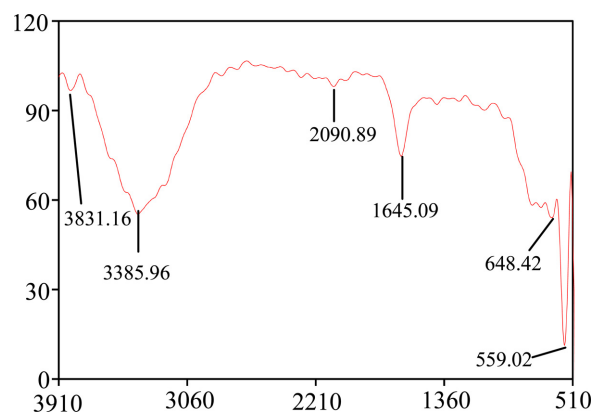


Fig. 3. FT-IR spectrum of the as-prepared C-dots.

### 3.2. Optimization of synthesis conditions

The optimum synthesis time for the as-prepared C-dots was experimentally determined and it takes approximately 20 min (Fig. 4). The time of 20 min was selected because at this time the as-prepared C-dots generated the highest fluorescence intensities, an indication of high photoluminescence properties of the nanomaterials at the optimized synthesis time. Optimization of the synthesis time for the C-dots is a very important aspect that should be carried out as reported in other previous

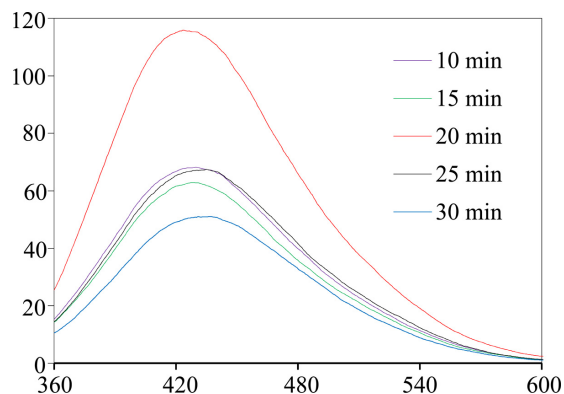


Fig. 4. Emission spectra of the as-prepared C-dots at different synthesis times.  $\lambda_{\text{ex}} = 330 \text{ nm}$ ; slit width = 2.5 nm.

studies.<sup>69</sup> There was no shift in the emission wavelength as synthesis time was varied between 10 and 30 min while holding the excitation wavelength constant at 330 nm.

### 3.3. Optical characteristics of the as-prepared C-dots

The UV–Vis spectrum of the as-prepared C-dots presented no absorption peak as shown in Fig. 5(a). The absence of an obvious absorption peak but rather a wide absorption band can be attributed to the possibility of a broad particle size distribution of the as-prepared C-dots.<sup>52,70,71</sup> The broad absorption spectrum that stretches into the visible region suggest the nonexistence of a well-defined band edge in the UV–Vis region.<sup>72</sup> A similar spectrum has been obtained in previous studies.<sup>73</sup> The excitation-emission spectra indicated relatively narrow Stoke's shift which implied the origin of the photoluminescence of the as-prepared C-dots may arise from band-gap transition [Fig. 5(b)].

The as-prepared C-dots revealed intense fluorescence intensity after excitation at 330 nm compared

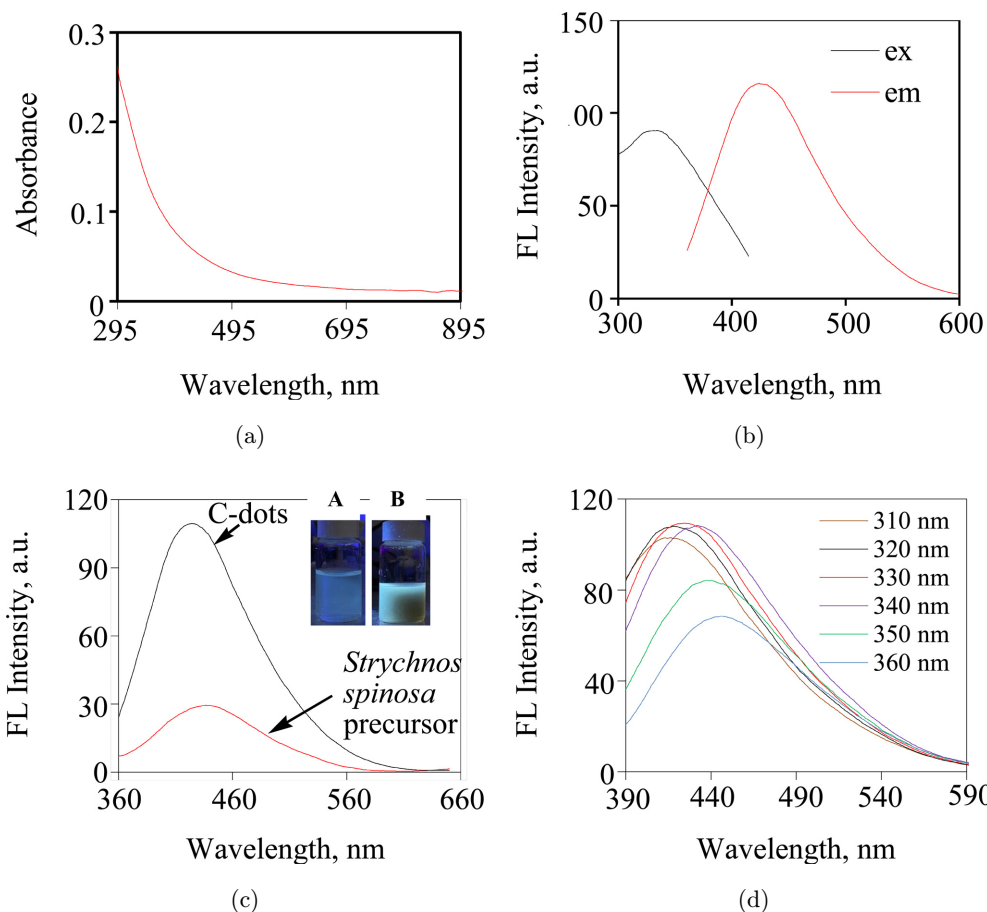


Fig. 5. Optical properties of the as-prepared C-dots; (a) U-Vis spectrum of the as-prepared C-dots; (b) fluorescence excitation-emission spectra of the as-prepared C-dots ( $\lambda_{\text{ex}} = 330 \text{ nm}$  and  $\lambda_{\text{em}} = 452 \text{ nm}$ ); (c) photoluminescence properties of the carbonized material (black) and the uncarbonized (red) ( $\lambda_{\text{ex}} = 330 \text{ nm}$ ) (insert **A** and **B** show the uncarbonized and carbonized *Strychnos spinosa* precursor material respectively under UV light at 365 nm); (d) emission spectra of the as-prepared C-dots at different excitation wavelengths ( $\lambda_{\text{ex}} = 310\text{--}360 \text{ nm}$ ).

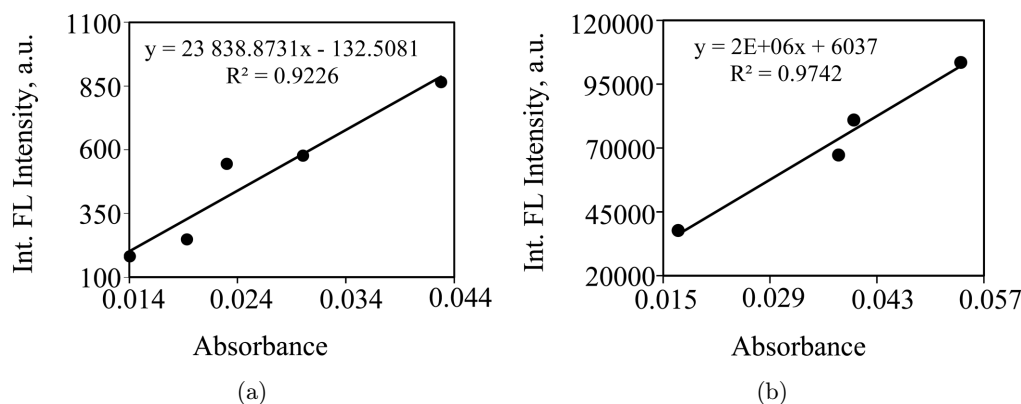


Fig. 6. Linear plots used in the determination of the fluorescence quantum yield of the as-prepared C-dots; (a) Plot of integrated fluorescence intensity versus absorbance for as-prepared C-dots ( $\lambda_{\text{ex}} = 330$  nm) and (b) Plot of integrated fluorescence intensity versus absorbance for the anthracene standard in ethanol ( $\lambda_{\text{ex}} = 350$  nm).

to the fresh *S. spinosa* precursor that had not undergone microwave irradiation [Fig. 5(c)]. The insert on Fig. 5(c) shows the appearance of the as-prepared C-dots under normal light, appearing as a light-yellow liquid with excellent water solubility and their blue emission under UV irradiation at 365 nm. The intense blue luminescence of the as-prepared C-dots demonstrates that there is no need for any further treatment such as surface passivation to introduce various functional groups on the surface of the C-dots.

In addition, the fluorescence emission spectra of the as-prepared C-dots are also broad and depict dependence on excitation wavelengths [Fig. 5(d)]. The broad and red shift of emission spectra with increasing excitation wavelength may reveal the intrinsic characteristics of the as-prepared C-dots such as varying particle size and distribution of different emissive sites on the surface of the C-dots.<sup>71</sup> Furthermore, the shift in the peak position with changes in the excitation wavelength illustrates the potential towards tuning of the C-dots photoluminescence through varying the excitation wavelength. The as-prepared C-dots revealed the strongest emission at the excitation wavelength of 330 nm which corroborated the findings from excitation-emission spectra [Fig. 5(b)].

The photoluminescence properties of C-dots have been thought to originate from the size of the C-dots, the presence of  $sp^2$  sites, the structural defects and in some cases the presence of the aromatic conjugate structure.<sup>67</sup> The fluorescence quantum yield (FQY) was determined experimentally using anthracene as the standard with literature value

of fluorescence quantum yield at 0.27 in ethanol (refractive index  $\sim 1.36$ ) as shown in Fig. 6.<sup>74</sup> The FQY for the as-prepared C-dots in water (refractive index  $\sim 1.33$ ) was found to be 0.31%. The FQY yield of the as-prepared carbon dots is quite low and its possible improvement can be achieved through surface passivation processes to introduce other functional groups on the surface of the carbon-dots to enhance their photoluminescent properties. The luminescence mechanism of fluorescent C-dots is still not well understood. Possible mechanisms have been proposed such as the radiative recombination of excitons,<sup>70</sup> quantum confinement effect,<sup>46</sup> poly-aromatic patterns,<sup>75</sup> emissive traps,<sup>71</sup> crooked edges<sup>76</sup> and structural defects of the carbon dots.<sup>67</sup> The band gap energy was determined using the equation  $E_g(\text{in eV}) = 1240/\lambda_g$  where  $E_g$  is the band gap energy in eV and  $\lambda_g$  is the wavelength (in nm) corresponding to the band gap energy at room temperature.<sup>77</sup>  $\lambda_g$  was obtained from a plot of absorbance versus wavelength for the as-prepared C-dots [Fig. 5(a)]. The tangent to this plot crosses the X-axis at a wavelength of 520 nm and therefore  $E_g = 1240/520 = 2.38$  eV.

### 3.4. Anti-counterfeit properties of the C-dots gel ink print

The as-prepared C-dots were then applied on a BWP 200 (P200) Botswana currency note specimen in the form of a UV-active ink which would otherwise be not noticeable under visible light. The P200 specimen currency note is shown on Fig. 7(a) under daylight and with no noticeable anti-counterfeit features. After UV irradiation (365 nm), three

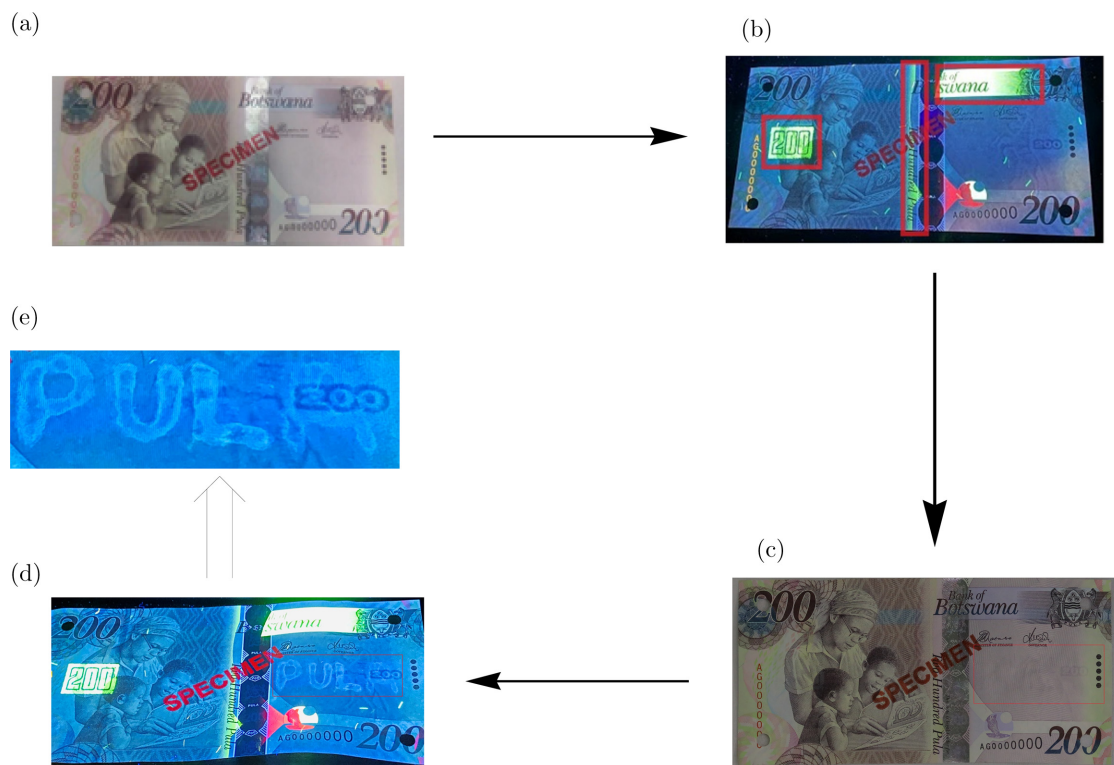


Fig. 7. A pictorial presentation of C-dot ink application on a Botswana currency of 'P200' (BWP 200.00) banknote specimen; (a) 'P200' banknote without C-dot ink and under daylight; (b) 'P200' banknote without C-dot under UV irradiation at 365 nm indicating the fluorescent anti-counterfeit features; (c) 'P200' banknote with the word 'PULA' written on it using C-dot ink and under daylight; (d) 'P200' banknote with the word 'PULA' written using on it C-dot ink and under UV irradiation at 365 nm; (e) an expanded view of the word 'Pula' written on 'P200.00' banknote using C-dot ink and under UV irradiation at 365 nm.

anti-counterfeit fluorescent prints that are already present in the specimen currency note are clearly visible on the currency note (enclosed in a red rectangle) [Fig. 7(b)]. The word "PULA" applied on the currency note using the C-dot gel ink is colorless, transparent, and not visible under daylight [Fig. 7(c)]. However, after UV irradiation at 365 nm, the word "PULA" becomes clearly visible, emitting blue-green light [Fig. 7(d)]. An expanded view of the gel ink print is shown clearly on Fig. 7(e). This reveals the unique optical characteristic of the C-dots and possible applications as security ink and thereby providing a technique to verify the authenticity of currency notes. It is important to note that advanced photoluminescent anti-counterfeiting requires costly and sophisticated equipment whereas in this case only a spectrofluorometer was used which is relatively less costly and dependable. In fact, a spectrofluorometer fitted with an array of fiber-optical accessories can provide a rapid and effective development of anti-counterfeiting ink printing.

### 3.5. Chemical and photostability of the as-prepared C-dots

The fluorescence intensity of the as-prepared C-dots was found to be stable after irradiation by UV light (365 nm) and daylight for an extended period of up to 6 h [Figs. 8(a) and 8(b)]. The degree of the fluorescence intensity of the as-prepared C-dots showed a slight change and becoming less intense after UV (365 nm) and daylight irradiation at time intervals of 1 h for an extended period of 6 h. This revealed the apparent photostability and resistance to photobleaching by the as-prepared C-dots that is noticeable on the small fluctuations of the fluorescence intensities [Figs. 8(a) and 8(b)]. The preservation of the photoluminescence intensity of the C-dot ink could be improved by doping or passivation and increasing the concentration of the C-dot ink applied. In addition, these findings show that the as-prepared C-dots can be suitable for either inkjet printing or counteract printing to satisfy the need for commercial use. Similar results have been obtained in previous studies.<sup>62,66</sup> Furthermore, a

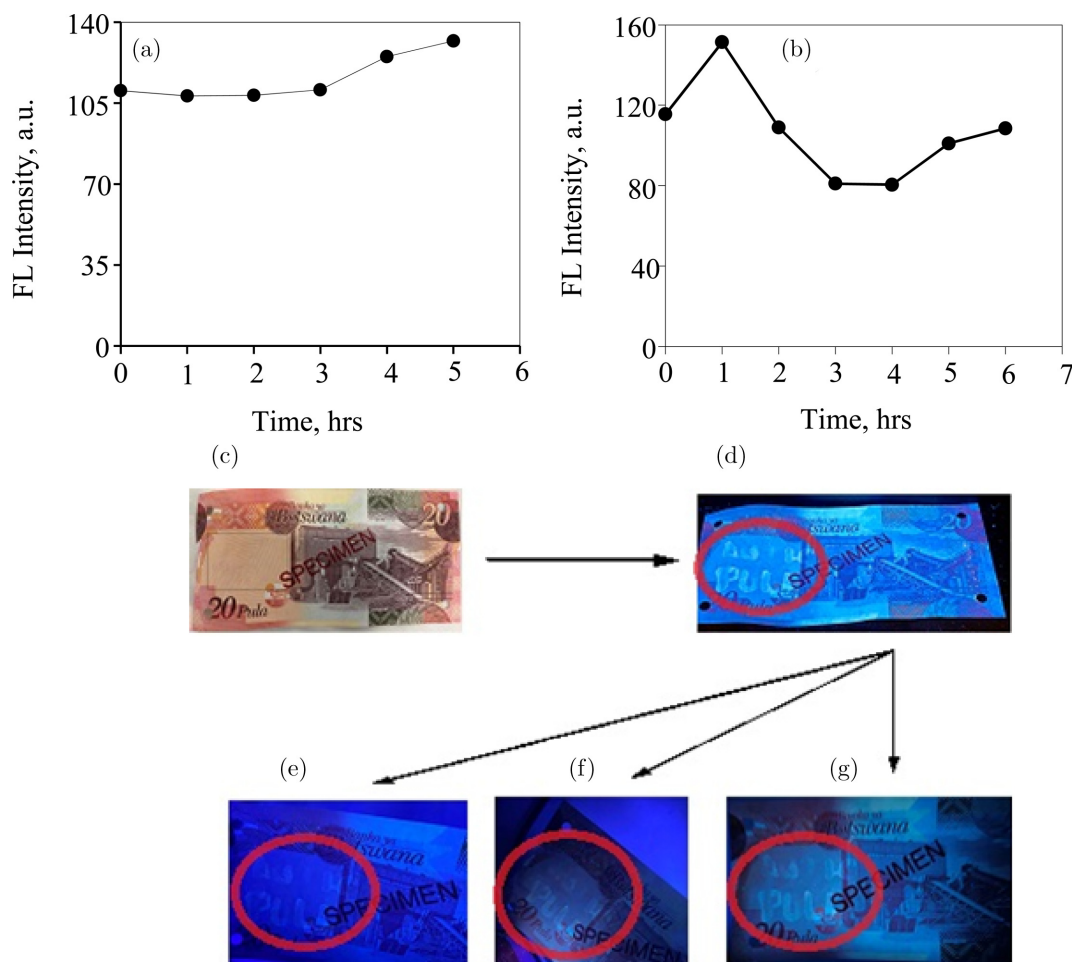


Fig. 8. Photostability and chemical stability tests; (a) fluorescence intensity of the asPrepared C-dots after exposure to UV light (365 nm); (b) fluorescence intensity of the asPrepared C-dots after exposure to daylight; (c) A Botswana currency of 'P20' (BWP 20.00) the word 'PULA' written on it using C-dot ink and under daylight; (d) 'P20' banknote with the word 'PULA' written on it using C-dot ink and under UV irradiation at 365 nm; (e) the word 'Pula' still visible after washing with acetone; (f) the word 'Pula' still visible after washing with ethanol; (g) the word 'Pula' still visible after washing with deionized water.

chemical stability test revealed the resistance of the as-prepared C-dot gel ink to washing away from organic solvents such as acetone and ethanol [Figs. 8(e) and 8(f)]. It is also important to mention here that even deionized water was not able to destroy the fluorescent ink printed on the banknote [Fig. 8(g)]. This gives an indication that the C-dot gel ink effectively adhered to the banknote such that after washing with both organic and inorganic solvents the C-dot print was still clearly noticeable. Therefore, it is reasonable to deduce that the facile synthesis approach, tunable luminescent properties accompanied by high photo and chemical stabilities make the C-dots gel ink good candidates for anti-counterfeiting applications.

#### 4. Conclusion

Fluorescent and durable C-dots were produced from wasted monkey orange fruit (*S. spinosa*) using the microwave assisted method. The process does not include any complex chemical oxidation or surface passivation procedures. The irradiation time played a crucial role in the degree of carbonization of the bulk biowaste. The use of readily available biowaste makes this synthesis approach green, economical and environmentally friendly. The as-prepared C-dots revealed excellent water solubility, intense blue luminescence, photo, and chemical stabilities making them a suitable anti-counterfeiting tool. The preparation of the gel ink using a mixture of chitosan and the C-dots illustrated the facile and versatility of its employment as a UV-sensitive marker

for anti-counterfeiting. The photoluminescence properties of the C-dots derived from the biowaste can be improved through surface passivation and modification. Finally, the fast synthetic approach, simplicity and generality provide great possibilities for large-scale fabrication and production of water-soluble fluorescent markers and prints that can be used in the fight against counterfeiting.

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