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Synthesis and Characterization of Carbon Nanoparticle/PVA/ Chitosan for Security Ink Applications

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Abstract. Security ink based using carbon nanoparticles (C-dots)/PVA/Chitosan composite based materials has been successfully synthesize. The C-dots powder were prepared using urea pyrolysis method. The precursors were synthesized using urea ($(NH_2)_2CO$, Mw=60.07 g/mol) and citric acid ($C_6H_8O_7{\cdot}H_2O$, Mw= 210.14 g/mol) as fuel and carbon sources, respectively. The carbon nanoparticle (C-dots) was prepared by heated the precursor solution at 250 °C for 90 min. The security ink was fabricated using C-dots, polyvinyl alcohol (PVA, $(CH_2CH(OH))_n$, with Mw= ~20000 g/mol) and chitosan as the dyes, resins, and binders, respectively. The morphology and optical properties of the security ink were measured using SEM and EDXs, PL Spectrometer, and UV-Vis spectroscopy. The viscosity properties of the security ink were measured using viscometer. The characterization showed that the C-dots has mono-disperse particle sizes, tetragonal structure and absorption spectra in UV light region. The viscosity properties show that the PVA:Chitosan concentration has a significant effect and optimized to the security ink viscosity. In additions, the security ink was studied using a commercial printer, the printing results show a good quality and blue emission (450 nm) appeared under UV light exposure at 365 nm. The security ink based C-dots/PVA/Chitosan composite has potential insight for the security application, panel display, optoelectronic and optical devices on an industrial scale.

Keywords: Carbon nanoparticles (C-dots), water based security ink, viscosity properties, PVA/Chitosan composite

1. Introduction

Luminescence materials are a semiconductor-like material, which has to change optical properties in response to the stimulus of external radiation such as UV light, thermal or nuclear radiations. Luminescence materials have optical security features that are difficult to imitate and duplicate. Therefore, they are widely used as non-colour security inks for applications in optical data recording, storage and security [1]. Some photoluminescence materials have been widely used as a fluorescent ink such as an organic dye [2], conjugated polymer [3] and inorganic quantum nanodots [4]. Organic dye has low photo-stability and small Stokes shift, while conjugated polymers and inorganic quantum nanodots have a characteristic of fluorescence that easily tuneable with narrow emission bandwidth and high photostability. In recent years, nanoparticles doped by lanthanide atoms and/or rare earth metal ions have been developed for an application as anti-counterfeiting security ink. However, there

are concerns regarding the risk of long-term cytotoxicity and potential environmental pollution of lanthanide or the rare earth ions -based security ink [5].

In the recent research, our group has succeeded in developing a new type of graphitic carbon nanoparticles (C-dots) as new type fluorescence materials without the use of rare earth ions [6]. The C-dots are the most stable allotropes of carbon and potentially developed due to their unique electronic and optical properties [7]. The C-dots could be synthesized on a large scale using nitrogen condensation process, including the melamine, urea, and thiourea [8]. The C-dots have been successful to develop for various application, such as solar absorber materials, bioimaging, and sensors [9-11]. Compared with inorganic quantum nanoparticles, the C-dots have many advantages such as simple fabrication process, high quantum efficiency, good biocompatibility, low cost and cytotoxicity, and high photostability [9].

In this paper, we report the synthesis and characterization of the C-dots/PVA/Chitosan composite based security ink prepared by the wet chemical method. We used PVA and Chitosan as an adhesive to control the oxidation and dissolution of the C-dots particles after printing. We varied the PVA/Chitosan concentration synthesis to determine the composite viscosity optimization of the C-dots/PVA/Chitosan composite based security ink. The morphology, viscosity and optical properties of the C-dots/PVA/Chitosan composite based security ink were measured using SEM and EDXs, Viscosity meter, PL Spectrometer, and UV-Vis spectroscopy.

2. Experiment

The C-dots powder were synthesized using citric acid and urea as carbon and fuel source, respectively. The precursor solution was prepared by mixing all raw materials with carbon-fuel (C/N) mass ratio at 3g/3g. The precursors were heated using the commercial oven at 250 ºC for 90 minutes to obtain black carbon powder [12]. The C-dots solution was prepared by dispersing the synthesized carbon powder with various of mass from 0.01g to 0.3g, into 20 mL of pure water. The C-dots solution were steers using a magnetic stirrer until all carbon powder disperse and become brown clear solutions.

The security ink was fabricated using prepared C-dots, polyvinyl alcohol (PVA, MW= ~20000 g/mol) and chitosan (β-(1-4)-linked D-glucosamine and N-acetyl-D-glucosamine) to form a colloidal composite of C-dots/PVA/Chitosan. The C-dots/PVA/Chitosan composite synthesis has several steps: (i) the chitosan powder slowly dissolved in pure water with 2% acetic acid at room temperature until getting homogeneous chitosan solution. Then, (ii) polyvinyl alcohol (PVA) and (iii) C-dots was mix to chitosan solution and stirred at 70 ºC. To optimize the viscosity security ink, the PVA/Chitosan concentration varied from 0% to 2.8 %wt/v shown in **Table 1**. The PVA and chitosan with a mass ratio at 4:1 used to produce a composite polymer with the best hydrophobic properties [13]. In additions, the prepared security ink were print into several types of commercial paper to determine the nature and the interaction of the C-dots/PVA/Chitosan composite with various type of papers.

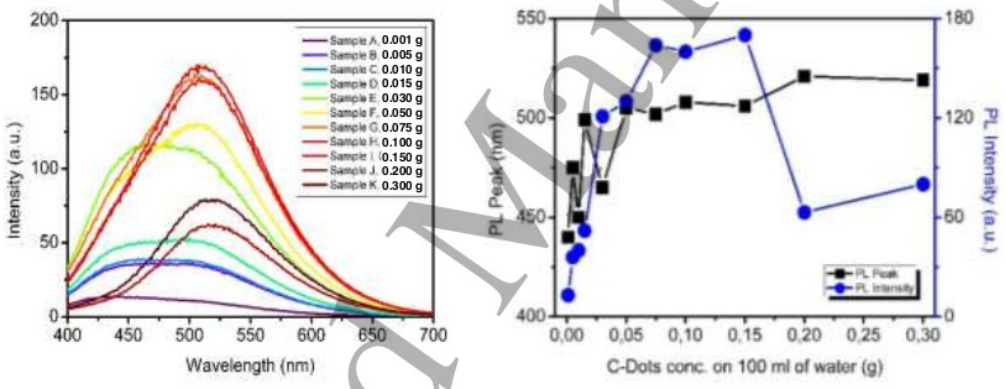
The photoluminescence (PL) spectra (Cary Eclipse Spectrofluorometer, Agilent, Australia), FT Infrared spectra (FTIR, Bruker Optics, Ettlingen – Germany), and scanning electron microscope (SEM, JEOL JCM-6000 Benchtop, Japan) were conducted to characterize the optical properties, chemical bonding and morphology of the prepared samples, respectively. The viscosity measurement to the optimized of C-dots/PVA/Chitosan-based security ink was conducted using rotational viscometer TV-20 Tokimec at room temperature.

Table 1. The various of PVA and chitosan mass concentration in 100 ml distilled water

Sample	PVA (g)	Chitosan (g)
Non Blend	0	0
Blend 1	0.4	0.1
Blend 2	0.8	0.2
Blend 3	1.6	0.4
Blend 4	2.8	0.7

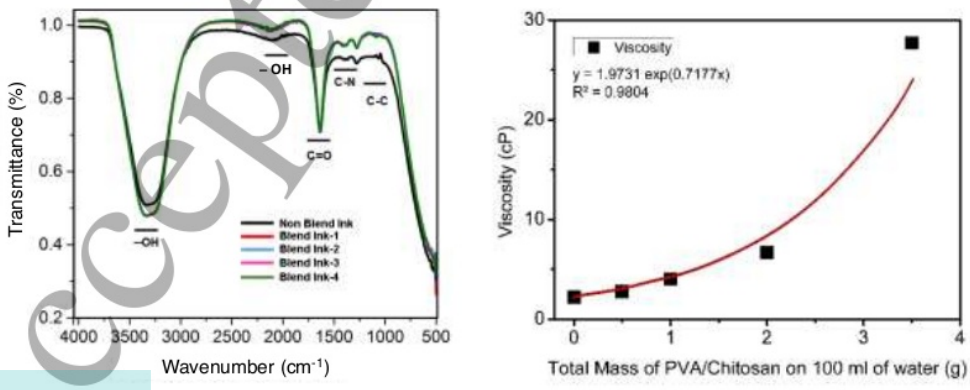
3. Results and Discussion

The C-dots solution was prepared by dispersing the synthesized carbon powder into pure water. **Figure 1(a)** shows the PL spectra of the C-dots solution for several of concentration from 0.01g to 0.3g into 20 mL of pure water. The PL spectra characterization shows that all prepared samples of C-dots solution has a blue luminescence with PL peak at 440 nm to 520 nm. Moreover, the blue luminescence properties of the prepared samples optimized by the increasing concentration of the C-dots solution shown in **Figure 1(b)**. At low concentrations, the C-dots solution has a wide range of PL emission peak and possibly have two PL peaks at 400 nm and 500 nm. The existence of two PL peaks caused by the interaction between C-dots and chitosan with excitation wavelength at 365 nm [13]. The PL properties showed that Sample-I with C-dots concentration at 0.75 %w/v has highest emission intensity. However, the PL intensity of the C-dots solution decreased for sample-J (1 %w/v) and sample-K (1.5 %w/v). The PL properties of the prepared samples shown that the electronic structure of C-dots particle unchanged, even the C-dots concentration was enlarged (see **Figure 1(b)**). However, the optimized the PL intensity of the C-dots solution caused by the photon-particle interactions probability between C-dots particle and excitation wavelength. The physical models for these phenomena are: (i) when low the C-dots particles number, thus the number of C-dots particles emission are lower as well. Then, (ii) when the number of C-dots particles increased, thus the number of C-dots emission photons would be higher as well. However, (iii) at the high amount of particles number, some emitted photons would be reabsorbed by the carbon particles and form a non-radiative recombination, where it causes the emission intensity has decreased (quenching effect recombination).



(a) (b)

Figure 1. (a) PL Spectra and (b) PL Properties of C-Dots solution for various of concentrations under UV light exposure at 365 nm.



(a) (b)

Figure 2. (a) The FTIR spectra of ink sample solutions and (b) The viscosity of C-dots/PVA/Chitosan composite as security ink.

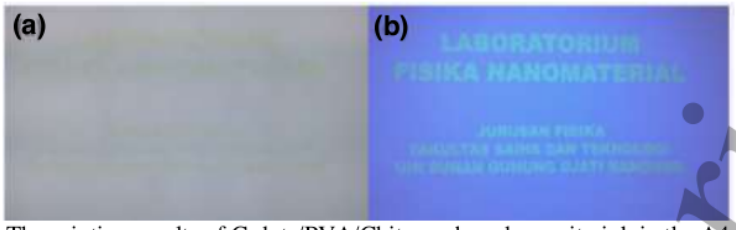


Figure 3. The printing results of C-dots/PVA/Chitosan-based security ink in the A4 commercial paper: (a) under visible light and (b) UV light exposure (365 nm).

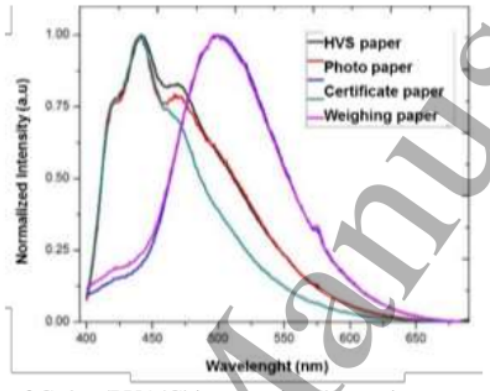


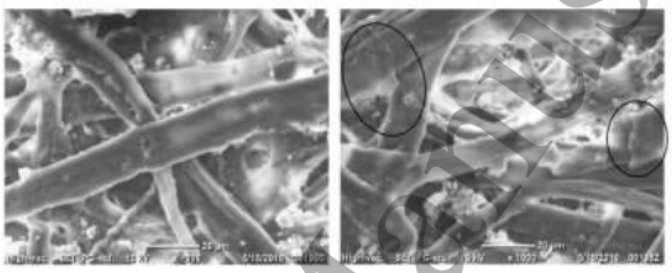
Figure 4. The PL spectra of C-dots/PVA/Chitosan printed at various types of paper under UV light exposure at 365nm.

To determine the existing functional groups (chemical bonding) of the security inks, the C-dots/PVA/Chitosan prepared samples were characterize using FTIR as shown in **Figure 2(a)**. The FTIR spectra results indicated several existing chemical bonds of C-dots, polymers and their interaction, such as C – C at 950-1030 cm^{-1} and C – N at 1400- 1420 cm^{-1}. In additions, the functional groups of ─OH (water combination band) appear at 3250-3420 cm^{-1} and 1655 cm^{-1}, this results shown the surface interaction between C-dots, polymers, and solvents [13]. This indicates that the C-dots particles have the capability to disperse in water, due to their dominant hydrophilic nature [14]. The chemical bond between PVA and Chitosan were expected to form a composite polymer with C-dots. Furthermore, when the prepared security ink was printed on a substrate such as paper, the PVA/Chitosan could be a thin layer of composite polymer with strong hydrophobicity. The hydrophobic nature of PVA/Chitosan composite were expected to prevent the re-dissolutions or the oxidation process of the C-dots particle. The viscosity of C-dots/PVA/chitosan composite measured for various of PVA/chitosan concentrations, shown in **Figure 2 (b)**. The viscosity results showed that the addition of PVA and Chitosan increases the viscosity of the security ink exponentially. The increasing viscosity of the C-dots/PVA/Chitosan composite might be caused by the increasing amount of PVA/Chitosan bonding crosslinks.

The solution of Ink Blend-1 was chosen as the security ink on the printing test using a commercial printer (HP Deskjet 1010). The printing stages consisted of: (i.) injection of the ink into an empty cartridge, (ii.) automatic printing on several papers, and (iv.) drying process at room temperature. **Figure 3** shows the printing result the security ink on an A4 paper sample. The initial observation proved that the security ink successfully printed on the paper and has blue emission under UV light exposure (365 nm). To understand the interaction between the security ink with the paper and its influence on the optical properties, the PL spectra were measured for various types of commercial papers. **Figure 4** shows the PL spectra of the manually printed of prepared security ink on various

types of commercial paper. In general, the PL spectra showed that the printed of security ink on various types of paper has blue emission with PL peak from 410 to 530 nm under UV light exposure (365 nm). However, the PL spectra showed that emission properties of printed results highly dependent on the security inks interaction with the commercial papers type. The PL properties shift was possible since a paper may contain material that can undergo a photoluminescence such as melamine and others. Therefore, a further study related to the interaction between the carbons nanoparticles based security inks with paper need to study closely.

Figure 5 shows a SEM image of uncoated and coated of A4 commercial paper by C-dots/ PVA/Chitosan composite based security ink using a commercial printer. The observation results showed that the uncoated and coated commercial paper had the same morphological characteristics. On deeper observation, the coated paper has a thin layer of polymer composite on the paper fibres. In addition, the porosity of the coated paper was lower, since the composite polymer filled in the pores. Therefore, it concludes that the C-dots/PVA/Chitosan based security ink could manual or automatic printed and the security ink composites strongly interacts with paper morphology.



(a) (b)

Figure 5. SEM images of (a) uncoated, and (b) coated of A4 commercial paper by C-dots/PVA/Chitosan composite based security ink materials.

4. Conclusions

Security ink based using carbon nanoparticles (C-dots)/PVA/Chitosan composite based materials has been successfully synthesize. The C-dots powder were prepared using urea pyrolysis method. The precursors were synthesized using urea ($(NH_2)_2CO$, Mw=60.07 g/mol) and citric acid ($C_6H_8O_7{\cdot}H_2O$, Mw= 210.14 g/mol) as fuel and carbon sources, respectively. The carbon nanoparticle (C-dots) was prepared by heated the precursor solution at 250 °C for 90 min. The security ink were fabricated using C-dots, polyvinyl alcohol (PVA, $(CH_2CH(OH))_n$, with Mw= ~20000 g/mol) and chitosan as the dyes, resins, and binders, respectively. The characterization showed that the C-dots has mono-disperse particle sizes, tetragonal structure and absorption spectra in UV light region. The viscosity properties show that the PVA:Chitosan concentration has significant effect and optimized the security ink viscosity. In additions, the security ink were study using a commercial printer, the printing results show a good quality and blue emission (450 nm) appeared under UV light exposure at 365 nm. The security ink based C-dots/PVA/Chitosan composite has potential insight for security application, panel display, optoelectronic and optical devices on an industrial scale.

5. Acknowledgment

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