



# Article Fluorescent Carbon Dots Ink for Gravure Printing

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**Abstract:** In the present article, we describe the use of highly fluorescent carbon dots (CDs) for the preparation of an effective water-based carbon dot ink (CD-ink) for gravure printing. Carbon dots were prepared hydrothermally from citrate and triethylenetetramine, and mixed properly with certain resins that are used in gravure inks. The as-produced CD gravure ink was used successfully for printing high quality fluorescent images.

Keywords: fluorescent inks; carbon dots; gravure inks

## 1. Introduction

Carbon dots (CDs) is a relatively new carbon nanomaterial that has been extensively studied the last decade, due to its unique characteristics and properties. Strong photoluminescence, easy and low-cost preparative methods, stability, biocompatibility, and low toxicity are the main characteristics and properties of CDs that have attracted a huge interest for their use in various potential applications, especially in bio sensing and imaging, as well as in light emitting devices, fluorescence probes, environmental engineering, and photocatalysis [1–7]. Among a plethora of different procedures that have been presented up to now, microwave or thermal pyrolysis, electrochemical oxidation, hydrothermal treatments, and laser ablation are the most common approaches to create CDs. As a precursor, a variety of organic compounds, from natural carbohydrates to specific chemicals, have been reported [1–3,5,8]. After the formation of carbon dots, a post purification step is often required, as it appears to significantly affect the fluorescence of final products [9,10].

Up to now, CDs, due to their excellent photoluminescence, high dispersibility in water, and non-toxicity, appear to be suitable candidates as fluorescent inks for printing applications [11,12]. Printing methods, in general, have a very high impact in the field of material science [11–16]. In the last few years, there has been tremendous interest about printing techniques and especially inks, as a new approach for large-scale, high-speed fabrication of printed electronics, in contrast with techniques already used (lithography, etc.). Carbon-based printing inks have already been studied extensively for the new era of printed electronics [13,14,17,18].

In this article, we present the use of CDs for the preparation of a fluorescent gravure ink. Highly dispersible in water CDs were easily mixed homogenously with water-based specific resins, and the final product was printed on several substrates (e.g., paper and plastic) or deposited on glass, with high homogeneity, and showed excellent photoluminescence, which remained after the evaporation of the solvent, in the solid printed material. Up to now, there are only a few reports in the literature that have used fluorescent inks for printing methods, most of them for anti-counterfeiting applications [19–26]. However, for the first time, CDs are used for the preparation of gravure printing ink. Gravure printing is one of the four predominant printing technologies used in the printing industry and is preferable for low-cost and high-speed mass productions of various products. It also has a wide range of applications,

such as floor coverings, newspapers, and flexible packaging, up to printed electronics [14,27]. A basic advantage of gravure printing is the excellent image quality and fine resolution that it offers, even for demanding printing jobs. Printing substrates used in gravure include polymers, glass, metal foils, and almost all types of papers. The gravure process requires low viscosity (0.05–0.20 Pa.s) and rapidly dried inks, formulated from soluble materials or nanoparticle dispersions [28]. Thus, the nanometer size of CDs is ideal for the development of gravure fluorescent inks, since the risk of cylinder cells clogging during printing is avoided. An additional advantage of CDs comes from the fact that it is feasible to be produced in large scale using simple synthetic methods and cheap precursors, favoring their use for low-cost and high-volume industrial applications where gravure is useful.

A brief description of the principle of the gravure method follows below. The printing unit includes an engraved cylinder, the ink fountain, a doctor blade, and an impression roller. The engraved cylinder is made up of recessed (engraved) cells that compose the desired printing image and fill with ink as the cylinder is immersed and rotated in the ink fountain. The excess ink is removed from the surfaces that do not have cells using the doctor blade. At the same time, when the substrate passes through the two cylinders (gravure and impression roller), due to the applied pressure, the ink is transferred to the substrate, forming the selected image.

#### 2. Materials and Methods

#### 2.1. Materials

Citric acid and triethylene tetramine (TETA) were purchased from Sigma-Aldrich Chemie GmbH, Germany. Water-based varnish NAB 056 L 0000 and corona-treated polyethylene terephthalate (PET) and polyethylene (PE) substrates were supplied from Druckfarben Hellas S.A, Aspropirgos, Attika, Greece. Optical brightening agent (OBA)-free coated paper was supplied from IGT Testing Systems, The Netherlands.

#### 2.2. Preparation of Gravure Ink

CDs were prepared by heating, in a teflon autoclave, a solution of 300 mg of citric acid and 200 mg of TETA in 7 mL of water at 150 °C for four hours. The reaction mixture was then purified by solid phase extraction using an alumina column, according to [9], and furthermore using dialysis membrane (3.5 kDa) for 24 h. One mL of the solution of CDs was mixed with 9 mL of the commercial water-based varnish NAB 056 L 0000 by stirring overnight. The commercial varnish contains a mixture of styrene-acrylic-emulsion, acrylic resins, and emulsion of polyethylene wax (solid content 58%). The percentage of the solids in the final suspension was about 1.4% w/w in the CDs.

#### 2.3. Gravure Printing

The fluorescent ink was printed onto an OBA-free coated paper (150 g/m<sup>2</sup>) obtained from IGT Testing Systems (404.012.030, CT 2846, black band, ISO 2846) that is used throughout the graphic industry as a standard paper and on various commercial craft papers. Additionally, corona-treated PET (12  $\mu$ m, 56 dynes cm<sup>-1</sup>) and PE (30  $\mu$ m, 50 dynes cm<sup>-1</sup>) substrates, available from Druckfarben Hellas S. A., were used.

## 2.4. Instrumentation

Optical absorption (OA) spectra in the UV-Vis spectral region were recorded on a Shimadzu 1650 spectrophotometer in the range 200–800 nm, at a sampling step of 0.5 nm with 1.5 nm slits, using a combination of halogen and deuterium lamps as sources. Photoluminescence (PL) spectra were obtained from solutions in quartz cuvettes, mounted in a Hitachi F-2500 FL spectrophotometer, employing a xenon 150 W lamp and a R928 photomultiplier. The excitation and detection slits were set at 2.5 nm and the accelerating voltage was set to 700 V. Microscopic analysis of the samples was performed using transmission electron microscopy (TEM) (JEOL-JEM 2100).

Printing tests were done using the IGT G1-5 printability tester with a raster patterned printing cylinder named by IGT as 402.153 (70 lines/cm, screen angle 53, stylus angle 140, and cell depth 33; 31; 30; 29; 26; 24; 20; 17; 14; 11  $\mu$ m). The printing force between the engraved disc and the substrate was selected between 100–1000 N and the printing speed was tested in the region 0.2–1.0 m/s.

Printing tests were done also using the IGT F1 printability tester with a ceramic, laser-engraved cylinder, with 4 different engravings. The printing force between the engraved disc and the substrate was selected between 10 and 500 N, and the printing speed was tested in the region 0.2–1.5 m/s. Before printing, the ink was applied with a pipette in front of a doctor blade and then transferred to the substrate.

#### 2.5. Adhesion of Ink on Polymeric Substrates

The adhesion of ink on the polymeric printed samples was evaluated according to the ASTMD3359 standard method [ASTM-D3359-09e2, Standard Test Methods for Measuring Adhesion by Tape Test, ASTM International, USA, 2009].

The printed samples were dried at 75  $^{\circ}$ C for 15 min. Then, a scotch tape (3M, width of 1.5 cm) was applied, pressed and removed. The evaluation of adhesion is indicated by the percentage of residual area of ink on film.

### 3. Results and Discussion

CDs were prepared by the hydrothermal heating of a mixture of citric acid and triethylenetetramine ( $CD_{CA-TETA}$ ) in water and purified by solid phase extraction using an alumina column [9]. The product was further purified by dialysis membrane for the removal of small molecular by-products. The as-prepared CDs exhibited intense blue fluorescence under UV-radiation (see Figure 1). TETA and citrate have been used previously for the preparation of CDs using microwaves [29,30].



**Figure 1.** Synthetic procedure of CD<sub>CA-TETA</sub>. Photos with dispersion of purified CDs in water under sunlight and UV lamp.

The as-prepared CDs had a mean diameter of 2–2.5 nm with a very narrow size distribution, as revealed by the characteristic transmission electron microscopy (TEM) image in Figure 2. In Figure 3, the UV-Vis absorption and photoluminescence spectra also appeared. The CD<sub>CA-TETA</sub> had an absorption maximum at 340 nm and a luminescence maximum at 451 nm after irradiation at  $\lambda_{max}$  (340 nm). The emission band was slightly shifted, from 448 to 458 nm, as excitation tuned from 330 to 390 nm, respectively. As a consequence, an intense blue light was emitted under UV light (Figure 1, inset).



Figure 2. TEM image of CD<sub>CA-TETA</sub>.



Figure 3. UV-Vis (a) and PL (b) spectra of CD<sub>CA-TETA</sub> dispersed in water.

The water solution of CD<sub>CA-TETA</sub> was then mixed with a common industrial acrylic resin suitable for gravure printing in several ratios. The as-prepared inks showed stable photoluminescence (PL) properties under the proper conditions. Because of their nanometer size (2–2.5 nm), CDs were formulated very easily into the low-viscosity gravure ink, giving an ideal dispersion in the solvent system and avoiding the settlement in the ink bottle for long periods of time (months). CD-ink was finally printed on various coated paper and polymeric substrates (polyethylene terephthalate, PET, polyethylene, PE) using gravure printability testers. The high-quality printed matters showed intense photoluminescence that remained, without obvious reduction, after at least two weeks (see Figure 4). The stability of the printed structures on paper, PET, and PE substrates were tested according to the standard ISO 2836/2004 [31]. In brief, a part of the printed surface was placed between two filter paper sheets soaked into different liquids, such as water, diluted alkali (1% NaOH in water), and alcohol (96% ethanol), and kept under pressure for 24 h or 10 min (the alkali exposure). All tests showed no obvious decrease of the luminescence of the printed samples. Furthermore, as shown in [Figure 5], luminescence intensity of the printed matters was directly proportional to the thickness of the ink layer.



**Figure 4.** Photos of paper (**a**,**b**) and polymeric (**c**,**d**) substrates, printed with fluorescent CDs ink, under visible (**a**,**c**) and UV (365 nm) (**b**,**d**) light.



**Figure 5.** (Upper) Schematic representation of gravure printing technique. (Lower) Paper substrate printed with fluorescent CDs ink, under UV (365nm) light, showing gradient luminescence in accordance to layer thickness.

In addition, CD-ink showed excellent ink adhesion to substrates (99% according to ASTM D3359 test method), a critical parameter in packaging applications. It should be noted that polymer substrates generally have low-energy surfaces, causing adhesion problems, due to the higher surface tension of water-based inks. This means that in the as-prepared CD-ink, basic parameters, such as ink viscosity, substrate surface energy, ink surface tension, interaction of ink-corona treated substrate, printing speed, and pressure, were perfectly combined.

### 4. Conclusions

In conclusion, in this work we showed that blue-emitting CDs were used successfully for the preparation of fluorescent inks suitable in gravure printing. CD-ink was printed on paper and polymer film showing intense and stable, luminescence, proportional to the thickness of the ink layer. The printed structures also showed stability in various liquids tested, according to the related ISO, and excellent ink adhesion to substrates.

**Author Contributions:** A.K. prepared the products and performed the characterization. V.B. performed the gravure printing and was responsible for the preparation of the ink. V.G. supervised the work and wrote the manuscript. All co-authors provided advice and helped write the manuscript.

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