Study of the Behavior of Cadmium-free Quantum Dots In Functional Inks

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Keywords: quantum dots, dots, nano, particles

Abstract

The following article is extracted from Laura Biscaldi's Master'sproject. After three year of engineering curriculum, students are required to perform a six-month individual project in a company or laboratory. During this project, they are expected to use the knowledge and skills they acquired during their studies at Pagora. Laura Biscaldi carried out her final year project in the LGP2 research laboratory (Laboratory of Pulp and Paper Science and Graphic Arts). She especially worked on the behavior of quantum dots (cadmium deprived) in functional inks.

The topic of this paper deals with Quantum dots and their behavior when introduced in printing inks. Quantum dots are nano-sized particles that have optical properties linked to their size, among which photoluminescence. For some years, quantum dots have been the subject of intensive research, because of their very interesting properties, as well as their various applications (such as lightning, healthcare, or photovoltaic energy). Introducing nano-particles in inks enables us to consider applications in the anti-counterfeiting area.

This project was realized in parternship with Damier Boyer, and Rodolphe Valleix, respectively researcher and PhD student at the Clermont-Ferrand Institute of chemistry, who synthesized quantum dots suspension in Isopropanol samples. Their particularity is that they are Cadmium deprived, which is important since cadmium is a heavy metal that can have harmful consequences.

The initial method consists in preparing ink formulation for different printing processes: inkjet, flexography and screen printing. Inkjet is considered in first place since it is the most common process used in research publications dealing with this topic. The first step of the experimental plan was to determine the optimal concentration of Quantum dots in inks as well as the optimal thickness of the ink

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film for each process in order to obtain the most intense fluorescence. Several substrates were used in order to identify different potential applications: special paper for anti-counterfeiting and polymers for intelligent signing and packaging.

In this article, only the first part of this project will be presented, i.e. the state of the art, which will enable us to understand theoretical aspects of quantum dots, notably how they work.

1. State of the Art

The addition of functional material such as active pigments in ink formulation has received a growing interest in recent years. This approach takes advantage of well-established printing processes used to create functional devices. (1) Some colloidal nanoparticles present very interesting properties such as conductivity or electroluminescence. However, the use of such particles to create functional devices remains a developing challenge. (2) Fluorescent nanoparticles were recently synthesized. In this article, their properties will be described as well as their possible applications and how they can be introduced in printing inks.

The studied nano-sized particles will be called « Quantum Dots » (QD) in this paper. They notably present interesting photoluminescence properties.

1.1 Photoluminescence

1.1.1. Definiton

Luminescence is a term introduced by Wiedmann in 1888 to design luminous phenomena which do not result from a raise in temperature. After having absorbed energy, a molecule elapses in an excited state, then retrocedes this energy as a radiation when going back to its fundamental state.

Luminescence depends on the chemical nature of the substance. Different types of luminescence are distinguished according to the initial excitation mode. When excitation is triggered by photons absorption, it is called photoluminescence (PL). PL can be either fluorescence or phosphorescence.

In the fluorescence phenomenon, the excited species go back very rapidly to their initial state of energy (from 10 psec to 100 nsec).

In phosphorescence, the excited species transit in an intermediate energy state called « triplet state » (Figure 1), where they stay during a certain amount of time before regaining their initial state (from µs to hours) (figure 1)(3).

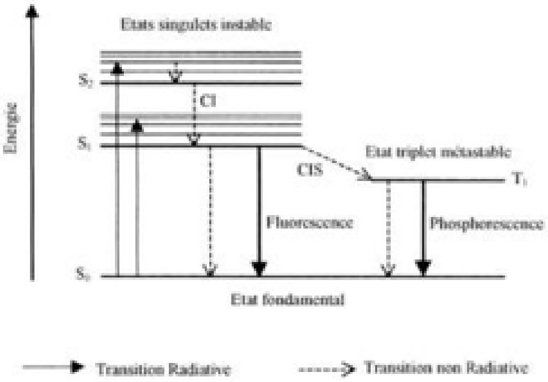


***Figure 1.** Perrin-Jablonski diagram describing the process of excitation and deactivation*

1.1.2 Measurement methods

A Fluorescent species can be characterized by its fluorescence emission spectrum which represents the wavelength distribution of emitted photons according to their absorption spectrum. Fluorescence can be characterized by several values :

- the fluorescence intensity depending on the excitation wavelength
- the excited state lifetime, which gives the characteristic time during which the molecule stays at the excited state before going back to its fundamental state (expressed in nanoseconds) (4).
- the fluorescence quantum yield specifying emission performance. It is defined as the ratio of the number of emitted photons on the number of photons absorbed by the sample. (5)

The measuring devices of fluorescence are called fluorometers. Fluorometry uses UV-visible radiation of the electromagnetic spectrum in order to study transitions between electronic levels in a molecule or an atom. (6)

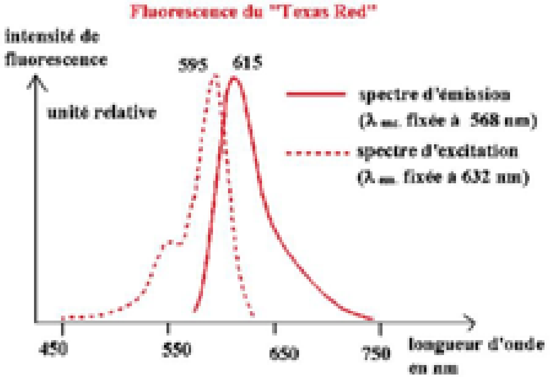


***Figure 2.** Fluorescence spectrum of Red Texas, fluorescent colorant used in Histology*

1.2 Quantum Dots

1.2.1. Definition

Quantum dots were discovered in 1981 by the Russian physician Alexey I. Ekimov (7). QD are semiconductor nanocrystals with a diameter generally between 2 and 10 nm. Their optical properties are linked to their size, as for photoluminescence. A quantum dot is excited by an incident light at a very specific frequency depending on its properties. A size, form or composition modification of these nanocrystals will change their emitting wavelength extending from 450 nm to 1500 nm (figure 3). The smaller the QD, the smaller the wavelength it emits : this phenomenon is called quantum containment (5).

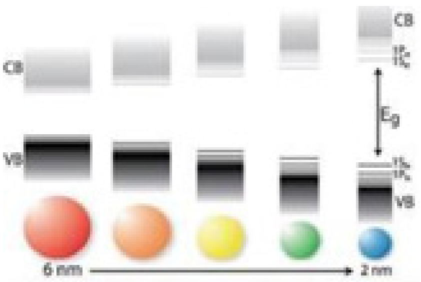


Figure 3. *Gap evolution between QD of decreasing sizes. Source : Chem. Soc. Rev., 2011*

Most of research carried out on quantum dots uses QD containing Cadmium (CdSe, CdTe, CdS). They are easy to synthesize and use precursors that are easy to obtain. However, studies show that QD containing cadmium may degrade and release Cd2+ cations, which are very toxic. One of the approaches to overcome this issue is to synthesize QD without cadmium, which have comparable properties . A possible alternative to replace cadmium is to use indium phosphore to create QD.(8)

QDs are semiconductors. In order to understand the notions of semi-conduction and electrical conductivity, it is necessary to study electronic band structure theory which is a quantic model in the physics of solids.

1.2.2 Electronic band structure theory

A semiconductor is a material presenting insulating characteristics but having a high probability that an electron may contribute to an electric current (9). Semiconductors' electrical behavior may be designed with electronic band structure theory (figure 4). In solid conductors, the valence band et conduction band are overlapped, electrons move vacantly. Whereas in semiconductors, the two bands are separated by a forbidden band called « gap ». This gap's width is still smaller than it is in an insulator (1,6 eV for CdSe and 1,3 eV for InP) (10). If energy is brought to the electrons (heat, light, magnetic field or electrical field), the latter can elapse from the valence band to the conduction band.

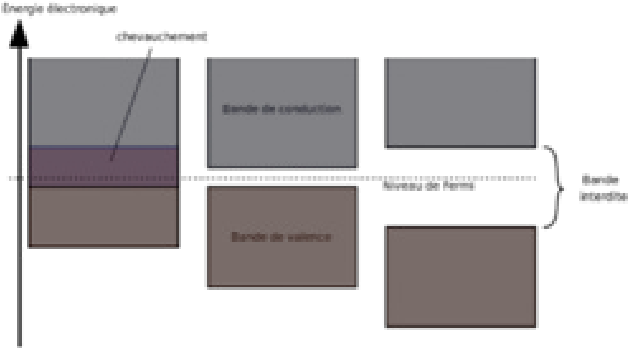


Figure 4. Band structure in a metal, a semi-conductor and an insulator.

1.2.3. QD structure

QD have a heart-shell structure composed of a semiconductor material surrounded by one or several envelopes with different compositions (Figure 5). It allows to minimize defects on the surface by reducing interactions between the exciton (electron-hole pair) and the external surface of the nano- crystal. This shell protects and reinforces photo-physical properties of the heart it encloses. Moreover, different relations between levels of energy in the heart and in the shell enable to control the wavelength, while it is not possible with a QD containing only one component. In general, heart-shell QD can be categorized by conduction band between elements. QDs of type I (InP/ZnS ; CdSe/ZnS) and type II (CdTe/CdSe) are most commonly used. In type I, the conduction band of the shell has a higher energy than the heart's energy whereas, the valence band of the shell has a lower energy. Thus, holes and electrons are confined in the heart. Zinc sulphide (ZnS) is the most commonly used material in type I of heart-shell QD. It has a strong chemical stability, extending the lifetimz of the shell. It is possible to link carbon chained molecules called « ligand », enablingQDs to bond with certain sites. The Ligand allows to stabilize the particles and inhibit aggregation.

In type II QDs , both valence and conduction bands have the highest energy in a material than in a - other one. One of the transporters (hole or electron) is confined in the heart while the other one is confined in the shell. This spatial division gives different properties in comparison with type I QDs.

Figure 5. Schematic structure of a fluorescent semiconductor colloidal heart-shell nano-crystal.

1.2.4. Synthesis

Only QD InP/Zn syntheses will be discussed since they will be used in this project.

Indium phosphide InP is a semiconductor from the category III-V. InP bare nanocrystals present a very low quantum yield (inferior to 1%). It is principally due to surface defects. Moreover, these nano- crystals are very sensitive to oxidation in the presence of water and oxygen. In order to enhance their optical properties and stability, a shell composed of another semiconductor is synthesized. This way, it is possible to strongly improve the quantum yield (up to 70-85%).(11)

QDs can be prepared as dispersions in an organic or aqueous phase. To suspend hydrophobic QDs, techniques such as exchange of ligands or encapsulation of QDs with hydrophilic or amphiphilic molecules wre used. The high specific surface of QDs provides numerous bonding sites which allow multiple bonds via several target fragments (8).

InP/Zn QDs can be obtained by a reaction of a complex (InCl3 and tris (triméthylsilyl) phosphine) in octadecene (ODE), in presence of zinc undecylenate. Zinc carboxylates have an important influence on surface defects and the size distribution of the resulting nanoparticles. An appropriate amount of

zinc carboxylate improves the photoluminescence quantum yield of InP nanocrystals. The size of the nanocrystal can be controlled by adjusting the initial concentration of zinc carboxylate. (12) As a rule, liquid-phase semiconductor nanocrystals can be synthesized :

- at room temperature by precipitating the nano-crystals in an aqueous environment, either in the presence of stabilizers or in reverse micelles;
- at high temperature in non-aqueous media, based on the separation in time of the nucleationand growth stages of the nano-crystals. In this case, organometallic precursors or complexes of inorganic precursors are used. (5) The synthesis of QDs makes it possible to give these nanoparticles specific properties, from which a variety of applications can be derived.

1.2.5 Applications

QDs are now used in devices containing display screens. This is because they can reproduce a much wider range of colors than a conventional LCD screen with 30% more saturated colors than the average. (13) It is estimated that the screen of a high definition television set can reproduce 35% of the color shades distinguishable to the eye, whereas screens containing QDs reach 55% of theses color shades. In displays, QDs are used to produce optimized white light in the backlight. A blue primary LED light excites two kinds of QDs which absorb this blue to emit green and red at a very specific wavelength. The white light which is then produced

(B+G+R) allows the filter system of the display to produce a maximal number of color shades.

Figure 6. *Comparison of a screen containing QDs (on the left) and without (on the right). Source: American Chemical Society, 2014*

QDs also hold great promises in medicine. Thanks to their powerful and stable fluorescence properties, they can be good biomarkers. QDs can be used for so-called "in vitro" diagnosis, which consists in detecting, quantifying and locating biological molecules on a sample. In this context, QDs are not injected into the human body, so that toxic metals such as cadmium can be used. These nanoparticles can also be used for "in vivo" diagnosis which, thanks to imaging techniques, allow real- time visualisation of tissues carrying a pathological molecule.

QDs could have a future in the photovoltaic sector by allowing better performance at lower cost. QD- based solar cells would replace more bulky materials such as silicone. US researchers at the National Renewable Energy Laboratory (NREL) have shown that nanotechnology can greatly increase the

amount of electricity produced by solar cells because QDs have a higher efficiency. Existing solar cells have a conversion efficiency of 33% on average, while the efficiency based on QDs is estimated at 65%. QD-based cells have a low energy consumption and allow versatile use (can be used on windows as well as roofs). However, cadmium cannot be used because of its cytotoxicity. A lot of work remains to be done before these cells can be marketed. (14)

1.3 QDs Printing : ink formulation requirement

The aim of this project is to manufacture inks based on QD InP/ZnS suspensions that can be printed using three processes : inkjet, screen printing and flexography. These printing techniques have very different characteristics and applications : ink formulations are therefore specific to each process.

1.3.1 Ink formulation

Generally, three categories of components compose an ink :

- Pigments or soluble colorants : pigments and colorant confer to inks their optical properties.
- The ink vehicle : the vehicle is composed of a mixture of polymers (resins) which act as binders and solvents. The vehicle enables the pigment to be transported and fixed to the substrate. It also allows pigment protection by forming a continuous film. It largely determines the rheological behavior of the ink.
- Additives : these components enable to optimize some ink properties at liquid or solid state.(20)

1.3.2 Screen printing inks

Screen printing is the printing process that allows the highest ink film thickness : between 10 and 100µm , which can be critical during drying. In screen printing, the preferred drying methods are solvent evaporation or photopolymerization. The viscosity of the inks varies between 1 and 100 Pa.s. (9) In addition, the inks must not contain highly volatile solvents and must have a non-negligible threshold flow constraint so that ink transfer can be controlled. For good print quality, screen printing inks must have specific rheological properties. In particular, the ink must have a rheofluidifying behavior in order to pass through the screen when the squeegee is scraping.

1.3.3 Flexographic inks

The inks used in flexography have a viscosity range between 50 and 500 mPa.s (9) and must be able to dry very quickly (spontaneous or forced evaporation of the solvent). Most of the inks are water- based, as they are better adapted to environmental and health standards. The printer adapts the viscosity of the ink by diluting it (20). Viscosity and surface tension can be modified by using different amounts of organic solvents and surfactants. For example, water or polyvinyl alcohol can be used to adjust the viscosity.

1.3.4 Study of the impact of the addition of polymeric resins on ink fluorescence

QDs suspension study

Many articles deal with the synthesis of QDs - polymer composites. Indeed, practical applications of QDs require nanoparticles to be stabilized in an appropriate matrix with conservation of their photoluminescence efficiency, without agglomeration.

A 2015 publication (24) describes the effects of different polymer matrices and the influence of K+ and Na+ ions on the fluorescence properties of QDs CdTe. Cations had no impact on the fluorescence intensity but, in high concentrations, they decrease the lifetime of QDs. Three commonly used polymer matrices, PEO (polyethylene oxide), PVA (polyvinyl alcohol) and epoxy resin, were used to study the effects of the polymer on QD lifetime and quantum yield. These matrices had a significant impact on these properties, probably due to the interaction between the surface ligand MPA (mercaptopropionic acid) of the QDs and the polymer molecule, which modified the surface of the QDs and thus increased the surface defects.

At 550 nm, the QD lifetime is 24.47 ns. In PEO and PVA, it is 17.33 and 17.12 ns, respectively. For epoxy resin, it drops to 0.74 ns. The quantum efficiency for 550 nm QDs has dropped from 34.22% to 7.45% and 7.81% in PEO and PVA, respectively. For the epoxy resin it is 2.25%.

Another study (25) describes the synthesis of composites (see Figure 8) using a polyurethane prepolymer (WPU). According to these researchers, quantum yield values are improved in composite films compared to aqueous suspensions of QDs. This also demonstrates that the WPU could further passivate the surface of CdTe QDs. Moreover, after irradiating the composites with UV light for more than a week, no significant decrease in photoluminescence intensity is observed, suggesting that the incorporation of CdTe QDs in the WPU matrix could protect them from photochemical oxidation.

Figure 8. *Image of composite films excited by a UV lamp at 363 nm (25)*

Fluorescent dye-based ink study

Two studies compared the effects of the resin in a conventional fluorescent dye ink composition. They agree that the impact of the resin on fluorescence depends mainly on the functional groups of the resin: -OH is a bathochrome effect group, fluorescence shifts to higher wavelengths. -CH (O) CH- is a chromophore; this group causes the light intensity of the fluorescence to increase. The -COOH group, present in the structure of acrylic resin, decreases the generation of fluorescence.

The first study compared different types of resin: an acrylic resin, a polyurethane resin and an epoxy resin. The wavelength of fluorescent emission is not influenced by the type of resin, but they all result in an increase in the emission intensity of the fluorescent ink. In both studies, the fluorescent emission intensity of the ink prepared by the epoxy reaches its maximum.

Although the surface tension of the three types of resin is almost identical, the surface tension of the ink prepared with these resins is different. It is situated between 27 mN/m and 30 mN/m, corresponding to inkjet basic requirements.

The viscosity of the ink depends mainly on the resins used. It can be controlled by selecting the type and amount of resin used. The order of viscosity, from largest to smallest, of three types of resin is: Polyurethane > Epoxy > Acrylic.

Ink adhesion depends on the interactions between the resin and the substrate. All five ink samples have high adhesion to the paper surface after drying. (31) (32)

In this project, we are mainly interested in the inkjet process. The aim is to study three different ink vehicles for this process. These three types of inks are detailed in the following paragraph.

1.4 Different types of ink for inkjet process

There are four types of ink for inkjet printing: water-based inks, solvent-based inks, UV inks and hot melt inks. For the high speed and industrial printing markets, aqueous and UV inks are the most commonly used. (33) Depending on the type of ink, the formulation may contain more or less volatile compounds. Many of the key performances are based on the way the solvent evaporates. In both water-based and solvent-based inks, the liquid vehicle of the ink is evaporated. In solid inks, there is no evaporation of solvent. UV and hotmelt inks change from liquid to solid state much faster, reducing some printing defects. And because both inks do not lose any volume, they can produce thicker ink films. (34) (35)

1.4.1 Aqueous inks

Water is a preferred solvent to counter environmental problems and health hazards. Water-based inks are also cheaper. However, water can also be a source of inconvenience when paper is used as a substrate. This can lead to numerous printing defects.

The aqueous environment does not allow for a wide variety of formulations because the solvent power of water is limited and the evaporation rate of water is too slow to take advantage of the high-speed printing possibilities that inkjet allows. (36) In addition, water-based inks have poor adhesion to non- porous substrates because water has no solvent power for non-porous materials such as PVC and other plastics. Organic solvents have better solvent power: this means that organic solvent-based inks offer better adhesion performance on these substrates than water-based inks. It is therefore possible to use organic solvents and co-solvents to partially or completely replace water in the ink formulation. (37) (38) The viscosity of water-based inks is low (about 10 mPa.s).

1.4.2 Solvent based inks

For this type of inks, the solvent evaporates after printing. The volatile solvents most often used in this case are low molecular weight alcohols, ketones or esters. Less volatile solvents with a drying retarding function are usually ketones, such as cyclohexanone, glycol ethers, ethers, acetals, glycols, lactones. (36)

In order for the printhead to work reliably, the resin must be able to be dissolved in the ink. If the resin is no longer soluble in the ink when it is dried, there is a high risk that the nozzles become clogged. For this reason, one generally uses polymer systems that cure by solvent evaporation and not by reactive cross-linking. The polymers used usually have a molecular weight of less than 50,000. They may be vinyl chloride or vinyl acetate copolymers, acrylic resins, polyketone resins and polyester resins. (39) (37) (36) Other resins can be used such as amino resin, phenolic epoxy resin as well as all cellulose derivatives (cellulose diacetate, nitro-cellulose, methyl cellulose, benzyl cellulose, etc.). These resins can be used in combination.

For this type of ink, the resin is present in the formulation preferably in an amount of 1 to 10% by weight. If the amount of resin is less than 1% by weight, adhesion to the substrate may become insufficient, while if the amount is more than 20% by weight, this can significantly increase the viscosity of the ink composition, leading to defects in the jettability performance of the ink. (40)

Solvent	Glycol ether 10% Hydroxyketone 10% Alkyl lactate 40% Acetoacetate 22%
Pigment	3,5 %
Diluent agent	Methanol, ethanol, or 2-propanol : 10%
Surfactant	Polyacrylate : 0.05%
Resin	Vinyl chloride/vinyl acetate copolymer : 4%

Table 1. *Solvent based ink formulation example*

In a patent concerning the synthesis of a fluorescent ink (36), the amount of polyamide resin is adjusted to regulate the viscosity while maintaining the effect of stable fluorescence. However, other European patents prefer polyurethane resins, polyvinylpyrrolidone or ethylcellulose.

1.4.3 UV inks

UV inks are nowadays used in many printing techniques thanks to their numerous advantages :

- Printing is possible on a wide variety of substrates.
- The ink is dried directly by UV exposure.
- The cross-linked ink forms a polymeric layer with good adhesion to the substrate and a good resistance to physical or chemical aggression.
- These inks contain few or no volatile organic chemicals or pollutants.
- Dangerous atmospheric conditions.
- Energy consumption is lower compared to that of of hot air dryers.

The current limitations concern edible and food contact applications. Disadvantages mainly include the cost of materials and the requirements of UV curing equipment. (35) Inks should be stored at temperatures between 5 and 25°C. (41)

The ink liquid is transformed into a polymerized solid after a short period of exposure to UV light. The curing process starts instantly thanks to the combination of 2 major components of the ink : the polymerizable compound (organic molecules) and the photoinitiators. UV inks contain monomers and oligomers (usually acrylate derivatives), functional materials (pigments or dyes dispersed in the vehicle), photoinitiators and various additives, which facilitate the photopolymerisation process. Polymerisation can be radical or cationic. UV inks for inkjet have a viscosity between 10 and 30 mPa.s.

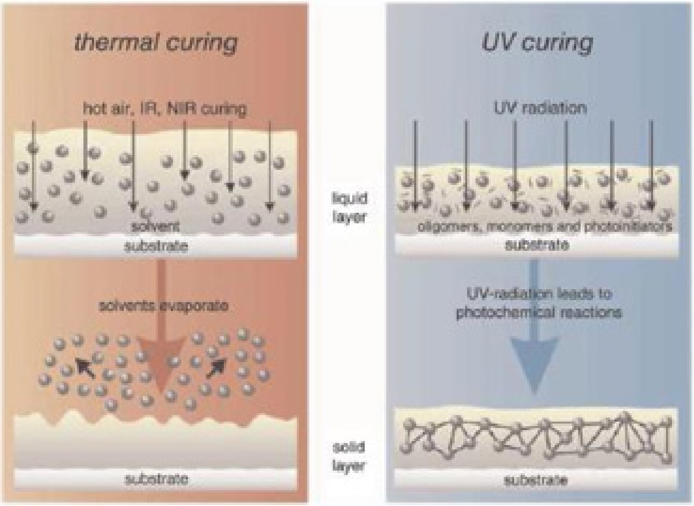


Figure 7. *Drying processes for solvent ink and UV ink.(Hönle AG.)*

The low viscosity required in the inkjet process limits the amount of high molecular weight compounds. The monomer plays an important role as it determines many aspects of ink performance.

The ink can be made using monomer mixtures to control viscosity. The monomers contain one or more unsaturated groups, allowing polymerization. The chemical nature of the unsaturations is variable, but acrylate groups are preferred as they are highly reactive.

The ink formulation can be improved by adding other types of monomers to the acrylate monomers, e.g. monomers containing vinyl groups (such as vinyl ether). Oligomers can also be added but their quantity is limited as they can cause ink jettability problems (increased ink viscosity). Commonly used oligomers contain acrylates, such as epoxy acrylates, urethane acrylates, polyesters and polyether acrylates. Table 2 summarises the compounds present in a UV ink formulation.

Components	Characteristics
Monomers	Monomers with low viscosity Mixture of monomers (most commonly used acrylates)
Oligomers	Limited quantity due to increased viscosity Improves adhesion to the substrate
Photoiniators	Present in mixture
Pigments	Coloring source
Polymeric dispersants	Polymers that disperse the pigments in the monomer to prevent pigment aggregation and increase ink stability.
Surfactants	Checking the ink wetting on the substrate surface Important for droplet formation in the nozzles
Adhesion additives	Additives to improve adhesion to specific substrates
Others additives	For specific purposes : anti-foaming agents, biocides...

Table 2. *Components present in UV ink formulation*

In a 2020 publication, a QD-UV ink is formulated with a solution of ethoxylated bisphenol A diacrylate resin mixed with PGMEA and an Irgacure Oxo-02 photoinitiator. (42)

In another publication (43), an epoxy-based ink was formulated and the amount of epoxy oligomer adjusts the viscosity. For the authors, an ink based on low molecular weight components such as epoxies exhibits stable behavior under a wide range of printing conditions.

The formulation of the inks plays a crucial role in print quality, but the substrate is just as important. In the following section, we will look at the properties of the printing substrate and its interactions with the ink.

1.5 Ink-subtrate interactions

1.5.1 Wettability

Wetting is here defined as the behavior of a liquid in contact with a solid surface, such as a drop of ink that comes into contact with the substrate. The quality of wetting is the degree to which the liquid is released from the solid.

Wetting is related to the surface energy of the solid. The contact angle is used to quantify the quality of the wetting liquid (see Figure 11). Contact angles from 0° to 90° represent good wetting, while 90° to 180° represent non-wetting. A contact angle of 90° represents partial wetting. (44)

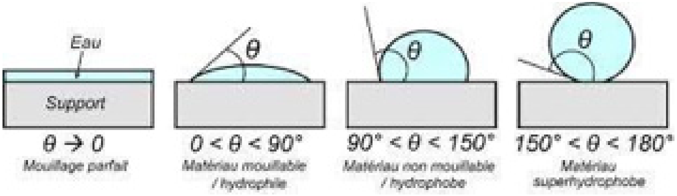


Figure 8. *Scheme describing different contact angle*

1.5.2 Inkjet

The substrate plays an important role in non-impact printing processes such as inkjet. The quality of the print is influenced by the porosity and surface condition of the substrate. The substrate surface is characterized by parameters such as roughness and surface energy. Generally, reducing surface roughness increases print quality.

Most inkjet inks have low viscosity and low surface tension, so the print quality is highly dependent on the surface properties of the paper. The print quality is strongly dependent on the absorption characteristics of the substrate. Other paper properties such as roughness, gloss, surface wettability and whiteness influence dot reproduction in inkjet printed images. (45)

1.5.3 Flexography

The application of aqueous flexographic inks to low energy surfaces can cause wetting problems due to the higher surface tension of the inks. To overcome this problem, pre-treatment, such as corona discharge treatment, is necessary. This treatment increases the polar characteristics of the surface by introducing new oxidized functions on the substrate surface.

According to a Swedish study (46) on flexographic inks, the level of corona treatment improves ink adhesion to the polymer substrate, but its effect is smaller than the effect of ink formulation (type of emulsion polymer and addition of silicone additive).

1.5.4 Screen printing

Stancic et al (48) compared 2 substrates, a matte coated paper and a PVC, as well as the influence of the number of threads on the quality of screen printing. The substrate has an influence on the roundness of the dots; more regular circular dots are obtained by printing on the PVC substrate.

By increasing the number of threads per cm of the screen, the non-uniformity of the print is more visible for PVC prints and varies non-linearly for the paper substrate. According to this study, using a

higher number of screen threads for a non-absorbent substrate does not significantly alter the reproduction of the image elements. The only exception is in solid color areas, where a higher number of screen threads results in lower uniformity.

1.6 Existing publications about QD printing

The vast majority of existing work on QD-based inks deals with the printing of QLEDs or photoconductors in inkjet and only using cadmium-based QDs. There are no publications dealing with QD printing in flexography.

One of the constraints to be mastered in inkjet is the halo phenomenon or "coffee ring effect" (49) (50) (51). The coffee ring effect is the result of the fluxes that occur inside the drop during the drying phase. The particles move from the center of the drop to the edges, resulting in an accumulation of material on the periphery of the printed pattern (21).

This effect can be limited in various ways: either by adding a solvent with a high boiling point, by heating the substrate, or by changing the surface state of the substrate via plasma treatment (to make the surface more hydrophobic). A volatile vehicle (such as toluene) should be avoided because it will accentuate the coffee ring effect. (52)

The solvent used in the ink formulation must have a high boiling temperature, enough so that it does not evaporate too quickly on the nozzles and thus limits particle accumulation. In addition, viscosity, surface tension and density must be compatible with the process (18). The QD must constitute between 1 and 7% by weight (53) and the surfactant 0.1% by weight of the total ink composition. Surfactant plays an important role in inkjet because it provides good surface tension to ensure good ink ejection through the nozzles and better penetration of the substrate.

Inks formulated for QD inkjet can be UV inks (29) or solvent inks (54) (50) (55) (56). QDs are preferably diluted in solvents such as water, glycols, acetates or alcohols.

Few different paper substrates are used in publications. One publication claims to obtain a result on standard printing paper with aqueous QD ink. However, a fading of the printed pattern after several days is observed (see Figure 13). (57)

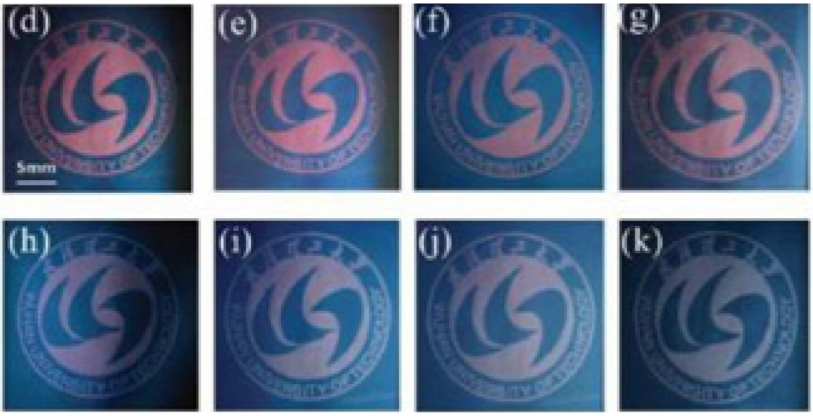


Figure 9. *Printed pattern on inkjet substrate viewed under UV light (365 nm) after 10 days (d), 20 days (f), 30 days (g), 40 days (h), 60 days (j), and 70 days (k). (57)*

Another work also uses a water-based QD ink, but the researchers only get a result on an inkjet photo substrate. (58) According to these researchers, the optimal parameters are to print two layers of ink, with a drop spacing of 15 µm and an operating temperature of 30 °C (see Figure 14).

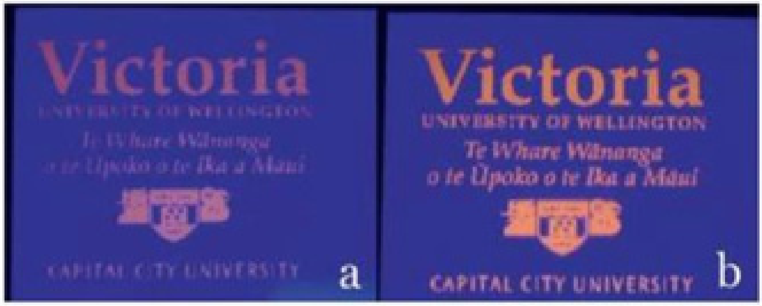


Figure 10. *Comparison of printed images with one layer (a) and two layers (b) of QDs. (58)*

Another research uses QD InP/ZnS to produce thermal curing ink. Through a ligand exchange process, the QDs can be dispersed in hydrophilic solvents. The QD dispersions are then mixed with other components to form a solution suitable for inkjet printing. In addition, in order to achieve the target set for certain optical properties, TiO2 particles (5 to 20%) and a dispersant are added and mixed using a stirrer. The ink is applied to glass substrates, then dried (100°C for 3 minutes) and cured (180°C for 10 minutes in nitrogen).(59)

Researchers have synthesized QD CdS/nanocellulose composites for photoelectric inks. The QDs act as pigments and the nanocelluloses as binders. The photo-induced current can reach 2 A and can be modified by playing on the carboxylate content of the nanocelluloses and the molar ratio of Cd2+/COOH. The photoelectric ink obtained is stable and can therefore be applied to screen and 3D printing. (60)

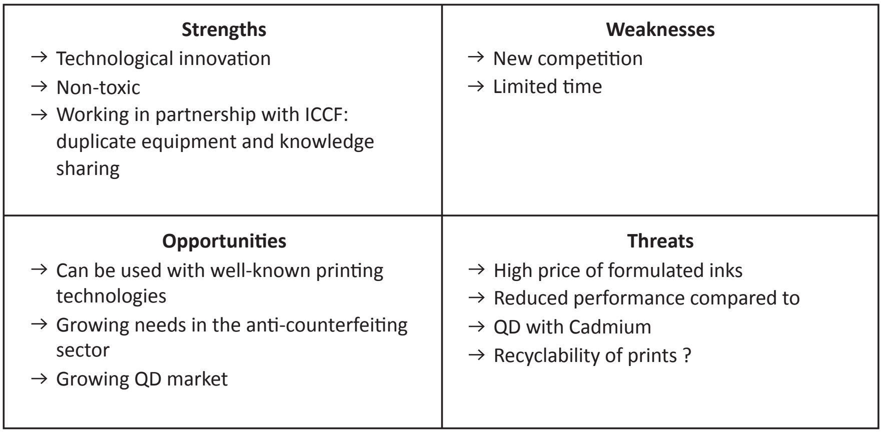
Sonication can be used to disperse nanoparticles in solvents. The nanoparticles must be in a well dispersed state, which can be difficult because they tend to form agglomerates. Ultrasound can be used to break up agglomerates of nanoparticles in aqueous dispersions. (61)

Conclusion

Quantum Dots are particles in full development. The attraction of research and industry for these nanoparticles makes them a particularly interesting issue.

According to the latest 2019 report of the European Union Office for Intellectual Property, counterfeiting costs €56 billion a yearfor eleven key sectors of the European economy . (70) This is why there is a great need in the anti-counterfeiting sector, where ink developed on the basis of QD InP/ZnS could be used.

However, if QDs develop on a large scale, it would be interesting to know how the recyclability of printed matter is achieved.



Strengths	Weaknesses
→ Technological innovation → Non-toxic → Working in partnership with ICCF: duplicate equipment and knowledge sharing	→ New competition → Limited time
Opportunities	**Threats**
→ Can be used with well-known printing technologies → Growing needs in the anti-counterfeiting sector → Growing QD market	→ High price of formulated inks → Reduced performance compared to → QD with Cadmium → Recyclability of prints ?

Table 4. *SWOT matrix of an anti-counterfeiting ink based on QD InP/ZnS*

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