Nanocolloid Quantum Dot Inks for Ink Jet: Recent Developments and Potential Applications

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Abstract

Quantum dots (QDs) represent a unique subset of nanomaterials characterized by their quantum confinement behavior. Most notably this manifests itself in nanocrystalline semiconductor materials which below a critical dimension (particle size typically < 10 nm), and in contrast to their bulk form, exhibit a remarkable transformation in optical, electronic or magnetic property behavior. From an applications/device perspective they can be predictably tuned according to their size, shape and intrinsic solid state properties. Originally exploitation of this unique behavior was limited to the fabrication of solid state electronic and optoelectronic devices incorporating, for example, epitaxially grown QDs. More significant however has been the recent advent of wet-chemically synthesized QDs, available in a colloidally dispersed form making them amenable to ink jet printing as well as other liquid deposition technologies. These colloidal products now promise to open up commercial opportunities for a myriad of new uses.

Introduction

Among digitally addressable, finite drop placement technologies, ink jet printing (IJP) has proven to be one of the most versatile precision microfluidic tools. IJ printhead technology provides a convenient means of dispensing pixel by pixel, micro-, nano-, pico- and even femto-liter drop volumes of a wide range of materials. As an example IJP is now being commercially developed for mass-producing inexpensive electronic products, reel-to-reel, with microscopically fine features on both rigid[1] and flexible substrates.[2] This process is also scalable allowing printing of large macroscopic areas.

In parallel with the recent progress in printhead technology there has been intensive effort in the research and development of new nanomaterials offering unprecedented properties. Among the most active materials subsets currently being exploited are carbon nanotubes and quantum dots. The latter will be the focus of this presentation and, in particular, the potential for printing nanocolloidal quantum dots in new device applications.

Potential applications for QDs are extremely pervasive and are currently generating considerable interest. As a metric Figure 1 shows U.S. patent activity compiled on the basis of a recently completed patent and extensive literature analysis of quantum dots.[3] Over 800 patents have been issued since Texas Instruments filed the first patent on this topic in 1986. Furthermore for the period 2001 to 2004 there remain almost 1000 pending U.S. patent applications. Their applications transcend biology/medical diagnostics, electronics, optoelectronics, optics, energy and many other industrial sectors. This presentation will focus on developments in two promising areas. These include security and electronic device applications, intimately associated with ink jet printing.

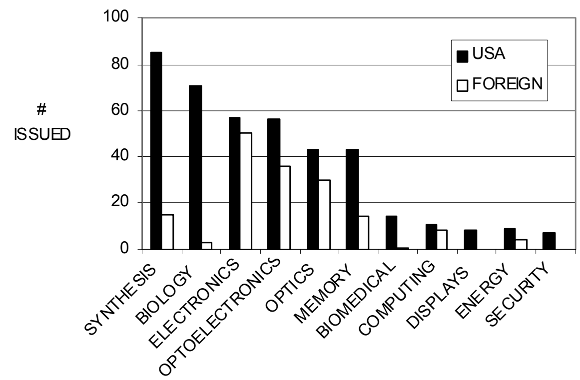

Figure 1. U.S. quantum dot patents issued between 1986 and 2004 classified according to commercial market application. [3]

What are Quantum Dots?

QDs refer to inorganic nanocrystalline materials fabricated to the smallest of dimensions, from only a few atom clusters and upwards.[4] At these tiny dimensions QDs behave according to the rules of quantum physics–which describe the behavior of atoms and sub-atomic particles, in contrast to classical physics which describes the behavior of bulk materials comprising many atoms. More specifically, quantum dots are structures where the electrons within *feel* a three dimensional confinement and hence can be thought of as an artificial atom. This phenomenon is limited to zero dimensions and is uniquely dictated by their exciton Bohr radius. Quantum confinement of both the electron and hole in all three dimensions leads to an increase in the effective bandgap of the material with crystallite size. It is this attribute in particular that is currently being exploited.

In material terms, quantum dots can be fabricated from semiconductor or metallic materials ranging in size from ~1 to 30 nm. Quantum confinement behavior will be observed, for example, with GaAs particles of ~14 nm diameter or less, with CdS particles with ~5 nm diameter or less, and for metallic Au particles, at even smaller particle diameters.

What makes quantum dots so fascinating is that they exhibit both chemical and physical differences with respect to the bulk material and the atomic/molecular material of the same chemical composition. Quantum confinement behavior is manifested in several unique, exploitable properties as shown in Table 1. For instance, the optical properties, such as the emission wavelength, can be simply altered by changing the size of the quantum dot.[5] In terms of electrical properties QDs can hold a single electron in addition to their normal atomic complement.[6]

Table 1: Commercially Promising QD Applications[1]

Sector	Exemplary Applications
Biology	Cell assaying
Biomedicine	In vivo imaging, targeting, disease diagnostics
Computing	QD nanoparticle array
Displays	Field emission
Electronics	Single electron transistor
Energy	QD tetrapod based solar cells QD super-lattice thermoelectric cells
Memory	Non-volatile flash memory
Optics/Tele-communication	Lasers and transistors for optical networks Quantum cryptography
Optoelectronics	Solid state white lighting
Security/ Bioterrorism	Covert identification tags Biopathogen detection

Quantum Dot Synthesis

Since their discovery 25 years ago the synthesis of QDs has followed essentially two pathways: in-situ *solid* state fabrication via molecular beam epitaxy or chemical vapor deposition (CVD); and *wet* state colloidal chemical methods. Typically semiconductor QDs have been synthesized from Groups IIB-VIA and IVA-VIA elements in the form of mixed alloys such as metal chalcogenides or individual elements such as silicon.

Nanocolloid QDs are typically synthesized from organometallic precursors injected into liquid surfactant nonpolar organic solvents.[7] Highly uniform-sized (monodispersed) particles can be prepared by a 2-step process: short nucleation at high temperature; and subsequent lower temperature size-selective precipitation to harvest highly monodispersed nanocolloid particles. The individual particle sizes can also be carefully controlled by selecting solvents with different boiling points. In many applications, particularly in photoluminescence, an inorganic coating (shell) is necessary to passivate the QD core.[8] Also for use in aqueous media various strategies are available for solubilizing and colloidally stabilizing QDs. These range for example from bilayer micelle encapsulation[9], shown in Figure 2, to more sophisticated colloid assemblies based on dendrimers and block copolymers.[10] This versatility in surface chemical functionalization makes QDs compatible with a variety of organic solvent or aqueous-based ink vehicle systems, and thus, suitable for a wide range of IJ-based applications.

Device Applications

The formulation of environmentally stable nanocolloids such as QDs, CNTs, metals, insulators, etc., compatible with various printing and coating environments, is critical. In the applications of QDs the following examples serve to illustrate how their unique properties and the advantages of IJP are coupled to fabricate novel devices.

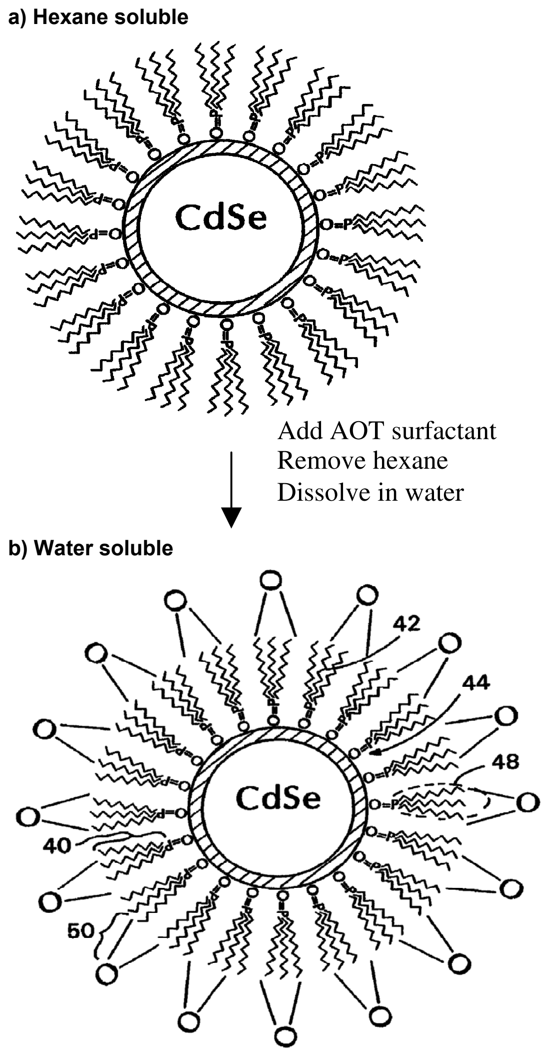

Figure 2. Structure of semiconductor nanocolloid QDs surface chemically functionalized by: a) tri-n-octyl phosphine oxide organic layer; and b) bilayer micelle formed by a displacement reaction with a hydrophilic dioctyl sulfosuccinate (Aerosol OT™) surfactant.[9]

Security

The first example evolved from graduate research conducted at the University of Hamburg and spin-off company, Nanosolutions which displayed its first prototype security printer at a Hanover trade fair in April 2002.[11] This used IJ inks based on colloidal dispersions of 5 nm nanocrystals of doped rare earth elements, e.g. $LaPO_4$:Eu or $CePO_4$:Tb. The inks are colorless and transparent and hence are not visible to the naked eye. Upon illumination with UV light they fluoresce and can be detected using appropriate sensing, e.g. a bar code scanner. The unique photo-emissive properties of the inks can be used to authenticate an invisible *spectroscopic fingerprint* on a variety of articles for security purposes, such as, art works, photographs, classified documents, CDs, etc. In contrast to organic fluorochromes, the photoluminescence of these inorganic nanocrystals provides a more prolonged and intense emission with a narrower detection wavelength and hence, higher detection sensitivity.

A more sophisticated approach using nanocrystalline QDs for optical coding is *color multiplexing,* based on using inks comprising mixtures of individual-sized monochrome QDs, to create secret cryptograms based on their individual absorption/emission signatures.[12] Practically indecipherable cryptograms are claimed because of the unique absorption excitation/spectral emission characteristics of the component, in this case metal chalcogenide, QDs. By assigning an undisclosed programmed sequence of excitation wavelengths (anywhere between 350 to 510 nm) the optical codes based on the intensity combination of individual fluorescent wavelengths are unreadable to a third party. The coding capacity and degree of sophistication can be designed according to the number of component QDs used and the number of respective emission intensities discriminated.

Electronics

IJP is already proving itself to be a viable technology in the burgeoning market of flexible electronics. Current applications range for example from interconnect devices, flat panel displays (OLED, PLED, EP), TFTs and RFIDs. Equally, advances in IJ printhead technology, as well as nanomaterials are aiding this development. Furthermore the possibility of employing differential surface energetics and surface capillary effects holds considerable promise in achieving small, sub-100 nm, feature resolutions.[13] In these so-called additive, non-lithographic, printing processes IJP may well prove an important future tool in bottom-up, self-assembly of basic nanostructures. One such example, shown schematically in Figure 3, is for a quantum device interference logic gate.[14] With the ability to adopt IJP for additively, and sequentially, patterning low-cost large area electronic circuits, integration of a QD-based device such as this is feasible.

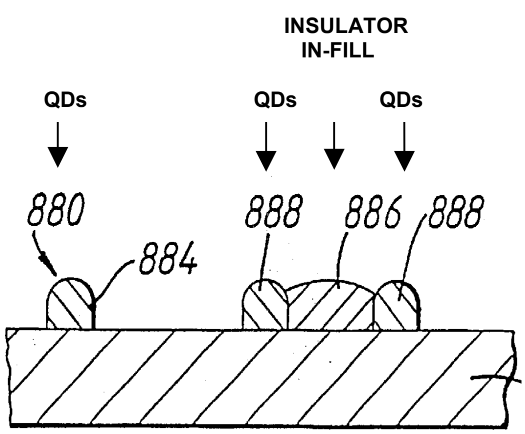

Figure 3. IJP fabrication of QD-patterned interference logic gate. device.[14]

Optoelectronics

Hybridizing an inorganic nanocrystal with a quantum dot has recently been proposed[15] as a new kind of optoelectronic device that could lead to a future generation of flat panel displays possibly superceding current liquid crystal displays. IJP with its precise positioning capabilities could prove an inexpensive and convenient means of incorporating discrete single layers of QDs sandwiched within the multilayer films that comprise QD-OLEDs.

Memory

A new generation of non-volatile flash memory chips based on CVD films of nanocystalline Si QDs dots are under commercial development.[16] Alternatively IJP with its economic advantages, and recent developments in the synthesis of monodispersed Si nanocolloids, might further enhance this technology especially in terms of achieving higher packing densities in self-assembling films.

Conclusions

Among the new generation of nanomaterials the synthesis of colloidal quantum dots opens up an exciting area of potentially new applications. The ability to formulate these materials into inks or coatings suitable for ink jet, as well as other printing technologies, provides the opportunity to exploit the unique properties of QDs in a range of new devices. In addition to the limited examples described here there are a host of other conceivable applications.

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