Research Article

Advanced Secure Information Retrieval Technology for Multilayer Information Extraction

Shoude Chang,1 Kui Yu,2 and Jiaren Liu1

1 Imaging Devices Group, Institute for Microstructural Sciences, National Research Council of Canada, Ottawa, ON, Canada K1A 0R6
2 Molecular & Nanomaterials Architecture Group, Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, ON, Canada K1A 0R6

Correspondence should be addressed to Shoude Chang, shoude.chang@nrc.ca

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Secure information retrieval technology aims at status identification and documentation authentication. Ideally, materials or devices used in these technologies should be hard to find, difficult to counterfeit, and as simple as possible. This manuscript addresses a novel information retrieval technology, with photoluminescent (PL) semiconductor quantum dots (QDs) synthesized via wet chemistry approaches used as its coding materials. Conceptually, these QDs are designed to exhibit emission at Fraunhofer line positions, namely, black lines in the solar spectrum; thus, the retrieval system can extract useful information under sunshine covering areas. Furthermore, multiphoton excitation (MPE) technology enables the retrieval system to be multilayer information extraction, with thin films consisting of QDs applied to various substrates, such as military helmets and vehicle and fingernails. Anticipated applications include security, military, and law enforcement. QD-based security information can be easily destroyed by preset expiration in the presence of timing agents.

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1. INTRODUCTION

There are two important issues in security technologies: information storage and retrieval. The visibility of the printed pattern of a barcode is vulnerable to counterfeiting; therefore, the most prevailing barcode technology is definitely not qualified in many security applications. Regarding high-level security, a hidden information carrier which is invisible to human eyes and is tiny in size is mandatory; moreover, the invariance of the information encoded by the carrier is critical to simplify the information retrieval procedure with enhanced reliability. For example, the information encoded including sequence- or pixel-based classification does not change with the position or rotation of its host object.

Multiplexed spectral coding technology that makes use of multiple wavelengths and multiple intensities as the coding space meets the invariant requirement for security, to a certain degree. Organic dyes and metal complexes are commonly used as fluorescence-sensing materials in various applications. Basically, they seem to be suitable in the multiplexed spectral coding technology; however, their intrinsic optical properties limit them to be ideal candidates. For example, different dye molecules require different excitation wavelengths; furthermore, it is difficult to retrieve information from a mixture of these fluorescent molecules due to their broad emission bandwidth and asymmetry. The limitation may also be related to the certain reaction of different dye molecules or the immiscibility of some of the dye molecules in a common matrix material. In order to meet the prerequisite for multiplexed encoding and decoding, the multiplexed spectral coding technology demands a set of luminescent materials with required properties, such as (1) single-light source for all materials to emit at different wavelength; (2) each emission independent of the excitation wavelength; (3) stable emission with narrow bandwidth from each luminescent material; (4) no chemical interaction among the fluorescent molecules; (5) no emission from matrix materials; (6) good miscibility of all luminescent materials in the selected matrix materials.

Recently colloidal photoluminescent (PL) semiconductor quantum dots (QDs) have demonstrated many of the
above-mentioned characteristics. For example, QDs exhibit emission with narrower bandwidth, broader absorption, and better photostability, compared to traditional luminescent materials. Furthermore, they are excellent with multiphoton excitation due to large multiphoton action cross-sections; accordingly, they are significant candidates for multilayer information extraction. Moreover, their bandgap emission and absorption peak positions can be easily and accurately tuned via the control of their size, structure, and composition. Due to their intrinsic optical properties, QDs are suitable in the multiplexed optical coding technology with potential in security and defence [1–5]. Basically, QDs are ultrasmall nanocrystals and are spherical in shape, usually in the range of 1–10 nm. Elements made up of QDs are often from Group IIB and Group VIA in the periodic table. QDs can be binary compounds, such as cadmium selenide (CdSe) and zinc sulfide (ZnS), or ternary compounds such as CdTeSe and ZnCdS, or layered structures such as core/shell CdSe/ZnS and CdTe/CdSe/CdTe [6–12]. When these nanocrystals dispersed in a transparent solution are excited, they provide coding information based on their emission position and intensity; such a solution with the secure information encoded is the so-called infoink. A mixture of various QDs with different emission positions can be dedicatedly designed to feature a special code with a set of data consisting of the emission positions and intensity. Such coding information is hidden in a fluorescence spectrum; accordingly, a spectroscopic device is needed rather than a scanner or camera to decode the encoded information. It is necessary to point out that such QD-based devices feature miniature in size and invisible to human eyes, demonstrating their potential in security applications.

Chan et al. proposed the idea of using colloidal QDs in multiplex bioimaging and biolabeling [13]; such a multiplex detection only involved single-photon excitation in solution. Bawendi and Jensen in MIT reported the design of using QDs for inventory control [14, 15]; however, no practical approaches were provided about their information retrieval system. Also, we demonstrated a QD-based information retrieval system with patents granted [16, 17]. In this manuscript, we describe, in detail, how to expand our patented technology to higher dimensional coding space, with its feasibility in sunlight-covering areas. In addition, we present the details of our advanced information retrieval system with QDs as the coding materials; a prototype system is acknowledged to extract information from an ID card.

2. INFOINKS CONSISTING OF QDs

Colloidal photoluminescent QDs as “infoinks” for biolabeling were proposed about ten years ago [18–20]; meanwhile, significant advances in solution-chemistry synthesis expand such applications of QD-based infoinks to many areas including security [9, 14–17, 21, 22]. Various photoluminescent QDs with different emission wavelengths provide a great number of combinations of wavelength and intensity. For example, an encoder using 6-wavelength and 10-intensity schemes has a theoretical coding capacity of about one million discrimination codes. The coding capacity can be even expanded by utilizing a third parameter, such as 1D sequence or 2D array of QDs. To be able to use QDs for the spectral coding of nonbiological objects such as banknotes, passports, certificates, and other valuable documents, paintable or printable QD/polymer/solvent infoinks are needed. The infoinks, consisting of different QDs, polymers, solvents, and additives, can be digitally printed onto various surfaces for coding purposes. A hybrid optic-electronic-digital system is used to extract the data from the resulting emission spectra. The detailed description is given in Section 3.

After the infoink is applied to a target surface and dried, the polymer becomes matrix materials, in which the mixture of different QDs with predesigned emission features is dispersed homogeneously [23]. The polymer used should not have quenching effects on the fluorescence of the QDs, and should satisfy other requirements, such as reasonable solubility in the selected solvent, long-term environmental stability, and good compatibility and miscibility with the QDs.

CdSe nanocrystals in the nanometer-sized range can be well dispersed in toluene, which is also a good solvent for polystyrene (PS). Therefore, the infoink prepared in our preliminary work consisted of CdSe nanocrystals (Evident Technologies [24]), high molecular weight PS, and toluene (both from Aldrich, St.Louis, Mo, USA). According to their individual emission intensity, the CdSe QD ensembles were mixed with different ratios, together with a certain amount of PS and toluene to engineer the infoinks with required emission spectral features and viscosity for testing. Furthermore, inhouse-synthesized CdSe-based nanocrystals and CdS nanocrystals were used in the present study [25–29]. The inhouse CdSe QDs were synthesized with a slow growth rate for high-quality and large-scale production. This nonorganometallic approach involved the addition of a solution with a chalcogen source in tri-n-octylphosphine (TOP) to a solution of CdO in TOP at one temperature, with subsequent growth at a lower temperature. A slow crystal growth rate was achieved with the zero growth rate accomplished via tuning the Cd-to-Se precursor molar ratios, as assessed by the temporal evolution of the optical properties of the growing nanocrystals dispersed in nonpolar hexanes (Hex) and polar tetrahydrofuran (THF). It has been acknowledged that a higher particle growth rate results in greater surface roughness, more surface defects, and lower PL efficiency. An approach for removing the surface defects is to control a small growth rate, ideally to achieve a zero growth rate, which means that the average rate of removal of atoms from the nanocrystal surface is equal to that of addition of atoms to the nanocrystal surface. The nanoparticles with the size close to a zero growth rate in an ensemble possess the smoothest and defect-free surfaces and highest PL efficiency. In general, the inhouse synthetic approach is excellent in terms of the control of the growth rate for the CdSe nanocrystals with high surface quality, a simple system but a rational choice for both fundamental understanding and tailoring applications. Also, such slow size growth is essential for large-scale production as well as for further in situ modification such as for core/shell materials. It is necessary to point out that the zero growth
rate methodology leads to our magic-sized QD ensembles, the latest in our synthetic laboratories; these single-sized QD ensembles exhibit bandgap emission with bandwidth as narrow as 8 nm are ideal for infoinks for security applications [9, 25, 26].

3. INFORMATION CODING AND RETRIEVAL

A 2D coding space could be spanned by the wavelengths and intensities of the mixed PL-QDs. Figure 1 illustrates, schematically, the designed infoink samples consisting of three different QDs with different emission wavelengths. Adjusting the various ratios of the three QDs can produce a series of 3 digital codes. The infoinks consisting of polymer, solvent, multiple QDs, and other additive are prepared and putting on the objects that need to be coded. A hybrid optic-electronic-digital system is used to extract the data. It is well acknowledged that one QD ensemble has a very broad absorption spectrum, with its single emission position (in wavelength, \( \lambda_{\text{em}} \)) independent of excitation wavelengths (\( \lambda_{\text{ex}} \)) as long as \( \lambda_{\text{ex}} \) is shorter than the excitation threshold (the first absorption peak) [5]. Accordingly, we proposed a new concept on using mixtures of multiple single-color QDs to create highly secret cryptograms based on their absorption/emission properties [30], in addition to the optical coding based on fluorescence of semiconductor quantum dots (QDs). The key to the readout of the optical codes is a group of excitation lights with the predetermined wavelengths programmed in a secret manner. The cryptograms can be printed on the surfaces of different objects such as valuable documents for security purposes.

Figure 2 shows a group of emission spectra collected from a mixture of three single-color QDs in toluene excited at a \( \lambda_{\text{ex}} \) ranging from 350 to 510 nm with a constant interval of 10 nm. The excitation peaks (\( \lambda_{\text{ex}} = 510, 500, 490, 480, 470, 460, \) and 450 nm) and three diffraction-induced second-order peaks (from \( \lambda_{\text{ex}} = 350, 360, \) and 370 nm) are also recorded in the measurement range. The inset illustrates two sets of selected spectral data normalized to a 10-level (0–9) intensity scale.

It is easy to understand that an \( \lambda_{\text{ex}} \)-dependent spectral change can be simply used to increase the coding capacity. Assuming that a 10-level (0–9) intensity scale is used for coding, a two-color QD system under the excitation of a single \( \lambda_{\text{ex}} \) can theoretically generate 99 codes, including those involving the fluorescence intensity level of 0. If multiple \( \lambda_{\text{ex}} \) elements can be applied to the system, the coding capacity is theoretically expanded to a multifold of 99. This should well accommodate all Latin characters, with a large redundancy. In the same way, thousands of the most frequently used Chinese characters could be coded with a tricolor QD system plus multiple \( \lambda_{\text{ex}} \) elements. Of course, from a practical point of view on the available single-color QD ensembles exhibiting narrow bandwidth and distinguishable intensity, using more spots spatially arranged in a particular way to represent a character could be a better way to increase the coding capacity, though at the cost of reducing the readout speed.

The coding capability can be furthermore extended from 2D surface to multiple layers by using two-photon exciting and 3D information extraction. The process of two-photon excitation is currently being examined for a variety of applications, for example, ultrahigh-density optical data storage.
biochemical imaging, and 3D microfabrication [31]. We have investigated the two-photon excitation characteristics of QDs, and have begun to explore their application for 3D information extraction. Theoretically, when laser light at a wavelength \( \lambda_p \) is tightly focused inside transparent QD materials so that its intensity in a small volume around the focus surpasses specific threshold, two-photon absorption is triggered if \( \lambda_p > \lambda_{em} > (\lambda_p/2) \), where \( \lambda_{em} \) is denoted as any of fluorescent emission wavelengths. Because the emission is localized in a part of the focal volume, 3D information could easily be extracted with the micron or submicron spatial resolution depending on focal optics and laser intensity. Experimentally, we demonstrated two-photon excitation based on CdSe, CdS, and/or CdSe/ZnS QDs, and an 800 nm femtosecond laser with the repetition rate of 78 MHz and the pulse duration of 120–150 femtoseconds. Figure 3 shows a typical image with one red spot, obtained from a CdSe QD dispersion by two-photon excitation. The volume of the focused spot can be manipulated by using various focusing objectives, laser beam diameter, and laser intensity. The emission and absorption spectra of one CdSe QD ensemble and one CdSe/ZnS QD ensemble are shown in the parts a and b of Figure 4, respectively, the emission spectra were collected with 800 nm two-photon excitation.

Obviously, the two fluorescence spectra by two-photon excitation shown in Figure 4 have little signal-to-noise ratios, with unambiguous recognition of fluorescence peaks and shapes. Moreover, the relationship between the emission intensity and the two-photon excitation pump intensity was investigated, with one CdS QD ensemble exhibiting an emission peak around 470 nm. While the fluorescent spectra of the CdS QD ensemble pumped by different pump power were shown in Figure 5(a), the fluorescent intensity versus the pump power shown in Figure 5(b) was calculated as

\[ y = 0.8515x^{1.4016} \]

Such a relationship does not agree with that of theoretical prediction \( y = \alpha \cdot x^2 \) under the coherently driven two-photon resonant absorption. The discrepancy could be explained by the detuning of the 470 nm emission peak from the coherent two-photon pumping at around 800 nm which is equal to 3723 cm\(^{-1}\) [32].
We reported a 2D information retrieving system [33], consisting of an exciting light, a spectrum sensor, and a signal-processing unit. Figure 6 shows a prototype of such a system for retrieving the information hidden in a tiny spot of a card. The exciting light is provided by a 370 nm LED light source. An optical fiber bundle guides the exciting light to the infoink spot applied on the surface of any object. The fluorescence emitted from the QDs is collected by the detecting fiber in the fiber bunch and fed to a spectrometer. The data generated by the spectrometer is further delivered to an intelligent instrument, namely, a microprocessor or a PC, which eventually extracts the information originally coded in the infoink. In order to obtain an even exciting light, the exciting fibers are arranged to surround the detecting fiber evenly to form an optical fiber bundle, as shown in Figure 6. A rubber cup is connected at the end of the fiber bundle to ensure that only the excited fluorescent light can enter the detecting fiber.

The raw data collected from spectrometer is processed by a computer with the following steps: (1) removing the noise by a digital filter; (2) separating the spectral center lines emitted by infoinks from the overlapped spectra; (3) finding the wavelengths ($W_s$) and intensities ($I_s$) of all the spectral center lines; (4) calibrating these $W_s$ and $I_s$, and retrieving the original data according to a prior known codebook.

Figure 7 shows a fluorescence spectrum measured from an infoink containing only one single-color QD ensemble with emission peak at 535 nm. Because of the Gaussian-like feature of the emission peak shape with a certain bandwidth, it is easy to understand that neighboring emission spectral...
profiles can mutually affect each other, including their emission intensity and peak position, when an infoink consisting of several single-color QD ensembles emitting at different positions. Figure 8 shows one example of such a spectral alias. The acquired emission spectrum from one infoink is the top/thick black curve; this infoink consists of two single-color QD ensembles, one is QDs 611 nm, the other is QDs 632 nm. As shown in Figure 8, the input spectrum can be deconvoluted into two spectra: one is with intensity of 1.0 (the gray curve), the other 0.2 (the thin black curve); these two deconvoluted spectra are resulted from the two QD ensembles. As the intensity of the spectrum represented by the thin black curve is only about 1/5 of that of the spectrum represented by the gray curve, the peak of the former could not be distinguished from the input spectrum. Such an ambiguous determination of the peak position will eventually result in a decoding error if no deconvolution is performed.

Let us turn our attention to spectrum deconvolution. A spectrum function of one infoink can be described as

\[ f(\lambda) = \sum_{i=1}^{N} k_i \cdot \delta(\lambda - \lambda_i) \otimes p(\lambda_i), \]

where \( \delta(\lambda) \) represents an impulse function, physically, a spectral line. \( k_i \) is the intensity of a \( \delta(\lambda) \) at \( \lambda_i \), \( p(\lambda_i) \) denotes the profile function centered at \( \lambda_i \), \( \otimes \) represents a convolution operation. As described above, the bandwidth of an emission profile of the infoink is the main reason for the spectrum alias. To get rid of the alias effect, the spectrum line must be separated by means of deconvolution operation.

Let \( F(u) \) and \( D(u) \) be Fourier transforms of \( f(\lambda) \) and \( \delta(\lambda) \), respectively, provided all the \( p(\lambda_i) \)'s have the same Fourier transformation \( P(u) \), the separated spectrum line at \( \lambda_m \) is obtained by the inverse Fourier transform (IFT) of (1):

\[ \text{IFT} \left[ \frac{F(u)}{P(u)} \right] = \sum_{i=1}^{N} k_i \delta(\lambda - \lambda_i). \]  

Equation (2) yields a serial of \( \delta(\lambda) \)'s, indicating that all the spectral lines are extracted and separated as individual impulses. However, as each spectrum profile of infoink is actually different from others, the deconvolution operation can only extract one narrow sharp impulse. To find all spectral lines, \( k_i \delta(\lambda - \lambda_i), i = 1 \cdots N \) times operations are needed.

For 3D information extraction using two-photon excitation, depth scanning devices are required, collaborated with a 2D extraction system. Controlled by a computer, the information encoded in layers will be retrieved layer by layer.

When applying QD-based labeling technology to sun-covering areas, there is a critical issue to be addressed: the brightness of sunlight may overpower most optics-based solutions. Specifically, detecting a return fluorescent signal can be very difficult as the return optical signal can get overwhelmed by sunlight. Fortunately, the sun is not a perfectly continuous white source. There are many black lines seen in the solar spectrum—the Fraunhofer lines. As shown in Figure 9, the solar spectrum has been split into pieces, from the blue (left) end to the red (right) end by these absorption lines, literally thousands, in fact, if one looks in fine enough detail. These black spectrum lines provide the coding space. Subsequently, the infoink will be engineered with QDs whose emission positions are located in those black lines. Although the encoding information provided by these wavelength positions could not be covered by the reflection of the powerful daylight, in our retrieving device proposed and patented, special filters are still used to extract the useful wavelengths, namely, Fraunhofer line signals while screen the others.

4. APPLICATIONS

A direct application is the ID card identification. In order to code the documents automatically and fast, a principal ink should be prepared first. The principal ink is an infoink that has a unique fluorescent wavelength. For an application using 6 wavelengths, 6 principal infoinks are
Figure 11: Emission spectra for the comparison of the photostability after UV-irradiation of CdSe QD ensembles from (a) SIMS-NRC and from (b) Evident Technologies. The two CdSe ensembles were dispersed in toluene with a similar concentration. The UV source is a 365 nm lamp, and the irradiation hours are indicated by the different color. NRC-QD ensemble exhibited little blue shift during UV-irradiation, as compared to that of Evident Technologies QD ensemble.

Another potential application is proposed for friend/enemy discrimination. The problem of identifying friendly from unfriendly forces becomes critical in the modern battles. The rise of the so-called “smart weapons” has enhanced the accuracy of ordnance delivery, but, sadly, has also increased the casualty rates of the so-called “friendly fire” incidents. After World War II, the use of precision weapons and advances in intelligence technologies for air and space has drastically revolutionized air warfare; meanwhile, the friendly fire casualty rate increased. The percent of casualties from 21% in World War II changes to 39% in Vietnam War and 49% in Persian War. (This percent was estimated by the American War Library on friendly fire casualties, both fatal and nonfatal, based on historic War Department, Department of the Navy, and Department of Defense casualty reports detailing various battle reports).

After Desert Storm, the Pentagon conducted extensive researches into developing ways for friend/enemy discrimination, but suspended many of them due to cost. One program—called the Battlefield Combat Identification System or BCIS—had been introduced to prevent friendly fire. However, to equip the Army with such automatic identification systems would have cost as much as $40,000 per vehicle. Up to date, the friendly fire is still playing a role as a critical “enemy” in the battlefield. One possible solution is the use of QD-based information coding and retrieving system. Instead of using expensively active radar technology, the QD-based system takes the advantages of the passive fluorescent features of QDs. To avoid friendly fire from aircraft attacking, the coded infoink is painted on the top surfaces of vehicles and soldiers helmets as their ID labels. By sending a probing beam and detecting the reflected spectrum, the aircraft could distinguish these labels before firing a missile or bomber. Even after the firing, the intelligent device built in the warhead could disable the deadly exploding if the ID signal is detected as friend army. The more soldiers and vehicles are involved in a battlefield, the higher level ID labels are demanded to enhance the discrimination and reduce a large-scaled casualty caused by friendly fire.

5. SUMMARY AND CONCLUSION

The present manuscript argues about basic ideas with preliminary experimental results about the use of semiconductor QDs for security and military applications. Photoluminescent QDs are suitable for security identification with, due to their intrinsic optical properties, such as narrow emission and broad absorption, good photostability, as well as easy tuning of their photoemission peak positions via the control of their size, structure, and composition. Thus, QDs satisfy the main requirements in security identification, such as easy encoding and decoding, large coding space, invisible, and translation-rotation invariant. Basically, our QD-based information retrieval technology has bright future in many applications; however, it is not a mature technology.
Additional experiments, such as sensitivity to nonuniform illumination, detection limitations, repeatability, and data collecting time, will be conducted in our future work.

Finally, we would like to discuss three critical factors for successful information retrieval, namely, an advanced methodology for multilayer information retrieval using QD-based infoinks with specially designed emission properties.

Factor one: long-term stability of QDs. The emission stability of QDs has been monitored for weeks. We are still making efforts on testing QD-based materials for longer stability. Different synthetic approaches lead to QDs with different surface properties and thus optical properties; Figure 11 shows the comparison of the photostability of the QDs developed by us (NRC-SIMS) and by Evident Technologies [24–26]. Recently developed magic-sized QD ensembles are very stable and should be excellent candidates [9].

Factor two: detection from a distance. At least, three factors are involved: (1) the quality/sensitivity of sensors, (2) the exciting beam, and (3) the QD quality including emission intensity and bandwidth. The first two are related to hardware development. Investigation will be carried out on concentrating the infoinks to enhance the fluorescent signals.

Factor three: the algorithm used for the deconvolution of an input spectrum plays an important role in information retrieval. The deconvolution procedure is adopted basically due to its ability of narrowing and separating the overlapped neighboring QD-emitting spectra. However, if one QD ensemble exhibits an emission spectrum with changes in its shape, errors may be introduced during deconvolution. Fortunately, QD-based infoinks have exhibited little changes in their individual emission shapes. Although many algorithms of signal detection and spectrum evaluation are available [34], they are basically designed for the purpose of improving the signal-to-noise ratio. For the present technology with QD-based emission, the algorithm for spectrum deconvolution is more needed. When a useful signal in the input is weak, a calibrating procedure should be introduced.

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