

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

185,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



# Carbon and Silicon Fluorescent Nanomaterials

Joaquim G. G. Esteves da Silva

*Centro de Investigação em Química da Universidade do Porto (CIQ-UP),*

*Department of Chemistry and Biochemistry,*

*Faculty of Sciences, University of Porto, Porto,*

*Portugal*

## 1. Introduction

The most known fluorescence nanoparticles are the semiconductor nanocrystals usually called quantum dots (QD) (Smith & Nie, 2010). These nanoparticles, with typical sizes between 1 to 12 nm, are being used in many advanced technological applications, for example in bioimaging (Gerion et al., 2001; Murcia et al., 2008; Williams et al., 2009). However, some of the materials that compose the QD are rare in the earth crust and highly toxic (Lovric et al., 2005).

Recently, the elements carbon and silicon, which are among the most abundant elements in the earth crust and are intrinsically non-toxic, become quite important elements in nanochemistry because they originate fluorescent nanostructures with relatively high quantum yield. Bulk carbon and silicon materials are not fluorescent but the corresponding nanomaterials are strongly fluorescent, allow emission colour tuning and are non-blinking nanoparticles with high scientific and technological potential.

Carbon nanomaterials are already well known, like for example the fullerenes, carbon nanotubes (CNT), either single-wall (SWNT) or multiple-wall (MWNT), carbon nanofibers and graphene (Liu et al., 2010). Highly fluorescent carbon nanomaterials, here called carbon dots (CD), were only accidentally discovered in 2004 during the electrophoretic purification of SWNT derived from arc-discharge soot (Xu et al., 2004). However, in the years 2000 and 2007, studies observed strongly fluorescence shortened MWNT and shortened SWNT (Luo et al., 2007; Riggs et al., 2000). Indeed, CD are carbon based nanomaterials that possesses similar size and surface functionality they constitute different families of nanomaterials and are constituted mainly by carbon with  $sp^2$  hybridization characteristic of monocristaline graphite with relatively high oxygen contents (Baker & Baker, 2010; Esteves da Silva & Gonçalves, 2011; Fan & Chu, 2010; Xu et al., 2004). CD are different from nanodiamonds because these last nanoparticles are constituted by about 98% carbon with a  $sp^3$  hybridization with small amounts of graphitic carbon on the surface that are synthesized from milling microdiamonds, chemical vapour deposition, shockwave or detonation processes (Baker & Baker, 2010). New simplified synthetic pathways are being proposed and the number of potential technological applications of CDs is increasing in the last years (Baker & Baker, 2010; Esteves da Silva & Gonçalves, 2011; Fan & Chu, 2010).

Another class of potentially non-toxic and biocompatible fluorescent nanoparticles are those of silicon (silicon dots - SD). One fluorescent silicon nanoparticle (silicon porous

nanoparticles) were first prepared in the 1950s by electrochemical etching in hydrofluoric acid and ultraviolet irradiation (Parkhutik & Timashev, 2000) but its red luminescence was only discovered in 1990 (Canham, 1990). However, porous silicon is fragile and highly reactive limiting its straightforward applications. SD with typical sizes in the order of 1 to 10 nm are mechanically more rough and show high quantum yields. Also, SD has one common property to QD, i.e. the emitted fluorescence is red shift with increasing size particles (Canham, 1999). These properties confer SD a quite interesting role for optoelectronic devices.

The research and modulation of SD is more advanced than CD and the application of computational theoretical methods to SD is a quite interesting research field (Pudzer et al., 2003; Belomoin et al., 2002; Trabi & Barone, 2011). Indeed, SD have been studied by density functional theory (DFT) and quantum Monte Carlo (QMC) methods to understand and simulate their structural and optical properties. This theoretical approach together with experimental confirmation will allow further developments in the understanding of the fluorescent properties tuning.

This chapter will focus on the description of the fluorescent nanoparticles carbon dots (CD) and silicon dots (SD) with a brief description of the synthesis methodologies, the current state of the art about the comprehension of the fluorescence mechanisms, their multiphoton excitation properties and its relevance to new bioimaging methodologies, and their most recent scientific and technological applications.

## 2. Synthesis of carbon and silicon nanomaterials

The synthesis of stable carbon and silicon based high fluorescent nanoparticles usually requires a two step methodology: the synthesis of the raw nanoparticle; and, reaction of the surface atoms with other substances to passivation and/or functionalization.

Raw nanomaterials can usually be obtained by top-down or bottom-up approaches. Top-down approaches usually include physical techniques, like for example laser ablation, or chemical reactions, like for example chemical catalyzed etching. Bottom-up approaches are usually chemical synthesis methods that use chemical precursors to synthesise the nanoparticles. Figures 1 and 2 show the main synthetic routes of CD and SD, respectively. (Baker & Baker, 2010; Esteves da Silva & Gonçalves, 2011; Fan & Chu, 2010; Gonçalves and Esteves da Silva, 2011; Kang et al., 2011)

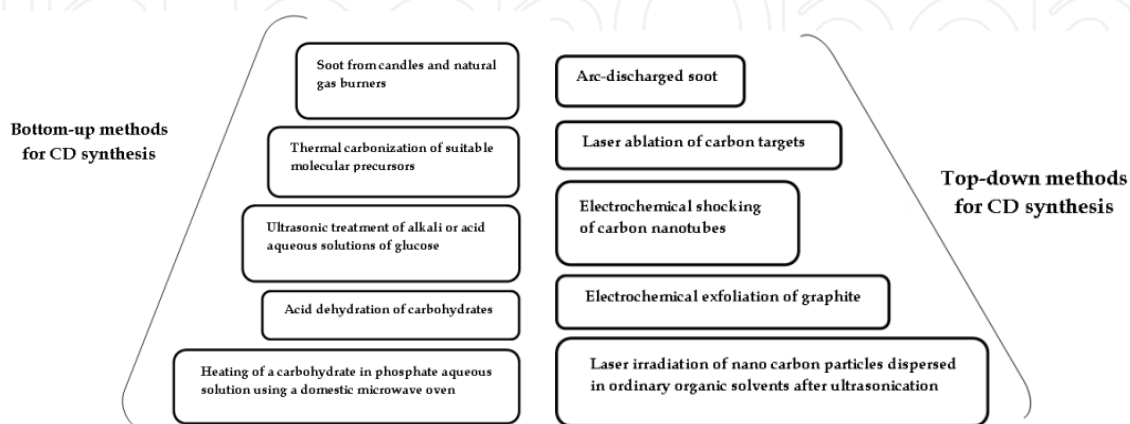


Fig. 1. Synthetic methodologies for CD.

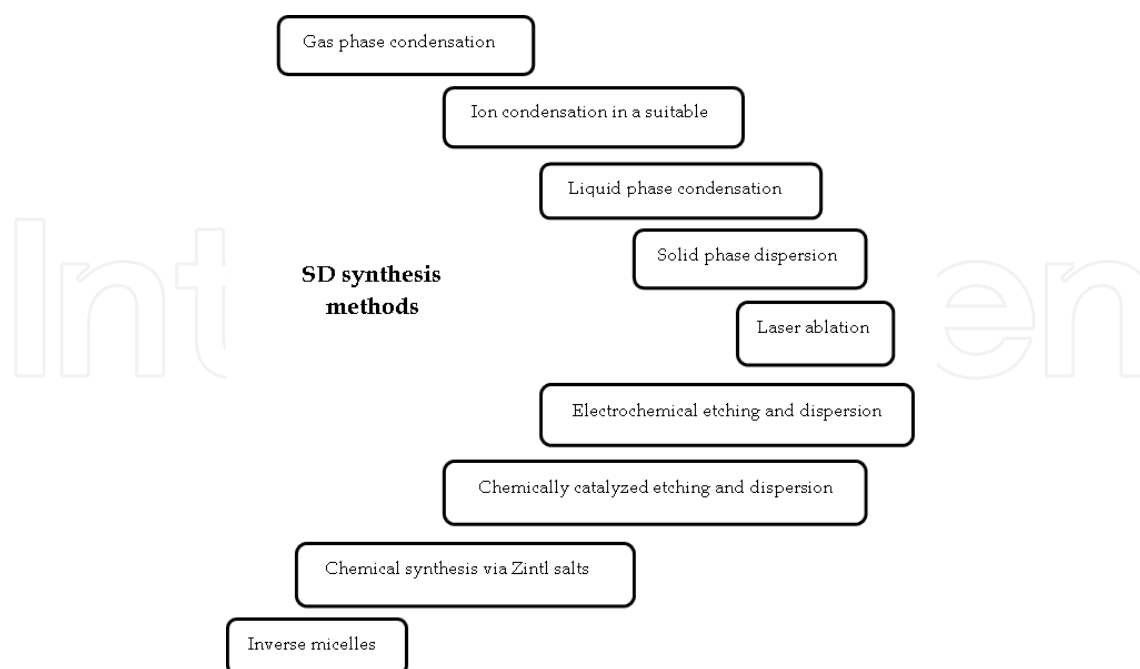


Fig. 2. Synthetic methodologies for SD.

### 3. Fluorescence mechanism of silicon and carbon nanomaterials

QD are usually constituted by elements from groups 12 to 16, for example III-V materials (GaN, InP, etc.), II-VI materials (ZnO, CdS, CdTe, etc.) and IV-VI materials (PbS, PbTe, etc.), (Smith & Nie, 2010). Two of the most spectacular properties of QD, which is not observed in the bulk material that is not fluorescent, are their quite strong luminescence and the dependence of their fluorescence properties with the size of the nanocrystal.

The dependence of the luminescence properties of QDs with their size is well established. QD show an electronic energy states distribution between that of a discrete molecule and of the bulk semiconductor, characterized by a bandgap energy ( $E_g$ ) corresponding to the energy difference between the valence and conduction band (Fig. 3). The absorption of energy higher than  $E_g$  by an electron in the valence band provokes its excitation into the conduction band originating a negative charge and a positive hole in the valence band (the pair negative charge and positive hole is called the exciton). In a nanoparticle the annihilation of the exciton corresponds to the emission of fluorescence. However, the exciton has a finite nanometric size defined by the Bohr exciton diameter that, for relatively small nanocrystals, may be greater than the size of the nanoparticle (Esteves da Silva and Gonçalves, 2011). When this condition is observed the nanoparticle is under a quantum confinement regime and their electronic properties are size dependent - the nanocrystal growth provokes a redshift in the emission of the fluorescence (Fig. 3) (Smith & Nie, 2010).

Another important characteristic of nanoparticles is that, due to its small size, a relatively high fraction of the atoms that constitutes the nanoparticle are localized at the surface. The atoms at the surface shows reduced coordination number and there is corrosion and imperfections which may affect the electronic properties of a nanoparticle - the smaller the nanocrystal the more important become the surface defects (Esteves da Silva and Gonçalves,

2011). Consequently, the electronic properties of QD may have contribution of surface defects besides quantum confinement effects.

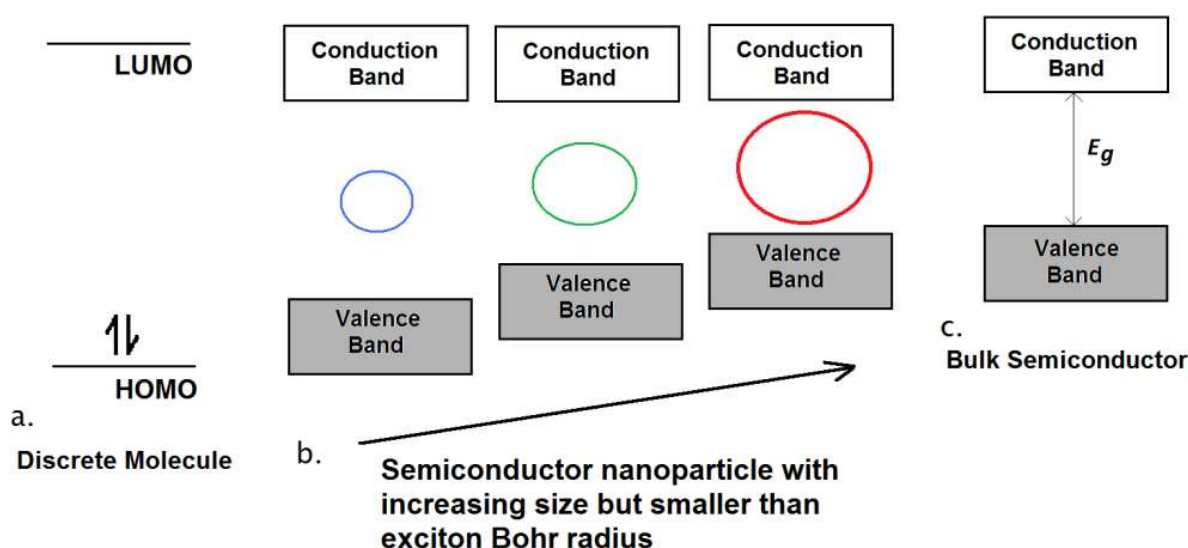


Fig. 3. Schematic representation of the electronic energy states in a semiconductor where quantum confinement is observed in the nanoparticles.

Silicon is a semiconductor with a bandgap energy of 1.14 eV (Shirahata et al., 2010; Wilcoxon et al., 1999). However, Silicon has no significant optical performance due to its indirect bandgap character (Fig. 4). The exciton Bohr radius of silicon is 4 nm and, under strong quantum confinement regime, the probability of radiative recombination through the direct bandgap transitions is increased and through phonon-assisted indirect bandgap transitions is reduced (Fig. 4) (Warner et al., 2005). Nanoparticles of silicon are highly luminescent and show quantum confinement size dependent properties resulting in the widening of the bandgap from 1.14 eV of the bulk to about 3.26 eV (380 nm) (Holmes et al., 2001; Shirahata et al., 2010).

Quantum confinement size dependent properties of SD have been observed for Si nanoparticles of size between 3 and 8 nm (Ledoux et al., 2002). Indeed, the energy of the emitted photons shifts to higher values when the size of the nanoparticles is reduced. However, for smaller SD, the surface composition becomes more important than the quantum confinement effect and the tuning of the emitted light becomes more difficult (Kang et al., 2011). SD of size between 1 and 4 nm showed quantum confinement effects, namely the maximum emission wavelength of 1 nm nanoparticles particles was 450 nm, 2 nm 520 nm, 3 nm 640 nm and 4 nm 740 nm (Kang et al., 2007; Kang et al., 2011). The emission of these SD could be tuned by chemically modification of the surface of the nanoparticles showing controllable surface effects.

The fluorescence of SD is still not complete understood but both quantum confinement effects and/or surface defects are involved in the fluorescence emission mechanism.

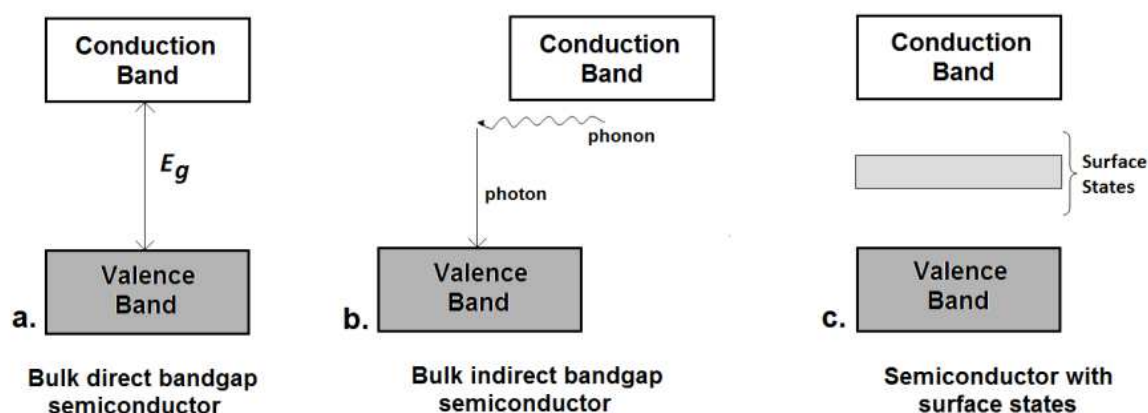


Fig. 4. Schematic representation of the electronic energy states in a direct (a.), indirect (b.) and with surface states semiconductor.

Similarly to QD and SD, CD are highly fluorescent nanoparticles. However, the fluorescence properties of CD do not show size dependency suggesting different fluorescence mechanism. Nevertheless, CD also shows the particular property of multicolour emission when different excitation wavelengths are used (Li et al., 2010; Liu et al., 2007; Liu et al., 2009; Mao et al., 2010; Peng & Travas-Sejdic, 2009; Zhu et al., 2009). Indeed, carbon is an insulator and quantum confinement effects are not expected for CD. Although the fluorescent mechanism of CD is still not clearly understood the fluorescence properties of these nanomaterials should be due to surface defects that originates energy levels that justifies the light emission (Fig. 4.c). These electronic levels distribution allow radiative recombination of excitons (Peng & Travas-Sejdic, 2009; Zhu et al., 2009). Also, and supporting the main effect of surface defects on the fluorescence properties, CD become fluorescent and the quantum yield increases when the nanoparticles are subjected polymer passivation and nitric acid treatment (Li et al., 2010; Liu et al., 2007; Liu et al., 2009; Mao et al., 2010; Peng & Travas-Sejdic, 2009; Zhu et al., 2009). Different starting materials and different fractions of similar size carbon nanoparticles also show different fluorescence emission properties.

#### 4. Multiphoton excitation phenomenon

When two low-energy photons arrive 'simultaneously' at a fluorophore and, through interaction with it, provokes the excitation of an electron that normally is excited by one higher energy photon, a two-photon excitation phenomenon (TP) is observed (Fig. 5) (Kim & Cho, 2009; Xu et al., 1996; Williams et al., 2001). TP based fluorescence microscopy using lower energy radiations as excitation sources (red or NIR photons) is becoming a quite popular technique for in vivo analysis (bioimaging) because of the following: (i) deeper penetration depth ( $>500\ \mu\text{m}$ ); (ii) lower tissue auto-fluorescence and self-absorption; (iii) reduced photodamage and photobleaching; and, (iv) localized excitation. One characteristic of the TP probes is the excitation cross sections ( $\delta\text{TP}$ ) usually expressed in GM (Göppert-Mayer) units ( $1\ \text{GM} = 10^{-50}\ \text{cm}^4\ \text{s/photon}$ ). Larger  $\delta\text{TP}$  the better because the TP probe is



more fluorescent and higher sensitivities are achieved. Apparently, the progress in this area is limited for the lack of appropriate probes (Kim & Cho, 2009).

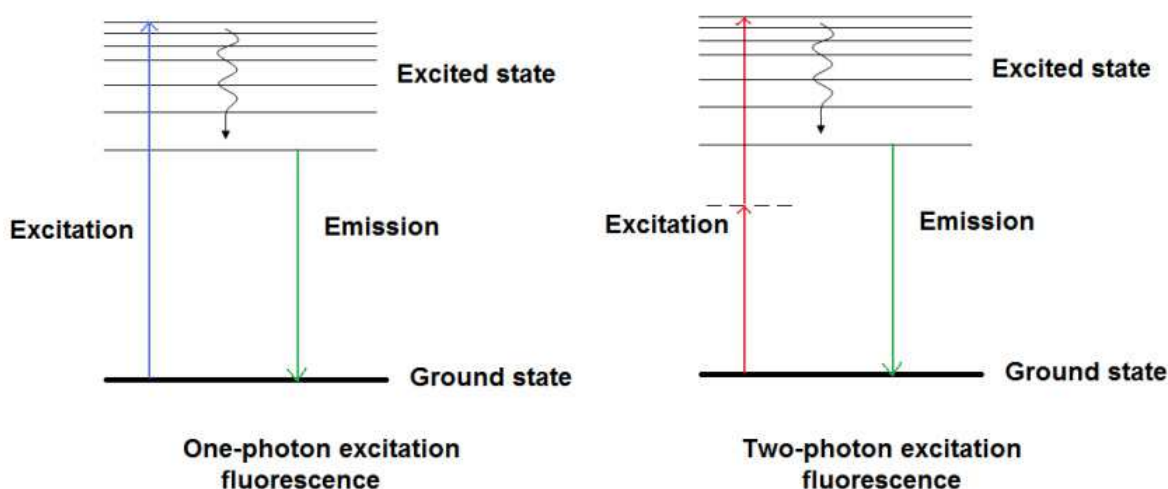


Fig. 5. Schematic representation of the electronic energy states of a fluorescent substance when one and two-photon excitation is observed.

Carbon and silicon nanoparticles can be excited by single (UV or near UV) or TP (red or NIR). TP and the low cytotoxicity and biocompatibility of carbon and silicon nanomaterials make them excellent sensors for bioimaging applications with a simple and straightforward application methodology (Fig. 6). CD and SD show luminescence with TP excitation in the NIR (800 nm femtosecond pulsed Ti:sapphire laser) (Cao et al., 2007) or long-wavelength light (from 500 to 1000 nm) (Akcakir et al., 2000; Li et al., 2010b). The maximum of the emission of fluorescence is in the 400 to 500 nm wavelength range as usually observed when one-photon excitation is used. The TP excitation is confirmed because a quadratic relationship between excitation laser power and the measured luminescence intensity is observed (Cao et al., 2007; Li et al., 2010b).

## 5. Applications of carbon and silicon nanomaterials

In this section some selected applications of fluorescent CD and SD are described. The selection criteria were their recent publication and potential for the future development of scientific and technological real applications. Indeed, taking into consideration the unlimited resources of both carbon and silicon in the earth crust, and their no toxicity and biocompatibility potential, major nanotechnological advances and future applications will have a strong contribution from CD and SD. These fluorescent nanoparticles will have an active role in the near future in bioimaging in biomedicine and bioanalytical applications, as nanocatalysts in technology and biochemistry, in sustainable energy devices and advanced analytical chemistry applications in general.

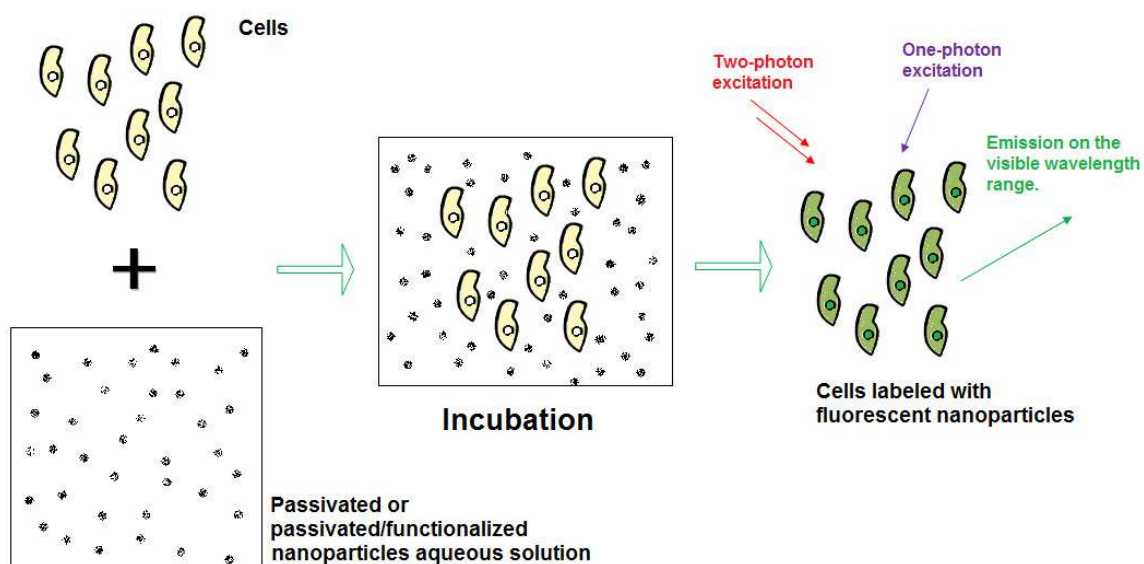


Fig. 6. Steps necessary to label cells with fluorescent nanoparticles before imaging with (either one-photon or two-photon excitation).

### 5.1 Carbon and silicon dots in bioimaging

Bioimaging sensors for *in vivo* diagnostics must be non-toxic and biocompatible. QDs based bioimaging methodologies have appeared in the last years together with toxicity concerns because they are constituted by intrinsically toxic elements like cadmium (Hardman, 2006; Lovric et al., 2005). CD and SD are constituted by intrinsically non-toxic elements which make them a particularly useful and promising bioanalytical tools as their performance approaches that of QDs. CD and SD have been demonstrated to have a very low cytotoxicity and were shown to internalize cells, probably by endocytosis mechanism, which, taking into consideration the MPE properties discussed above, makes these nanoparticles suitable for bioimaging purposes (Akcair, 2000; Erogbogbo, 2011; Li et al., 2010; Li & Ruckenstein, 2004; Manhat, 2011; Ray et al., 2009; Sun et al., 2006; Veinot, 2006; Yang et al., 2009a; Yang et al., 2009b).

The development of bioimaging agents that are selectively uptake by cancer cells is a particularly active research field. Usually CD or SD are functionalized with an aminoacid (lysine or glutaric acid), folic acid, antimesothelin or transferring to be selectively uptake by cancer cells (Erogbogbo, 2011; Li et al., 2010a; Manhat, 2011).

### 5.2 Carbon dots as peroxidase mimetics

Surprisingly CDs have shown to possess enzymatic properties because they have a peroxidase like activity (Shi et al., 2011). Indeed, CDs catalyses the oxidation of peroxidase substrates by hydrogen peroxide. For example, 3,3',5,5'-tetramethylbenzidine (TMB) is oxidised by hydrogen peroxide in the presence of CDs and detected by the production of a blue coloured compound (oxidised TMB). This new function of CDs opens new perspectives in their bioanalytical potential as a nanosensor for hydrogen peroxide and glucose (Shi et al., 2011).



The comparison of CDs with horseradish peroxidase (HRP) showed that CDs required a hydrogen peroxide concentration about two orders of magnitude higher than HRP to reach a maximum level of peroxidase activity (Shi et al., 2011). This result suggested that CDs are more stable than HRP at high hydrogen peroxide concentration. Also, CDs are much more stable than HRP.

Because the colour development (absorbance at 652 nm) was found proportional to the hydrogen peroxide concentration when TMB was used as substrate a quantitative method was obtained with a limit of detection of 0.2  $\mu\text{M}$  (linear plot in the hydrogen peroxide concentration between 0.0010-0.10 mM) (Shi et al., 2011).

The coupling of CDs with other enzymes can generate new bioanalytical methodologies, like for example for the quantification of glucose. Indeed, by combining CDs and TMB with glucose oxidase a straightforward colorimetric method for glucose is obtained with a limit of detection of 0.4  $\mu\text{M}$  (linear plot in the glucose concentration between 0.0010-0.50 mM) (Shi et al., 2011). This method is sensible enough for serum glucose quantification because the concentration in healthy and diabetic individuals range from 3 to 8 mM and 9 to 40 mM.

### 5.3 Silicon dots as nanocatalyst and photodynamic therapy

SD shows great potential as nanocatalyst with strong and tunable chemical activity, specificity and selectivity (Kang et al., 2011). These properties of SD are attributed to their tunable band gap energy and photoconductivity properties.

Due to the larger exciton (electron/hole pair) energy of SD with 1 to 2 nm size, these nanoparticles induces the photochemical reduction of carbon dioxide to carbonate anion and degradation of methyl red. Also, SD with 3 to 4 nm size photocatalyses the hydroxylation of aromatic hydrocarbons – benzene is transformed to phenol with a 100% yield with high selectivity. (Kang et al., 2011)

These catalyst properties of SD are probably due to their efficient photosensitizers of singlet oxygen (Timoshenko et al., 2006). This property has been used to suppress the division of cancer cells as consequence of the oxidation of cell material by singlet oxygen (Steller, 1995). Also, the formation of superoxide ions was observed when SD are present (Fujii et al., 2005). The photochemical synthesis of reactive oxygen species appears promising for use in photodynamic therapy of cancer.

### 5.4 Metallic plasmons and carbon dots luminescence interaction

An important recent scientific result was the successful coupling of plasmonic metal nanoparticles with luminescent CD (Zhang et al., 2011; Li et al., 2011). Indeed, the coupling of CD with plasmon metals enhances the CD brightness (metal enhanced fluorescence - MEF) and photostability resulting into better detectability in bioanalytical applications. Two different coupling strategies have been successfully tested that show MEF: CDs immobilized in glass substrates containing silver islands films (SiFs) (Zhang et al., 2011); and, deposition of CDs on the surface of silver nanoparticles mediated with a silica layer (Li et al., 2011).

MEF results from the interaction, within the wavelength of light (near-field conditions), of the luminescent material with the metallic surface plasmons. This interaction provokes an enhancement of the fluorescence of the nanoparticle and reduces the corresponding excited decay times leading to enhanced photostability (Zhang et al., 2011). When the fluorescent nanoparticle is more than one wavelength of light way (far-field conditions) the corresponding quantum yield ( $Q_0$ ) is given by (Zhang et al., 2011):

$$Q_o = \Gamma / (\Gamma + K_{nr})$$

where  $\Gamma$  is the fluorophores' radiative decay rate and  $K_{nr}$  are the nonradiative decay rates for excited state relaxation. Under near-field conditions the quantum yield ( $Q_m$ ) is given by:

$$Q_m = (\Gamma + \Gamma_m) / (\Gamma + \Gamma_m + K_{nr})$$

where  $\Gamma_m$  is the system modified radiative rate. The corresponding far ( $\tau$ ) and near-field ( $\tau_m$ ) lifetimes are given by (Zhang et al., 2011):

$$\tau = 1 / (\Gamma + K_{nr})$$

$$\tau_m = 1 / (\Gamma + \Gamma_m + K_{nr})$$

These equations show that when  $\Gamma_m$  increases, the quantum yield increases (MEF) and the lifetime is reduced (enhanced photostability).

### 5.5 Silicon dots coupled with multi-polar plasmonic hot spots

The metal enhanced fluorescence (MEF) has been investigated for SD (Nychyporuk et al., 2011). Indeed, as discussed above for CD, the photo-stimulated emission of fluorescence of fluorophores suffers a significant enhancement when they are in the vicinity of metal nanoparticles. Stronger fluorescence enhancement is achieved when SD are localized in regions where the photo-induced electric fields from several metal nanoparticles are superimposed (hot spots) (Nychyporuk et al., 2011).

SD were embedded in a silicon nitride matrix ( $\text{SiN}_x$ ) and deposited on a quartz substrate using a chemical vapour deposition technique followed by the fabrication of a monolayer of silver nanoislands on the surface of the  $\text{SiN}_x$  dielectric film and covered by a thin silicon nitride film ( $\text{SiN}_y$ ) containing SD dispersed inside it (Nychyporuk et al., 2011). This procedure resulted in the preparation of 208 nm films ( $\text{SiN}_x$  - 170 nm;  $\text{SiN}_y$  - 38 nm) containing SD with mean diameters between 2 and 4 nm, silver nanoclusters with a mean diameter of  $18 \pm 3$  nm and two adjacent silver islands are separated by about 20 nm distance. Strong MEF was observed in the mean distance between two adjacent silver islands because these places correspond to the photoexcited plasmon hot spots (Nychyporuk et al., 2011). The local plasmon resonance of the silver islands could be tuned in the visible spectral range (400 to 600 nm) by adjusting the  $\text{SiN}_y$  dielectric constant allowing an optimization of the MEF for the SD.

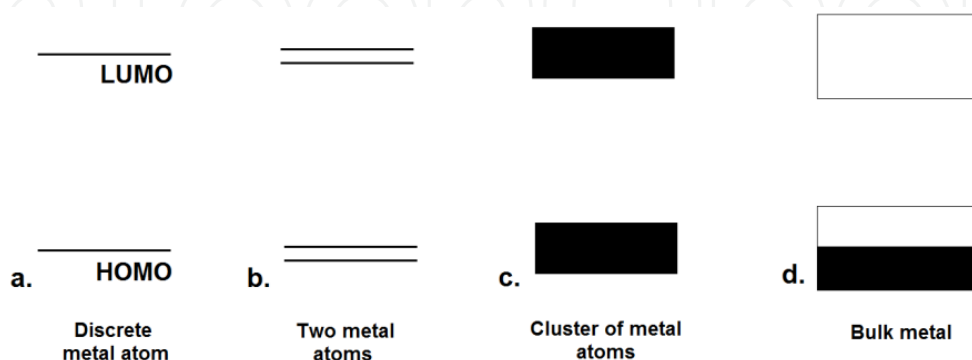


Fig. 7. Schematic representation of the electronic energy level diagram of discrete metal atoms (a.), two metal atoms (b.), clusters of metal atoms (c.) and bulk metallic element (d.).

### 5.6 Carbon dots immobilized in fiber optics

The use of optical sensors in chemical and biological analytical measurements is an expanding area of research with growing importance, especially in biomedical and environmental applications. Indeed, optical sensors are intrinsically immune to electromagnetic interferences and, if properly designed, can show an increased sensitivity, fast response times and suitability to remote monitoring when used with optical fibers (Jorge et al., 2005). The combination of optical fiber technologies with fluorescence spectroscopy has greatly contributed to the progress of optical chemical sensors (Gonçalves et al., 2010; Jorge et al., 2005; Maule et al., 2010). However, the design of sensing heads based on fiber optics requires high quantum yield fluorescent sensors and fluorescent nanomaterials are strong candidates to be coupled to fiber optics (Gonçalves et al., 2010; Jorge et al., 2005; Maule et al., 2010).

CD synthesised by laser ablation and functionalized with N-acetyl-L-cysteine were successfully immobilized (thin of about 750 nm) in the tip of a fiber optic using a sol-gel technology (Gonçalves et al., 2010). Due to the CD functionalization the sensing head selectively and reversibly responds to mercury(II) ions by a quenching mechanism. The response of the nanosensor is fast (less than 10s) and stable. Also, submicromolar concentrations of mercury(II) could be detected and quantified - Stern-Volmer constant (pH=6.8) of  $5.3 \times 10^5 \text{ M}^{-1}$ .

### 5.7 Carbon dots for photocatalyst design

Photoexcited CD have been shown to have redox active properties namely as electron-donor capabilities in reduction reactions (Wang et al., 2009). This property was observed when silver ion was reduced to silver metal upon irradiating with a Xe arc lamp (450 and 600 nm) an aqueous solution of CD silver ions (Wang et al., 2009).

The upconverted photoluminescent and redox properties of CD opened interesting perspectives in its application as energy-transfer agents in photocatalyst design (Li et al., 2010). CD were dispersed on the surface of  $\text{TiO}_2$  and  $\text{SiO}_2$  and their potential in the photocatalytic degradation of methyl blue was assessed using a 50 mg/L solution - after 25 minutes the reduction of methyl blue was almost completed (Li et al., 2010). When undoped  $\text{TiO}_2$  and  $\text{SiO}_2$  or CD alone were used the reduction of methyl blue was nearly inexistent. The observed difference in the reduction yield is due to the relatively large intrinsic band gap of  $\text{TiO}_2$  which has as consequence of only less than 5% of the sunlight is used. When  $\text{TiO}_2$  is doped with CD the full spectrum of sunlight can be used because the nanoparticles absorb visible light and emit at shorter wavelength (325 to 425 nm) which can be used by  $\text{TiO}_2$  and  $\text{SiO}_2$  originating the exciton. This excitation species is responsible for the formation of reactive oxygen species that provokes the degradation of the dyes (Li et al., 2010). Moreover, the presence of CD attached to the oxides surfaces permits the transfer of electrons allowing charge separation, stabilization and hindered recombination with an overall higher activity of the photocatalyst (Li et al., 2010).

### 5.8 Carbon dots for white LED

White light-emitting devices (WLED) are currently an alternative as low energy consumption light sources and liquid-crystal displays among many other technological applications with significant economical advantages (Jang et al., 2010; Wang et al., 2011). CD have been successfully used in the fabrication of an electroluminescent (EL) device that emits a spectrum that approximates natural sun light (Wang et al., 2011).

WLED based CD were assembled using a tri-layer nanocrystal EL device (Wang et al., 2011): a 40 nm thick poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer on the anode; CD with 5 nm diameter with a quantum yield of more than 60%, dispersed in toluene, were spun-casted onto the PEDOT:PSS forming a 20 nm thick film; a 40 nm thick 1,3,4-tris(N-phenylbenzimidazol-2-yl) benzene (TPBI) was used as the electron transporting layer; finally, a 1 nm thick LiF and 120 nm thick Al electrodes were deposited by thermal evaporation. The EL spectrum of this device covers the entire visible zone with a turn-on voltage of about 6 V and a maximum brightness output of 35 cd m<sup>-2</sup>.

### 5.9 Silicon dots for photovoltaic applications

The use of solar cells for the sustainable production of electric energy is a well known strategy that is characterized by its relatively high cost due to the cost of the cell material and relatively low efficiency. SD may contribute significantly for efficiency improving and cost reducing of solar cells (Luo et al., 2011).

One of the most important properties of SD useful for solar cells is their tunability because different bandgap layers, with chemical and thermal compatibility (the same material), can be assembled in multi-junction solar cells. Indeed, a large number of different bandgap layers that match the solar spectrum and raising the efficiency can be assembled using the same growth process because the same SD are being used. Another property of SD, that is common to QDs, is the multi-exciton generation (MEG) and consists in the generation of multiple electron-hole pairs from the absorption of a single photon. MEG may increase considerably the power conversion of solar cells. Also, the possibility of MPE of SD constitutes another factor for increasing the efficiency of solar cells.

## 6. Perspectives

The progresses that are being observed in the synthesis of high quantum yield fluorescent carbon and silicon nanoparticles are opening new technological applications for these intrinsically non-toxic and highly abundant materials. Indeed, in the very near future CD and SD will have an important role in energy conversion systems, new illumination apparatus and catalytic processes.

In the human health sector, namely in medical diagnosis and imaging, CD and SD are becoming an important area of scientific and technological development. Indeed, these nanomaterials with a suitable functionalization can be used in bioimaging methodologies replacing the already established protocols including classical organic dyes and the potentially toxic cadmium based QD. Moreover, CD and SD show multiphoton excitation properties which markedly increase their bioimaging potential.

Consequently, fluorescent carbon and silicon nanomaterials will play an important role in a sustainable development of the earth.

## 7. Acknowledgments

Financial support from Fundação para a Ciência e a Tecnologia (FCT, Lisbon) (Programa Operacional Temático Factores de Competitividade (COMPETE) e participado pelo Fundo Comunitário Europeu FEDER) (Project PTDC/QUI/71001/2006) is acknowledged.

## 8. References

- Akcakir, O.; Therrien, J.; Belomoin, G.; Barry, N.; Muller, J.D.; Gratton, E. & Nayfeh, M. (2000) Detection of luminescent single ultrasmall silicon nanoparticles using fluctuation correlation spectroscopy. *Applied Physics Letters*, 76, 1857-1859, ISSN: 1077-3118.
- Baker, S.N. & Baker, G.A. (2010) Luminescent Carbon Nanodots: Emergent Nanolights. *Angewandte Chemie International Edition*, 49, 6726 – 6744, ISSN: 1521-3773.
- Belomoin, G.; Rogozhina, E.; Therrien, J.; Braun, P.V.; Abuhassan, L. & Nayfeh, M.H. (2002) Effects of surface termination on the band gap of ultrabright Si<sub>29</sub> nanoparticles: Experiments and computational models, *Physical Review B*, 65, 193406, ISSN: 1550-235X.
- Canham, L.T. (1990) Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers, *Applied Physics Letters*, 57, 1046-1048, ISSN: 1077-3118.
- Canham, L.T. (1999) Lewis Acid Mediated Hydrosilylation on Porous Silicon Surfaces. *Journal of the American Chemical Society*, 121, 11491-11492, ISSN: 1520-5126.
- Cao, L.; Wang, X.; Meziani, M.J.; Lu, F.; Wang, H.; Luo, P.G.; Lin, Y.; Harruff, B.A.; Veca, L.M.; Murray, D.; Xie, S.Y. & Sun, Y.P. (2007) Carbon dots for multiphoton bioimaging. *Journal of the American Chemical Society*, 129, 11318-11319, ISSN: 1520-5126.
- Erogbogbo, F.; Tien, C.-A.; Chang, C.-W.; Yong, K.-T.; Law, W.-C.; Ding, H.; Roy, I.; Swihart, M.T. & Prasad, P.N. (2011) Bioconjugation of luminescent silicon quantum dots for selective uptake by cancer cells. *Bioconjugate Chemistry*, 22, 1081-1088, ISSN: 1043-1802.
- Esteves da Silva, J.C.G. & Gonçalves, H. (2011) Analytical and bioanalytical applications of carbon dots. *Trends in Analytical Chemistry*, doi:10.1016/j.trac.2011.04.009, ISSN: 0167-2940.
- Fan, J & Chu, P.K. (2010) Group IV Nanoparticles: Synthesis, Properties, and Biological Applications. *Small*, 6, 2080-2098, ISSN: 1613-6829.
- Fujii, M.; Kovalev, D.; Goller, B.; Minobe, S.; Hayashi, S. & Timoshenko, V.Y. (2005) Time-resolved photoluminescence studies of the energy transfer from excitons confined in Si nanocrystals to oxygen molecules. *Physical Review B*, 72, 165321-165329, ISSN: 1550-235X.
- Gerion, D.; Pinaud, F.; Williams, S.C.; Parak, W.J.; Zanchet, D.; Weiss, S. & Alivisatos, A.P. (2001) Synthesis and Properties of Biocompatible Water-Soluble Silica-Coated CdSe/ZnS Semiconductor Quantum Dots. *Journal of Physical Chemistry B*, 105, 8861-8871, ISSN: 1520-5207.
- Gonçalves, H. & Esteves da Silva, J.C.G. (2011) A New Insight on Silicon dots. *Current Analytical Chemistry*, In revision, ISSN: 1573-4110.
- Gonçalves, H.; Duarte, A. & Esteves da Silva, J.C.G. (2010) Carbon dots based optical fiber sensor for Hg(II). *Biosensors and Bioelectronics*, 26, 1302-1306, ISSN: 0956-5663.
- Hardman, R. (2006) A Toxicological Review of Quantum Dots: Toxicity Depends on Physicochemical and Environmental Factors. *Environmental Health Perspectives*, 114, 165-172, ISSN: 0091-6765.
- Holmes, J.D.; Ziegler, K.J.; Doty, R.C.; Pell, L.E.; Johnston K.P. & Korgel, B.A. (2001) Highly Luminescent Silicon Nanocrystals with Discrete Optical Transitions. *Journal of the American Chemical Society*, 123, 3743-3748, ISSN: 1520-5126.



- Jang, E.; Jun, S.; Jang, H.; Lim, J.; Kim, B. & Kim, Y. (2010) White-Light-Emitting Diodes with Quantum Dot Color Converters for Display Backlights. *Advanced Materials*, 22, 3076–3080, ISSN: 1521-4095.
- Jorge, P.A.S.; Caldas, P.; Esteves da Silva, J.C.G.; Rosa, C.C.; Oliva, A.G.; Farahi, F. & Santos, J.L. (2005) Luminescence-based optical fiber chemical sensors. *Fiber and Integrated Optics*, 24, 201-225, ISSN: 1096-4681.
- Kang, Z.; Liu, Y. & Lee, S.T. (2011) Small-sized silicon nanoparticles: new nanolights and nanocatalysts. *Nanoscale*, 3, 777-791, ISSN: 0306-0012.
- Kang, Z.; Tsang, C.; Wong, N.; Zhang, Z. & Lee, S. (2007) Silicon Quantum Dots: A General Photocatalyst for Reduction, Decomposition, and Selective Oxidation Reactions. *Journal of the American Chemical Society*, 129, 12090-12091, ISSN: 1520-5126.
- Kim, H.M. & Cho, A.B.R. (2009). Two-photon probes for intracellular free metal ions, acidic vesicles, and lipid rafts in live tissues. *Accounts of Chemical Research*, 42, 863-872, ISSN: 1520-4898.
- Ledoux, G.; Gong, J.; Huysken, F.; Guillois, O. & Reynaud, C. (2002) Photoluminescence of size-separated silicon nanocrystals: Confirmation of quantum confinement. *Applied Physics Letters*, 80, 4834-4836, ISSN: 1077-3118.
- Li, Z.F. & Ruckenstein, E. (2004) Water-Soluble Poly(acrylic acid) Grafted Luminescent Silicon Nanoparticles and Their Use as Fluorescent Biological Staining Labels. *Nano Letters*, 4, 1463-1467, ISSN: 1530-6984.
- Li, Q.; Ohulchanskyy, T.Y.; Liu, R.; Koynov, K.; Wu, D.; Best, A.; Kumar, R.; Bonoiu, A. & Prasad, P.N. (2010a) Photoluminescent carbon dots as biocompatible nanoprobe for targeting cancer cells in vitro. *Journal of the Physical Chemistry C*, 114, 12062-12068, ISSN: 1932-7447.
- Li, H.; He, X.; Kang, Z.; Huang, H.; Liu, Y.; Liu, J.; Lian, S.; Tsang, C.H.A.; Xiaobao, X. & Lee, S.T. (2010b) Water-soluble fluorescent carbon quantum dots and photocatalyst design. *Angewandte Chemie International Edition*, 49, 4430-4434, ISSN: 1521-3773.
- Li, J.; Zhang, B.; Wang, F. & Liu, C. (2011) Silver/carbon-quantum-dot plasmonic luminescence nanoparticles. *New Journal of Chemistry*, 35, 554-557, ISSN: 1369-9261.
- Liu, H.; Ye, T. & Mao, C. (2007) Fluorescent Carbon Nanoparticles Derived from Candle Soot. *Angewandte Chemie International Edition*, 46, 6473-6475, ISSN: 1521-3773.
- Liu, R.; Wu, D.; Liu, S.; Koynov, K.; Knoll, W. & Li, Q. (2009) An Aqueous Route to Multicolor Photoluminescent Carbon Dots Using Silica Spheres as Carriers. *Angewandte Chemie International Edition*, 48, 4598-4601, ISSN: 1521-3773.
- Liu, Z.; Zhou X. & Qian, Y. (2010) Synthetic Methodologies for Carbon Nanomaterials. *Advanced Materials*, 22, 1963-1966, ISSN: 1521-4095.
- Lovric, J.; Bazzi, H.S.; Cuie, Y.; Fortin, G.R.A.; Winnik, F.M. & Maysinger, D. (2005) Differences in subcellular distribution and toxicity of green and red emitting CdTe quantum dots. *Journal of Molecular Medicine*, 83, 377-385, ISSN: 1432-1440.
- Luo, Y.; X. Xia, X.; Liang, Y.; Zhang, Y.; Ren, Q.; Li, J.; Jia, Z. & Tang, Y. (2007) Highly visible-light luminescence properties of the carboxyl-functionalized short and ultrashort MWNTs. *Journal of Solid State Chemistry*, 180, 1928-1933, ISSN: 0022-4596.
- Luo, J.-W.; Stradins, P. & Zunger, A. (2011) Matrix-embedded silicon dots for photovoltaic applications: a theoretical study of critical factors. *Energy & Environmental Science*, doi:10.1039/C1EE01026C, ISSN: 1754-5706.



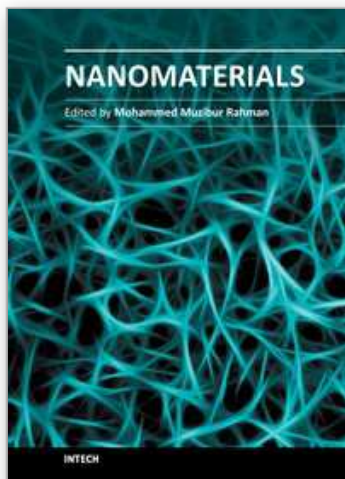
- Manhat, B.A.; Brown, A.L.; Black, L.A.; Ross, J.B.A.; Fichter, K.; Vu, T.; Richman, E. & Goforth, A. (2011) One-step melt synthesis of water-soluble, photoluminescent, surface-oxidized nanoparticles for cellular imaging applications. *Chemistry of Materials*, 23, 2407-2418, ISSN: 1520-5002.
- Mao, X.J.; Zheng, H.Z.; Long, Y.J.; Du, J.; Hao, J.Y.; Wang, L.L. & Zhou, D.B. (2010) Study on the fluorescence characteristics of carbon dots. *Spectrochimica Acta Part A*, 75, 553-557, ISSN: 1386-1425.
- Maule, C.D.; Gonçalves, H.M.R.; Mendonça, C.; Sampaio, P.; Jorge, P.A.S. & Esteves da Silva, J.C.G. (2010) Wavelength encoded analytical imaging and fiber optic sensing with pH sensitive CdTe quantum dots. *Talanta*, 80 1932-1938, ISSN: 0039-9140.
- Murcia, M.J.; Shaw, D.L.; Long, E.C. & Naumann, C.A. (2008) Fluorescence correlation spectroscopy of CdSe/ZnS quantum dot optical bioimaging probes with ultra-thin biocompatible coatings. *Optics Communications*, 28, 1771-1780, ISSN: 0030-4018.
- Nychyporuk, T.; Zakharko, Y.; Serdiuk, T.; Marty, O.; Lemiti, M. & Lysenko, V. (2011) Strong photoluminescence enhancement of silicon quantum dots by their rear-resonant coupling with multi-polar hot spots. *Nanoscale*, 3, 2472-2475, ISSN: 0306-0012.
- Parkhutik, V. & Timashev, S. (2000) Kinetics of porous silicon growth studied using flicker-noise spectroscopy. *Journal of Applied Physics*, 87, 7558-7560, ISSN: 1089-7550.
- Peng, H. & Travas-Sejdic, J. (2009) Simple Aqueous Solution Route to Luminescent Carbogenic Dots from Carbohydrates. *Chemistry of Materials*, 21, 5563-5565, ISSN: 1520-5002.
- Pudzer, A.; Williamson, A.J.; Grossman, J.C. & Galli, G. (2003) Computational studies of the optical emission of silicon nanocrystals. *Journal of the American Chemical Society*, 125, 2786-2791, ISSN: 1520-5126.
- Ray, S.C.; Saha, A.; Jana, N.R. & Sarkar, R. (2009) Fluorescent carbon nanoparticles: synthesis, characterization, and bioimaging application. *Journal of the Physical Chemistry C*, 113, 18546-18551, ISSN: 1932-7447.
- Riggs, J.E.; Guo, Z.; Carroll, D.L. & Sun, Y.P. (2000) Strong Luminescence of Solubilized Carbon Nanotubes. *Journal of the American Chemical Society*, 122, 5879-5880, ISSN: 1520-5126.
- Shi, W.; Wang, Q.; Long, Y.; Cheng, Z.; Chen, S.; Zheng, H. & Huang, Y. (2011) Carbon nanodots as peroxidase mimetics and their applications to glucose detection. *Chemical Communications*, 47, 6695-6697, ISSN: 1364-548X.
- Shirahata, N.; Hasegawa, T.; Sakka, Y. & Tsuruoka, T. (2010) Size-Tunable UV-Luminescent Silicon Nanocrystals. *Small*, 6, 915-921, ISSN: 1613-6829.
- Smith, A.M. & Nie, S. (2010) Semiconductor nanocrystals: structure, properties, and band gap engineering. *Accounts of Chemical Research*, 43, 190-200, ISSN: 1520-4898.
- Steller, H. (1995) Mechanisms and genes of cellular suicide. *Science*, 267, 1445-1449, ISSN: 0036-8075.
- Sun, Y.P.; Zhou, B.; Lin, Y.; Wang, W.; Fernando, K.A.S.; Pathak, P.; Meziani, M.J.; Harruff, B.A.; Wang, X.; Wang, H.F.; Luo, P.J.G.; Yang, H.; Kose, M.E.; Chen, B.L.; Veca, L.M. & Xie, S.Y. (2006) Quantum-sized carbon dots for bright and colourful photoluminescence. *Journal of the American Chemical Society*, 128, 7756-7757, ISSN: 1520-5126.

- Timoshenko, V.Y.; Kudryavtsev, A. A.; Osminkina, L. A.; Vorontsov, A. S.; Ryabchikov, Y.V.; Belogorokhov, I.A.; Kovalev, D. & Kashkarov, P.K. (2006) Silicon nanocrystals as photosensitizers of active oxygen for biomedical applications. *JETP Letters*, 83, 423-426, ISSN: 0370-274X.
- Trani, F. & Barone, V. (2011) Silicon Nanocrystal Functionalization: Analytic Fitting of DFTB Parameters, *Journal of Chemical Theory and Computation*, DOI: dx.doi.org/10.1021/ct1006086, ISSN: 1549-9626.
- Veinot, J.G.C. (2006) Synthesis, surface functionalization, and properties of freestanding silicon nanocrystals. *Chemical Communications*, 4160-4168, ISSN: 1364-548X.
- Wang, X.; Cao, L.; Lu, F.S.; Meziani, M.J.; Li, H.; Qi, G.; Zhou, B.; Harruff, B.A.; Kermarrec, F. & Sun, Y.P. (2009) Photoinduced electron transfers with carbon dots *Chemical Communications*, 3774-3776, ISSN: 1364-548X.
- Wang, F.; Chen, Y.H.; Liu, C.Y. & Ma, D.G. (2011) White light-emitting devices based on carbon dots' electroluminescence. *Chemical Communications*, 3502-3504, ISSN: 1364-548X.
- Warner, J.H.; Dunlop, H.R. & Tilley, R.D. (2005) Highly Luminescent Silicon Nanocrystals with Discrete Optical Transitions. *Journal of the Physical Chemistry B*, 109, 19064-19067, ISSN: 1520-5207.
- Wilcoxon, J.P.; Samara, G.A. & Provencio, P.N. (1999) Optical and electronic properties of Si nanoclusters synthesized in inverse micelles. *Physical Reviews B*, 60, 2704-2714, ISSN: 1550-235X.
- Williams, Y.; Sukhanova, A.; Nowostawska, M.; Davies, A.M.; Mitchell, S.; Oleinikov, V.; Gun'ko, Y.; Nabiev, I.; Kelleher, D. & Volkov, Y. (2009) Probing cell-type-specific intracellular nanoscale barriers using size-tuned quantum dots. *Small*, 5, 2581-2588, ISSN: 1613-6829.
- Williams, R.; Zipfel, W.R. & Webb, W.W. (2001). Multiphoton microscopy in biological research. *Current Opinion in Chemical Biology*, 5, 603-608, ISSN: 1367-5931.
- Xu, X.Y.; Ray, R.; Gu, Y.L.; Ploehn, H.J.; Gearheart, L.; Raker, K. & Scrivens, W.A. (2004) Electrophoretic Analysis and Purification of Fluorescent Single-Walled Carbon Nanotube Fragments. *Journal of the American Chemical Society*, 126, 12736-12737, ISSN: 1520-5126.
- Xu, C.; Zipfel, W.; Shear, J.B.; Williams, R.M. & Webb, W.W. (1996). Multiphoton fluorescence excitation: new spectral windows for biological nonlinear microscopy. *Proceedings of the National Academy of Sciences*, 93, 10763-10768, ISSN: 1091-6490.
- Yang, S.T.; Wang, X.; Wang, H.; Lu, F.; Luo, P.G.; Cao, L.; Meziani, M.J.; Liu, J.H.; Liu, Y.; Chen, M.; Huang, Y. & Sun, Y.P. (2009a) Carbon dots as nontoxic and high-performance fluorescence imaging agents. *Journal of the Physical Chemistry C*, 113, 18110-18114, ISSN: 1932-7447.
- Yang, S.T.; Cao, L.; Luo, P.G.; Lu, F.S.; Wang, X.; Wang, H.F.; Meziani, M.J.; Liu, Y.F.; Qi, G. & Sun, Y.P. (2009b) Carbon dots for optical imaging in vivo. *Journal of the American Chemical Society*, 131, 11308-11309, ISSN: 1520-5126.
- Zhang, Y.; Gonçalves, H.; Esteves da Silva, J.C.G. & Geddes, C.D. (2011) Metal-enhanced photoluminescence from carbon nanodots. *Chemical Communications*, 47, 5313-5315, ISSN: 1364-548X.

Zhu, H.; Wang, X.; Li, Y.; Wang, Z.; Yanga, F. & Yang, X. (2009) Microwave synthesis of fluorescent carbon nanoparticles with electrochemiluminescence properties. *Chemical Communications*, 5118–5120, ISSN: 1364-548X.

IntechOpen

IntechOpen



## **Nanomaterials**

Edited by Prof. Mohammed Rahman

ISBN 978-953-307-913-4

Hard cover, 346 pages

**Publisher** InTech

**Published online** 22, December, 2011

**Published in print edition** December, 2011

The book "Nanomaterials" includes all aspects of metal-oxide nano-structures, nano-composites, and polymer materials instigating with materials survey and preparations, growth and characterizations, processing and fabrications, developments and potential applications. These topics have utilized innovative methods of preparation, improvement, and continuous changes in multidimensional ways. The innovative frontiers are branching out from time to time to advanced nanotechnology. It is an important booklet for scientific organizations, governmental research-centers, academic libraries, and the overall research and development of nano-materials in general. It has been created for widespread audience with diverse backgrounds and education.

### **How to reference**

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Joaquim G. G. Esteves da Silva (2011). Carbon and Silicon Fluorescent Nanomaterials, Nanomaterials, Prof. Mohammed Rahman (Ed.), ISBN: 978-953-307-913-4, InTech, Available from:  
<http://www.intechopen.com/books/nanomaterials/carbon-and-silicon-fluorescent-nanomaterials>

**INTECH**  
open science | open minds

### **InTech Europe**

University Campus STeP Ri  
Slavka Krautzeka 83/A  
51000 Rijeka, Croatia  
Phone: +385 (51) 770 447  
Fax: +385 (51) 686 166  
[www.intechopen.com](http://www.intechopen.com)

### **InTech China**

Unit 405, Office Block, Hotel Equatorial Shanghai  
No.65, Yan An Road (West), Shanghai, 200040, China  
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元  
Phone: +86-21-62489820  
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](https://creativecommons.org/licenses/by/3.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen