Isabel Costas-Mora, Vanesa Romero, Isela Lavilla and Carlos Bendicho*

Luminescent assays based on carbon dots for inorganic trace analysis

DOI 10.1515/revac-2015-0003
Received February 26, 2015; accepted June 24, 2015; previously published online July 22, 2015

Abstract: Carbon dots (CDs) are a recently discovered class of fluorescent nanomaterials with great potential to be applied in the analytical field. CDs have demonstrated to be a promising alternative to conventional organic fluorophores or quantum dots as optical nanoprobes for sensing different chemical species. In this overview, we review the progress in the design of novel nanoprobes based on fluorescent CDs for inorganic trace analysis. Representative examples of CD-based assays are described and the different sensing strategies are discussed.

Keywords: carbon dots; chemiluminescence; fluorescence; inorganic trace analysis; optical sensing.

Introduction

Carbon dots (CDs) are a new type of fluorescent nanostructured material with a size smaller than 10 nm, which have shown interesting properties for their application as optical nanoprobes. These are also known as carbon nanodots, fluorescent carbon nanoparticles (CNPs), or carbon quantum dots (QDs).

CDs were accidently discovered by Xu et al. (2004) during electrophoretic purification of single-walled carbon nanotubes fabricated from arc-discharge soot. Since then, several synthesis pathways have been proposed for obtaining fluorescent CDs, and application for these was found in several areas, including biological, medical, or chemical fields (Baker and Baker 2010, Silva and Gonçalves 2011, Li et al. 2012, Wang and Hu 2014c, Lim et al. 2015).

Semiconductor nanoparticles, also known as QDs, have been extensively used as optical probes due to their interesting optical properties (Freeman and Willner 2012, Frigerio et al. 2012, Li and Zhu 2013, Costas-Mora et al. 2014b). Nevertheless, QDs possess some limitations related to its potential toxicity since these usually contain toxic elements within their composition such as Cd, Se, Te, or As, among others. Compared to QDs and conventional organic dyes, CDs exhibit superior features in terms of high aqueous solubility and resistance to photobleaching, as well as easy functionalization and low toxicity (Bourlinos et al. 2008, Baker and Baker 2010).

In addition, CDs can be fabricated from simple and nontoxic precursors such as carbohydrates (e.g. glucose, fructose, sucrose). The use of this kind of precursor suggests the low toxicity of this nanostructured material and its potential in different areas related with biology and biochemistry.

In the last years, CDs have gained increasing popularity in a wide variety of areas, including photocatalysis, optoelectronic, and especially optical sensing. In this sense, CDs have been applied for detection of biological (Cai et al. 2015, Han et al. 2015, Ma et al. 2015, Mehta et al. 2015, Nandi et al. 2015, Niu et al. 2015, Wu et al. 2015), organic (Huang et al. 2013 Huang et al. 2014a, Hu et al. 2014, Wei et al. 2014, Zhang et al. 2014a, Zhang et al. 2015), and inorganic (Yin et al. 2013, Liu et al. 2014b, Zhang and Chen 2014c, Zhao et al. 2014a, Cui et al. 2015, Gogoi et al. 2015) species. Regarding inorganic trace analysis, a dramatic increase in the number of publications describing CD-based systems has occurred in the last 2 years (Figure 1).

To date, several review articles focused on the synthesis procedures, properties, and general applications of CDs have been published (Baker and Baker 2010, Silva and Gonçalves 2011, Li et al. 2012, Wang and Hu 2014c, Lim et al. 2015), but none of them has tackled specific applications of CDs for detection of inorganic species. In this review, we present an insight into CD-based systems for inorganic trace analysis.

***Corresponding author: Carlos Bendicho,** Facultad de Química, Departamento de Química Analítica y Alimentaria, Área de Química Analítica, Universidad de Vigo, Campus As Lagoas-Marcosende s/n, 36310 Vigo, Spain, e-mail: bendicho@uvigo.es
Isabel Costas-Mora, Vanesa Romero and Isela Lavilla: Facultad de Química, Departamento de Química Analítica y Alimentaria, Área de Química Analítica, Universidad de Vigo, Campus As Lagoas-Marcosende s/n, 36310 Vigo, Spain

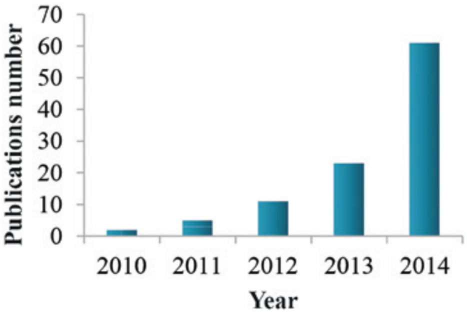

Figure 1: Evolution of the number of publications involving the use of CD-based assays for inorganic trace analysis.

Optical properties of CDs

The main feature accounting for the great interest of many researchers concerning CDs lies on their ability to emit fluorescence. In spite of the fact that the exact mechanism involved in the emission of CDs is still unknown, it is generally attributed to the presence of surface defects generated from chemical oxidation or functionalization (Sun et al. 2006). In addition, the presence of carbon-oxygen bonds seems to be necessary for obtaining fluorescent CDs.

There are several synthetic pathways to synthesize fluorescent CDs, which can be classified as top-down and bottom-up methods. The first group includes treatments by arc-discharge, laser ablation, or electrochemical exfoliation, whereas the latter involves thermic carbonization, electrochemical treatment, and different synthesis methods involving microwave and ultrasound energies (Baker and Baker 2010, Silva and Gonçalves 2011, Li et al. 2012, Wang and Hu 2014c).

Generally, application of top-down methods leads to the formation of nonfluorescent CDs, so additional chemical treatments are essential in order to get fluorescent CDs. Therefore, surface activation and subsequent fluorescence emission are achieved through changes in the superficial states of CDs. To this end, there are three different strategies: (i) acid oxidation of nonfluorescent CDs (Xu et al. 2004, Sun et al. 2006, Bourlinos et al. 2008), (ii) doping of oxidized CDs with inorganic salts (Sun et al. 2008, Wang et al. 2009), and (iii) covering the surface of CDs with an organic polymer (Sun et al. 2006, Sun et al. 2008, Wang et al. 2009). On the other hand, most of the bottom-up procedures are based on the simultaneous synthesis and passivation of CDs leading to the formation of fluorescent CDs via a one-step procedure. Among the synthesis pathways proposed for CDs, bottom-up methods are the most widely used due to their simplicity and low cost, as well as ease of controlling the size, shape, and optical properties of synthesized CDs. One of the properties affected by synthesis procedures is the fluorescence quantum yield (QY). This property depends on the synthesis pathway (Sun et al. 2006, Li et al. 2012) and surface ligand nature (Sun et al. 2006, Hu et al. 2009, Peng and Travas-Sejdic 2009).

As is shown in Table 1, the main limitation of CDs resides on the relatively low fluorescence QY, which usually are lower than 15%, so new synthesis and doping procedures for CDs are currently being investigated.

Thus, Bhaisare et al. (2015) synthesized CDs with a QY of 42% by hydrothermal treatment of sucrose, whereas Yu et al. (2015) developed a novel synthesis pathway making use of a plant of Jinhua bergamot as carbon source, which allows obtaining highly fluorescent CDs, with a QY of about 50%.

In addition, Wang et al. (2015c) fabricated organosilane functionalized CDs, which are amphiphilic so that they can display multisolvent dispersibility. These CDs are dispersable in water and other common organic solvents (i.e. dimethyl sulfoxide, methanol, dimethylformamide, acetone, ethanol, tetrahydrofuran, toluene, and hexane). As-prepared CDs have a QY of 51%.

Another synthesis strategy providing highly fluorescent CDs (QY=52%) was proposed by Zhou et al. (2015). These workers used citric acid and Tris as precursors to generate CDs by hydrothermal treatment.

On the other hand, several studies have been carried out for doping CDs so that their optical properties are improved. As occurs with QDs, coating of CD surface with inorganic compounds such as ZnS, ZnO, or TiO_2 causes a significant improvement in the fluorescence properties of the CDs (Anilkumar et al. 2011, Shen et al. 2012). As mentioned above, the ability of CDs to emit fluorescence seems to be related to the presence of energy traps or superficial defects. The covering of these traps during passivation allows the radiative recombination of trapped electrons and holes, thus facilitating fluorescence emission. For this reason, the improvement of surface passivation causes the enhancement of CD fluorescence intensity. Among the different doping strategies applied so far, doping with inorganic species and further passivation with organic ligands are the ones providing a relevant increase in fluorescence QY, which can reach values up to 78% (Anilkumar et al. 2011).

Undoubtedly, N is the doping species most widely used to improve the optical properties of CDs, since experimental procedures to introduce N in the CD structure are relatively fast and simple (Barman and Sadhukhan 2012, Barman et al. 2014, Liu et al. 2014a, Qian et al. 2014a, Tang

Table 1: Properties of CDs synthesized from different precursors under different synthesis treatments.

Synthesis method	Precursor	Size (nm)	Surface ligand	QY (%)	References
Laser ablation	Graphite powder and cement	5	PEG_{1500N}	4–0	Sun et al. 2006
	Graphite powder and cement	5	PPEI-EI	4–10	Sun et al. 2006
	Graphite	3.2	PEG_{200}	3–8	Hu et al. 2009
Arc-discharge	SWCNTs			1.6	Xu et al. 2004
Electrochemical treatment	CNTs	2.8		6.4	Zhou et al. 2007
	Graphite	2–10		2.8–5.2	Lu et al. 2009
	Graphite	5		0.81	Wang et al. 2014b
	Glycine	2.4		27.1	Wang et al. 2014a
	Ethanol	2.1–4.3		4–15.5	Deng et al. 2014
Hydrothermal treatment	MWCNTs	3	Acetone	10	Cayuela et al. 2013
	Lactose	1.5	Tris	12.5	Zhang et al. 2013
	EG	0.7–4		25	Liu et al. 2012c
	Glucose	7.5	PEI	3.5	Han et al. 2012
	Glucose	1.8–3.8		2.4–1.1	Yang et al. 2011
	Dopamine	3.8		6.4	Qu et al. 2013
	Sucrose	1.84		21.6	Chen et al. 2013
	Sucrose	5		42	Bhaisare et al. 2015
	Bergamot	10		50.87	Yu et al. 2015
Ultrasonic treatment	Glucose	<5		7	Li et al. 2011a
	Active carbon	5–10		5	Li et al. 2011b
Microwave treatment	Citric acid	2.2–3	EDA	30.2	Zhai et al. 2012
	Glycerol	3.5	TTDDA	12.02	Liu et al. 2011
	Glycerol	7	BPEI	7–15.3	Liu et al. 2012a
	Glycerol	2.1		3.2	Chen et al. 2011
	Saccharide	2.7–3.6	PEG	3.1–6.3	Zhu et al. 2009
	Glycerin	3–4	PEG	12	Lin et al. 2011
	Citric acid	12	PEI	30	Salinas-Castillo et al. 2013
	[BMIM][Br]	2–6		19.76	Zhao et al. 2014a
	[BMIM][BF_4]	2–6		25.8	Zhao et al. 2014a

[BMIM][BF_4], 1-butyl-3-methylimidazolium tetrafluoroborate; [BMIM][Br], 1-butyl-3-methylimidazolium bromide; BPEI, branched poly(ethyleneimine); CNTs, carbon nanotubes; EDA, ethylenediamine; EG, ethyleneglycol; MWCNTs, multiwalled carbon nanotubes; PEG, poly(ethyleneglycol); PEI, poly(ethylenimine); PPEI-EI, poly(propionylethyleneimine-co-ethyleneimine); SWCNT, single-walled carbon nanotubes; Tris, tris(hydroxymethyl)aminomethane; TTDDA, 4,7,10-trioxa-1,13-tridecanediamine.

et al. 2014, Wu et al. 2014b, Yang et al. 2014, Xu et al. 2015b). It must be mentioned that despite these advantages, QY reached are lower than those achieved by the introduction of inorganic compounds. Usually, these vary in the range of 30%–40%, although some works reported QYs of up to 64% (Barman et al. 2014). The QY of doped CDs depends on the introduced species. Yang et al. (2014) investigated the effect of doping CDs with different species over QY. CDs synthesized prior to doping procedure had a fluorescence QY of 6%, whereas the introduction of N, S, or Se caused an enhancement of QY reaching values of 39%, 24% and 19%, respectively. In addition, the introduction of these doping species affects the emission wavelength. Although N is the most extended doping species used up to date, in the last years, some works dealing with doping species such as B (Shan et al. 2014), S (Xu et al. 2015a), P (Zhou et al. 2014), or Si (Qian et al. 2014b) have been published.

Another strategy that allows achieving high fluorescence QY lies on the introduction of two doping species. To date, some combinations have been reported, including N-S (Dong et al. 2013, Ding et al. 2014, Mohapatra et al. 2015), N-P (Barman et al. 2014), N-Al (Wang et al. 2015b), N-B (Barman et al. 2014), and N-Mn (Li et al. 2014). Among the mentioned combinations, QYs obtained by the combinations of N-S, N-P, and N-Mn, which are 54%–73%, 70%, and 83%, respectively, must be highlighted.

Table 2 shows the QYs of doped CDs following the different strategies mentioned above. Therefore, the doping of CDs offers a way to solve the limitation of the low fluorescence QY that is generally reached.

Table 2: Quantum yield of doped CDs with several species and following different strategies.

Doping species	QY (%)	References
ZnO	45	Sun et al. 2008
ZnS	50	Sun et al. 2008
ZnS	78	Anilkumar et al. 2011
TiO_2	70	Anilkumar et al. 2011
N	32	Xu et al. 2015b
N	29	Barman and Sadhukhan 2012
N	35	Tang et al. 2014
N	15.7	Zhang and Chen 2014c
N	13–22	Teng et al. 2014
N	36.3	Qian et al. 2014a
N	37.4	Liu et al. 2014a
N	36.5	Wu et al. 2014b
N	64	Barman et al. 2014
N	39	Yang et al. 2014
S	24	Yang et al. 2014
S	67	Xu et al. 2015a
Se	19	Yang et al. 2014
B	14.8	Shan et al. 2014
P	25	Zhou et al. 2014
Si	19.2	Qian et al. 2014b
N, S	54.4	Ding et al. 2014
N, S	69	Mohapatra et al. 2015
N, S	73	Dong et al. 2013
N, P	70	Barman et al. 2014
N, Al	25.7	Wang et al. 2015b
N, B	39	Barman et al. 2014
N, Mn	83	Li et al. 2014

A relevant feature of CDs is the strong influence of excitation wavelength over both emission wavelength and fluorescence intensity (Sun et al. 2006, Chen et al. 2011, Li et al. 2011a,b, Han et al. 2012, Lai et al. 2012, Lin et al. 2012, Liu et al. 2012c, Ma et al. 2012, Shen et al. 2012, Zhai et al. 2012, Du et al. 2013, Liu et al. 2013b, Zhang et al. 2013). Therefore, it is possible to change the emission wavelength merely by modification of the excitation wavelength, which allows working in a wide spectral range, i.e. from UV to near-infrared. It must be mentioned that several synthesized CDs have up-conversion properties, so they are able to emit fluorescence at a wavelength shorter than that of excitation (Li et al. 2011a,b, Ma et al. 2012, Liu et al. 2013b, Zhang et al. 2013). The up-conversion properties can be ascribed to multi-photon activation process, in which the simultaneous absorption of two or more photons leads to the emission at a shorter wavelength, which is known as anti-Stokes type emission. This attractive optical property enables promising applications.

As was mentioned, one of the most interesting features of CDs is their high stability. The pH of the medium is one of the main factors influencing both the stability and optical properties of CDs due to the protonation or deprotonation of capping ligands. This limitation is overcome by the selection of the appropriate capping ligand depending on the working pH. To date, several CD-based pH sensors have been developed taking advantage of this limitation (Jia et al. 2012, Mao et al. 2013, Kong et al. 2014, Nie et al. 2014, Pedro et al. 2014, Wu et al. 2014b, Wang et al. 2015a, Jin et al. 2015).

Application of CDs as optical probes for inorganic analysis

The optical properties mentioned in the previous section have been exploited for developing several CD-based optical nanoprobes.

Even though fluorescence is the optical property most widely exploited to develop CD-based probes, their ability to emit chemiluminescence (CL) and electrochemiluminescence (ECL) has also been used to construct novel detection approaches for inorganic species (Figure 2).

As can be observed, most of CD-based nanoprobes developed to date are based on fluorescent sensing, with metal ions such as Cu(II), Hg(III), and Fe(III) being the analytes most widely investigated. Table 3 shows some features of selected works based on the use of CDs as optical probes for the detection of inorganic species.

CDs as fluorescent probes

Besides sensing approaches making use of quenching or fluorescence enhancement, assays based on fluorescence resonance energy transfer (FRET), ratiometric, reversible

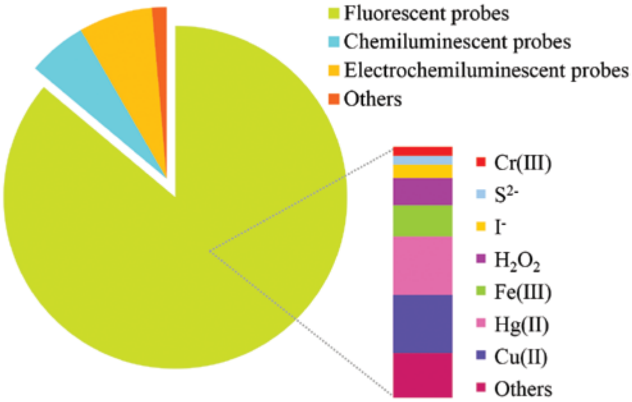

Figure 2: Inorganic species studied by different detection techniques involving the use of CD-based assays.

Table 3: CD-based systems developed for inorganic species detection.

Analyte	CD synthesis method/ precursor	Capping ligand	Effect on CD emission	Linear range	LOD	Sensing mechanism	References
Ag(I)	HT/EG		Fluorescence enhancement	$0–9\times10^{-5}$ M	3.9×10^{-7} M	Reduction of Ag^+ to Ag nanoclusters on the surface of CDs	Gao et al. 2015
ClO^-	HT/pepper		Fluorescence quenching	$1\times10^{-7}–1\times10^{-5}$ M $1\times10^{-5}–3\times10^{-4}$ M	5×10^{-8} M 6×10^{-8} M	Oxidation of functional groups of CDs	Yin et al. 2013
ClO^-	MW/sucrose		Fluorescence quenching	$2\times10^{-7}–2\times10^{-6}$ M	1.5×10^{-8} M	Oxidation of CDs	Huang et al. 2014b
CH_3Hg^+	US/fructose-PEG-NaOH	PEG	Fluorescence quenching	$2.3\times10^{-8}–2.8\times10^{-7}$ M	5.9×10^{-9} M	Ultrasound-assisted permeation of CH_3Hg^+ through PEG passivation coating leading to electron transfer process	Costas-Mora et al. 2014a
Co(II)	HT/cysteine		Fluorescence quenching	$10\times10^{-9}–1\times10^{-4}$ M	10×10^{-9} M	Formation of Co_xS_y NPs and aggregation of CDs	Li et al. 2015
Cu(II)	HT/citric acid	BPEI	Fluorescence quenching	$1\times10^{-8}–1.1\times10^{-6}$ M	6×10^{-9} M	Complex formation between capping ligand and Cu(II)	Dong et al. 2012
Cu(II)	MW/glucose	BSA-Lys	Fluorescence quenching	$2\times10^{-12}–1.5\times10^{-9}$ M	5.8×10^{-13} M	Coordination of Cu(II) with $-NH_2$ and -COOH groups of lysine	Liu et al. 2012b
Cu(II)	EC/graphite	TPEA	Fluorescence quenching	$1\times10^{-6}–1\times10^{-4}$ M	1×10^{-8} M	Binding of Cu(II) and TPEA	Qu et al. 2012
Cu(II)	MW/citric acid	PEI	Fluorescence quenching	$3\times10^{-7}–1.6\times10^{-6}$ M	9×10^{-8} M		Salinas-Castillo et al. 2013
					1.2×10^{-7} M		
Cu(II)	HT/bamboo leaves	BPEI	Fluorescence quenching	$3.3\times10^{-7}–6.6\times10^{-5}$ M	1.1×10^{-7} M	Displacement of capping ligand due to its coordination with Cu(II)	Liu et al. 2014c
Cu(II)	MW/[BMIM][Br]	IMD groups	Fluorescence quenching		5×10^{-9} M	Binding of Cu(II) with N of IMD groups	Zhao et al. 2014a
Cu(II)	AO/CNPs N-doped		Fluorescence quenching	$1\times10^{-8}–2\times10^{-7}$ M	5×10^{-9} M	Cu(II) interaction with C-N groups of CDs	Yang et al. 2014
Cu(II)	HT/OPD	OPD	Fluorescence enhancement	$2\times10^{-9}–8\times10^{-8}$ M	1.8×10^{-9} M	Complex formation of $Cu(OPD)_2$ in the CD surface	Vedamalai et al. 2014
Cu(II)	HT/AEAPMS	EDA groups	Ratiometric	$0–3\times10^{-6}$ M	3.5×10^{-8} M	Cu(II) interaction with superficial EDA groups	Liu et al. 2014b
Cu(II)	EQ/graphite	TPEA	Enhancement of electric current	$1\times10^{-6}–6\times10^{-5}$ M	1×10^{-7} M		Shao et al. 2013
F^-	MW/glucose-PEG	PEG	Fluorescence quenching	$1\times10^{-4}–1\times10^{-2}$ M	3.1×10^{-8} M	Interaction between F^- and CD capping ligand	Liu et al. 2013a
Fe(III)	Heating of banana peel and further MW		Fluorescence quenching	$2\times10^{-6}–1.6\times10^{-5}$ M	2.1×10^{-7} M	Interaction of Fe(III) with CD capping ligands	Vikneswaran et al. 2014
Fe(III)	MW/[BMIM][BF_4]	OH groups	Fluorescence quenching		2×10^{-8} M	Binding of Fe(III) with superficial OH groups	Zhao et al. 2014a
Fe(III)	MW/AA-PEG	PEG	ECL ratio	$5\times10^{-6}–8\times10^{-5}$ M	7×10^{-7} M		Zhang et al. 2014b
Fe(III)	MW/Bergamot		Fluorescence quenching	$2.5\times10^{-8}–1\times10^{-4}$ M	7.5×10^{-8} M		Yu et al. 2015
Hg(II)	MW/Bergamot		Fluorescence quenching	$1\times10^{-8}–1\times10^{-4}$ M	5.5×10^{-9} M		Yu et al. 2015
Hg(II)	HT/citric acid	AEAPMS	Fluorescence quenching	$0–5\times10^{-6}$ M	1.35×10^{-9} M	Complex formation between amino groups and Hg(II)	Wang et al. 2015c

Table 3: (continued)

Analyte	CD synthesis method/ precursor	Capping ligand	Effect on CD emission	Linear range	LOD	Sensing mechanism	References
Hg(II)	HT/folic acid	EG	Fluorescence quenching	$0–2.5\times10^{-7}$ M	2.3×10^{-7} M	Superficial changes of CDs	Zhang and Chen 2014c
Hg(II)	HT/EDTA salts		Fluorescence quenching	$0–3\times10^{-6}$ M	4.2×10^{-9} M	Charge transfer between Hg(II) and CDs	Zhou et al. 2012
Hg(II)	AO/CNPs S-doped		Fluorescence quenching	$2\times10^{-9}–2\times10^{-6}$ M	2×10^{-9} M	Hg(II) interaction with superficial SH groups	Yang et al. 2014
Hg(II)	HT/PEG-NaOH		Fluorescence quenching	$0–1\times10^{-8}$ M	1×10^{-15} M	Hg coordination with oxygen-rich superficial groups of CDs	Liu et al. 2013b
Hg(II)	MW/flour		Fluorescence quenching	$5\times10^{-10}–1\times10^{-8}$ M	5×10^{-10} M		Qin et al. 2013
Hg(II)	HT/citric acid-EG	ODN	Fluorescence recovery	$5\times10^{-9}–2\times10^{-7}$ M	2.6×10^{-9} M	Complex formation of Hg(II)/ODN and subsequent displacement of GO	Cui et al. 2015
H_2O_2	AO/carbon		Colorimetry	$1\times10^{-8}–1\times10^{-5}$ M	1×10^{-8} M	Catalysis of TMB substrate oxidation leading to formation of blue solution	Zheng et al. 2013
I^-	MW/citric acid-EG		Turn off-on	$5\times10^{-7}–2\times10^{-5}$ M	4.3×10^{-7} M	Complex formation and subsequent Hg(II) displacement causing fluorescence recovery	Du et al. 2013
K^+	HT/candle	EDA	FRET (fluorescence recovery)	$5\times10^{-5}–1\times10^{-2}$ M	1×10^{-5} M	Inhibition of FRET process due to the binding of the analyte in the place of crown-ether	Wei et al. 2012

AO, acid oxidation; EC, electrochemical treatment; HT, hydrothermal treatment; MW, microwave treatment; US, ultrasound treatment; AA, ascorbic acid; AEAPMS, *N*-(β-aminoethil)-γ-aminopropyl methyldimethoxy silane; [BMIM][BF_4], 1-butyl-3-methylimidazolium tetrafluoroborate; [BMIM][Br], 1-butyl-3-methylimidazolium bromide; BPEI, branched poly(ethylenimine); BSA, bovine serum albumin; CNPs, carbon nanoparticles; EDA, ethylenediamine; EG, ethyleneglycol; GO, graphene oxide; IMD, imidazole; Lys, lysine; NP, nanoparticle; ODN, oligodeoxyribonucleotide; OPD, o-phenylenediamine; PEG, poly(ethyleneglycol); PEI, poly(ethylenimine); TMB, 3,3,5,5-tetramethylbenzidine; TPEA, *N*-(2-aminoethyl)-*N*,*N'*,*N'*-tris(pyridine-2-yl-methyl) ethane-1,2-diamine).

and up-conversion nanoprobes have also been developed. Figure 3 shows relevant sensing mechanisms involved in the use of CDs as fluorescent nanoprobes to detect inorganic species.

Probes based on changes of CDs fluorescence

As is shown in Figure 2, most CD-based fluorescent probes use direct measurements of fluorescence changes caused by the interaction with the target analyte.

The most widely observed effect is the fluorescence quenching of CDs when these interact with inorganic species. This effect is observed in 90% of the CD-based systems developed to date. Analytes mostly investigated are Cu(II), Hg(II), and Fe(III).

Recently, Zhao et al. (2014a) reported a novel fluorescent assay using CDs synthesized from two different ionic liquids (i.e. 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF_4], and 1-butyl-3-methylimidazolium bromide, [BMIM][Br]). The use of different precursors leads to the formation of different functional groups. CDs fabricated from [BMIM][Br] have imidazol groups in the CD surface, whereas those synthesized from [BMIM][BF_4] are rich in hydroxyl surface groups. These CDs obtained from [BMIM][Br] have a great selectivity for Cu(II), whereas those fabricated from [BMIM][BF_4] allow the selective detection of Fe(III).

As was mentioned, several novel methods have been developed for the sensitive detection of Cu(II). Among them, the work performed by Dong et al. (2012) must be highlighted since it allows the detection of Cu(II) at picomolar levels (LOD=0.58 pM). This assay is based on the use of CDs functionalized with bovine serum albumin (BSA) and lysine. In the presence of Cu(II), the fluorescence intensity of the system was quenched probably due to the coordination of Cu^{2+} with the carboxyl group and amino group of lysine and glycine of partial uncoated CD-BSA. The applicability of this approach for Cu(II) detection in hair and water samples was demonstrated.

As indicated above, Hg(II) has also been detected using CD-based systems. Among the developed methods, those relying on changes in fluorescence intensity are mostly employed for detection.

The fabrication of N-doped CDs from folic acid, which acts as C and N source at the same time, has been reported

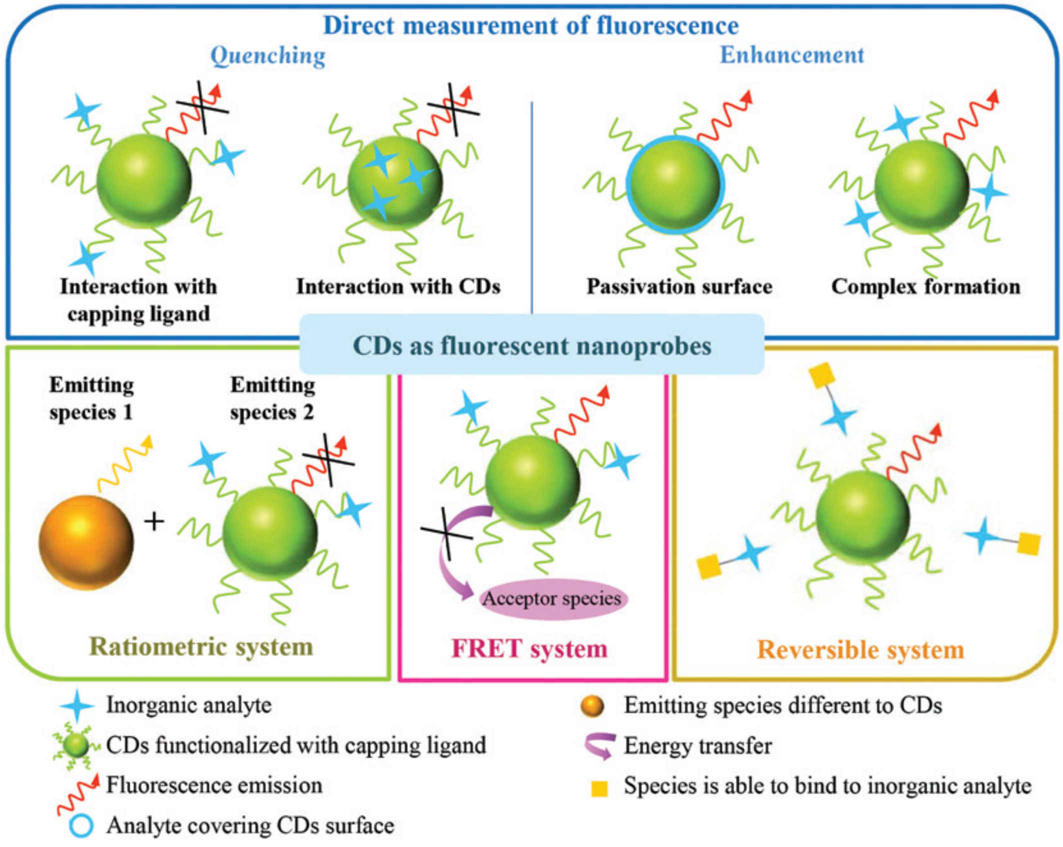

Figure 3: Processes involved in the sensing mechanisms using CD-based assays.

(Zhang and Chen 2014c). As-prepared CDs display great sensitivity toward Hg(II), thus allowing its detection.

Another interesting method was designed by Zhou et al. (2012) for detection of Hg(II) and biothiols in complex matrices. In this system, the presence of Hg(II) causes the fluorescence quenching of CDs due to a charge transfer process. Initial fluorescence intensity is recovered when CD-Hg interact with biothiols due to the great affinity of thiol groups toward Hg(II), which causes the displacement of Hg(II) from the CD surface.

Liu et al. (2013b) have reported an extremely sensitive assay for the detection of Hg(II). In this assay, a detection limit of 1 fM is reached using CDs synthesized from poly(ethylene glycol) (PEG) and NaOH. In addition, the applicability of the proposed method was demonstrated in different water samples. Other assays showing high sensitivity for Hg(II) detection were developed by Qin et al. (2013) and Yang et al. (2014). The former group synthesized CDs from flour to generate a fluorescent probe that allows reaching a detection limit (LOD) of 0.5 nM Hg(II). In the second paper, CDs doped with different heteroatoms including N, S, or Se were tried for detecting metal ions. The obtained results suggest that N-doped CDs display a great sensitivity toward Cu(II), whereas S-doped CDs are suitable for Hg(II) detection. LODs were 5 and 2 nM for Cu(II) and Hg(II), respectively.

Yu et al. (2015) used a plant of Jinhua bergamot as carbon source to obtain highly fluorescent CDs with a QY of about 50%. As-prepared CDs were applied as optical probes for Hg(II) and Fe(III) detection through fluorescence quenching effects. LODs were 0.075 μM and 5.5 nM for Fe(III) and Hg(II), respectively.

Another CD-based system that allows the detection of Hg(II) at nanomolar levels was recently developed by Wang et al. (2015c). This system is based on CDs functionalized with organosilane and allows achieving a LOD as low as 1.35 nM.

Moreover, our group developed a novel assay for the sensitive and selective detection of CH_3Hg^+ (Costas-Mora et al. 2014a). This method is based on the integration of synthesis and detection processes in a single step, which is accomplished by the use of high-intensity ultrasound energy. The applicability of the proposed method for CH_3Hg^+ detection was demonstrated by analyzing different reference certified materials of water and marine animal tissues. Some remarkable features of the method are its simplicity, sensitivity, and rapidity. A LOD of 5.9 nM CH_3Hg^+ was reached with this assay.

Besides metal ions, other inorganic species have been detected by CD-based systems. Among them, H_2O_2 is one of the most widely studied. B-doped CDs were used for H_2O_2 and glucose detection (Shan et al. 2014). One of the most relevant features lies in the increased sensitivity achieved due to the CD doping process. The LOD reached with B-doped CDs is 10 mM. Yeh et al. (2013) have reported another CD-based system for H_2O_2 and glucose detection. In this work, reduced graphene oxide (RGO) with incorporated CDs (CDs@RGO) is employed to accomplish the recognition event. Fluorescence quenching of CDs is produced due to its interaction with reactive oxygen species (ROS). Nevertheless, the presence of H_2O_2 in the reaction medium inhibits the ROS effect, and thus, a fluorescence enhancement is observed. A LOD of 140 nM H_2O_2 is reached.

In spite of the fact that fluorescence enhancement caused by inorganic analytes is scarcely observed, there are some relevant approaches reported to date.

Gao et al. (2015) observed that Ag(I) caused the fluorescence enhancement of CDs, which can be attributed to the reduction of Ag(I) to generate silver nanoclusters on the CD surface. The LOD obtained following the above strategy was 320 nM of Ag(I).

Probes based on FRET processes

Until now, FRET processes have been scarcely used to detect inorganic species. A novel sensor has been described by Cui et al. (2015) using CDs functionalized with oligodeoxyribonucleotide (ODN) for the detection of Hg(II). When CDs are in the presence of GO, fluorescence quenching is produced due to a FRET process. Nevertheless, when Hg(II) is introduced in the mixture, the displacement of GO occurs due of the formation of a complex between Hg(II) and thymine from ODN, so the recovery of fluorescence is produced. With this detection strategy, a LOD of 2.6 nM is achieved.

Another work based on FRET was conducted by Wei et al. (2012). This system uses CDs in conjunction with an ion-selective crown ether and graphene to develop a FRET system that is highly selective for K^+ detection. CDs act as donor species, whereas graphene does it as acceptor ones. Therefore, FRET is inhibited by the presence of K^+ due to a competitive process between the ammonium group of crown-ether and the target analyte, hence causing the fluorescence recovery of CDs.

Ratiometric probes

Ratiometric probes are based on the calculation of a fluorescence ratio of the quenched and constant reference fluorescence signals. It allows correction of some instrumental variations and provides improved sensitivity.

A ratiometric probe to detect Hg(II) was reported by Cao et al. (2013) using CDs and QDs as emitting species. The solution containing blue-emission CDs and red-emission CdSe/ZnS QDs exhibits dual emissions at 436 nm and 629 nm under a single excitation wavelength. The interaction of Hg(II) with QD functional capping groups causes the fluorescence quenching of QDs, whereas CD fluorescence remains constant, so Hg(II) can be monitored by fluorescence color evolution from red to blue. This strategy constitutes a simple way for visual detection of Hg(II).

In addition, Yan et al. (2015) reported a novel nanohybrid ratiometric fluorescence probe for NO_2 determination. This system uses blue-colored CDs in conjunction with red-colored QDs. CD fluorescence is not affected by NO_2, whereas it causes the fluorescence quenching of QDs. This leads to a distinguishable color change from orange-red to blue in the presence of NO_2, which allows achieving a LOD of 19 nM. Moreover, this system allows the visual detection of NO_2 with a LOD of 1 ppm.

Lastly, a FRET-based ratiometric probe for H_2O_2 detection was recently fabricated by Wu et al. (2014a). Herein, CDs act as energy donor and recognition element for H_2O_2. It was demonstrated for the first time that this FRET-based nanoprobe serves to detect H_2O_2 *in vivo* using zebrafish as a vertebrate model. It was found that CDs are accumulated in the abdominal region of the zebrafish, and the majority of them are excreted within 4 h without causing apparent toxicity. The LOD of the method is 0.5 μM H_2O_2.

Reversible probes

In recent years, reversible systems have emerged as a new detection strategy, which is characterized by its high selectivity. These systems involve two steps: (i) fluorescence quenching and (ii) fluorescence recovery.

Regarding CD-based reversible probes, it should be mentioned that a few systems based on the use of turn off-on strategies have been developed to date.

There are some works that exploit the fluorescence quenching caused by Cu(II) and the further recovery of CD fluorescence to develop novel CD-based reversible probes (Hou et al. 2013, Zong et al. 2014). On the one hand, Zong et al. (2014) reported a new method for Cu(II) and L-cysteine detection by a turn off-on strategy. Quenching of CD fluorescence is due to Cu(II) adsorption onto the CDs surface (off). The addition of L-cysteine causes the fluorescence recovery of CDs (on) as a result of its great affinity toward Cu(II), which is displaced from CD surface. Herein, LODs for Cu(II) and L-cysteine are 23 and 0.34 nM, respectively.

On the other hand, a novel reversible sensor for S^{2-} detection has been reported by Hou et al. (2013). This system is based on the use of CDs whose capping ligand has great affinity toward Cu(II). When it is present in the sample, Cu(II) binds to CD capping ligand, causing fluorescence quenching. Nevertheless, the subsequent addition of S^{2-} causes the displacement of Cu(II) to form CuS and, in turn, the recovery of CDs fluorescence.

In addition, Teng et al. (2014) synthesized N-doped CDs from pyrolyzed flour to develop a turn off-on system. This is based on the quenching of CD fluorescence caused by the presence of Fe(III) as a result of an electron transfer process and the fluorescence recovery due to the interaction with L-cysteine, which also causes a shift in the emission wavelength.

Another turn off-on CD-based system was described by Du et al. (2013). This assay is focused on iodide detection using CDs whose fluorescence was previously quenched by Hg(II). Therefore, the formation of a complex between iodide and Hg(II) causes the elimination of Hg(II) from CD surface and, thus, the recovery of CD fluorescence. This system allows detection of iodide in urine samples at very low concentrations, with a LOD of 430 nM of iodide being achieved.

Moreover, Wang et al. (2015d) synthesized polyaniline/CD nanocomposites, which are nonfluorescent due to the quenching caused by the presence of polyaniline. Nevertheless, the addition of Hg^{2+} caused the release of polyaniline from CDs due to the strong binding affinity between Hg^{2+} and amino groups and, in turn, the fluorescence restoration of CDs. This strategy allows reaching a LOD of 0.8 nM.

Recently, Gu et al. (2015) designed an off-on fluorescent probe to detect Au(III) and glutathione. The introduction of Au(III) on fluorescent CDs leads to fluorescence quenching due to the formation of the complex Au(III)/CD. Nevertheless, when biothiols are added to the mixture, fluorescence restoration occurs, being especially significant for glutathione. Following this strategy, LODs of 0.48 and 2.02 μM for Au(III) and glutathione are reached.

Up-conversion probes

As was mentioned above, many synthesis approaches give rise to CDs that are able to emit fluorescence at low wavelength when they are excited at larger wavelength. This phenomenon is known as up-conversion fluorescence.

An assay using the down- and up-conversion properties of CDs was proposed by Yin et al. (2013) to determine hypochlorite. The authors found two linear ranges, which allow the determination of hypochlorite in a wide concentration range (i.e. 0.1–10 and 10–300 μM of hypochlorite). As in the work mentioned above, the sensitivity of the CD-based assay depends on the excitation wavelength. LODs of 0.05 and 0.06 μM were achieved using down- and up-conversion properties, respectively.

CDs as chemiluminescent probes

To date, only a few works have been reported based on the use of CDs in conjunction with CL to detect inorganic species.

Recently, Zhao et al. (2014b) demonstrated the ability of CDs functionalized with branched poly(ethyleneimine) to detect Fe(III) in alkaline medium by direct measurements of CL. It was found that Fe(III) is retained onto the CD surface and it acts as oxidant species, thus causing the enhancement of the CL signal. This new method allows the selective and sensitive detection of Fe(III), with a LOD of 66.7 nM being reached.

In addition, Lin et al. (2015) proposed the use of peroxynitrous acid-carbonate-CDs system for nitrite sensing. In this system, CDs act as energy acceptor. This method allows achieving a LOD of 5.0 nM of nitrite.

Lastly, some works based on the use of ECL have been reported. Zhang et al. (2014b) developed a novel method where a dual peak of ECL is used to detect Fe(III). The use of ECL dual peak allows achievement of higher sensitivity in comparison with those based on the use of single-peak. Therefore, a linear range of 5–80 μM and LOD of 0.7 μM were achieved. The main feature of the proposed system is the minimization of the typical instability of ECL methods to detect metal ions, since Fe(III) determination is performed after establishing the ratio of ECL peaks.

An ECL probe based on the use of Ag-CD nanocomposite was described by Wang et al. (2014d) to detect S^{2-}. The affinity of the target analyte and Ag attached to CDs was the responsible for ECL changes and the subsequent ability of the proposed system to detect S^{2-}.

Other strategies for detection of inorganic species

A minor group of detection strategies making use of CDs are commented in this section. Regarding colorimetric detection, Zheng et al. (2013) designed a CD-based system for sensitive determination of H_2O_2, reaching a detection limit of 10 nM. This method is based on the catalytic effect produced by H_2O_2, which leads to the formation of a colored solution. In addition, the applicability of the proposed system in biological samples was demonstrated.

On the other hand, Shao et al. (2013) developed a novel method based on the use of CDs functionalized with *N*-(2-aminoethyl)-*N*,*N′*,*N′*-tris(pyridine-2-yl-methyl)ethane-1,2-diamine) (TPEA) for detection of cerebral Cu(II) using an electrochemical assay. CDs-TPEA were immobilized in the electrode showing a great selectivity toward Cu(II).

Recently, Gogoi et al. (2015) developed a solid sensing platform for on-site detection of heavy metals. To this end, CDs were immobilized in an agarose hydrogel film. The presence of different metal ions causes color changes, i.e. Cr^{6+}, green; Cu^{2+}, blue; Fe^{3+}, brown; Pb^{2+}, white; and Mn^{2+}, tan brown. The achievement of low LODs should be highlighted, i.e. 1 pM for Cr^{6+}, 0.5 μM for Cu^{2+}, and 0.5 nM for Fe^{3+}, Pb^{2+}, and Mn^{2+}.

Detection of inorganic species in biological systems

Several fluorescent nanoparticles, including QDs, metallic nanoclusters, and other CNPs, have been used for imaging and detection in biosystems. In this sense, the use of CDs as optical probes has greatly increased within the last few years due to their nontoxic nature.

Recently, Mohapatra et al. (2015) developed a novel method for Hg(II) determination in water and living cells using nitrogen and sulfur co-doped CDs. Hg(II) interacts with sulfur to cause fluorescence quenching. This sensing strategy allows reaching a LOD of 0.05 nM of Hg(II). The suitability of the reported method for Hg(II) detection in living cells was demonstrated by evaluation of N,S-CD cytotoxicity in HaCaT cells.

In addition, a new method based on the use of CDs functionalized with TPEA was developed for imaging and detection of Cu(II) in cells. In this system, TPEA acts as selective recognition unit for Cu(II), and the binding of the target analyte causes the fluorescence quenching of CDs (Qu et al. 2012). Another work focused on the detection of intracellular Cu(II) was recently developed by Vedamalai et al. (2014). In this work, the formation of the $Cu(OPD)_2$ complex in the CD surface causes the fluorescence enhancement and color change from yellow to orange.

Gong et al. (2015) used N-doped CDs for Fe(III) sensing and cellular imaging. The presence of Fe(III) causes the fluorescence quenching of CDs, a LOD of 1.8×10^{-7} M being reported. Another approach centered on the detection of Fe(III) was recently described by Zhou et al. (2015), in which a LOD of 0.32 μM for Fe(III) is reached.

Moreover, Salinas-Castillo et al. (2013) developed a novel CD-based system to detect Cu(II) using fluorescence measurement generated by down- and up-conversion. This system offers low cytotoxicity and it is suitable for intracellular detection and imaging of Cu(II) in biological species. LODs of the proposed system vary with the excitation wavelength used. LODs of 0.09 and 0.12 μM Cu(II) are achieved by excitation with UV light (down-conversion) and NIR irradiation (up-conversion), respectively. On the other hand, the use of UV light as excitation source does not prevent the strong interference caused by Fe(II), whereas the use of NIR excitation allows the selective detection of Cu(II).

Among ratiometric probes, the system developed by Liu et al. (2014b) should be highlighted. These workers proposed a ratiometric strategy for Cu(II) detection at low concentrations. This probe is based on the use of CDs and silica nanoparticles functionalized with Rhodamine B. The proposed system showed two different bands upon excitation at the same excitation wavelength, one in the blue region corresponding to CD emission and the other in the red region corresponding to Rhodamine B. CDs have surface ethylenediamine groups, which have a great affinity toward Cu(II), hence acting as recognition element. The binding of Cu(II) with the capping ligand causes the fluorescence quenching of CDs, whereas the Rhodamine band remains unchanged, so a ratiometric signal is obtained. A LOD 35.2 nM Cu(II) was achieved using this strategy. This system provided good results when it was applied for imaging and detection of Cu(II) in cells and water samples.

Conclusions

Since discovery of CDs around 10 years ago, these fluorescent nanomaterials have emerged as a suitable alternative to conventional organic dyes and QDs for optical sensing. A variety of simple synthetic pathways for obtaining fluorescent CDs from natural starting materials have been proposed so far. Given their low cost, ease of synthesis and functionalization, high stability, and nontoxicity, CDs show a great potential to be exploited in several fields. Among them, CDs have encountered application in the analytical field as optical probes for the detection of several species. Remarkable progress in the application of CDs for inorganic trace analysis has been achieved in the last years.

To date, several detection strategies based on fluorescence and CL changes have been proposed with this aim. Thus, fluorescent, chemiluminescent, FRET-based, reversible, and up-converted fluorescence probes have been designed. As a result of their interesting properties, it is expected that CDs will play an increasing role in the analytical field in the near future. The extension of CD applicability as optical probes for the sensitive and selective detection of inorganic species still needs further investigation, especially adequate functionalization strategies and further studies on sensing mechanisms.

Acknowledgments: Financial support from the Spanish Ministry of Economy and Competitiveness (project CTQ2012-32788) and the European Commission (FEDER) is gratefully acknowledged. V. Romero thanks the Spanish Ministry of Education, Culture and Sports, for predoctoral research grant.

References

Anilkumar, P.; Wang, X.; Cao, L.; Sahu, U.; Liu, J.-H.; Wang, P.; Korch, K.; Tackett, K. N. II; Parenzan, A.; Sun, Y.-P. Toward quantitatively fluorescent carbon-based “quantum” dots. *Nanoscale* **2011**, *3*, 2023–2027.

Baker, S. N.; Baker, G. A. Luminescent carbon nanodots: emergent nanolights. *Angew. Chem. Int. Ed.* **2010**, *49*, 6726–6744.

Barman, S.; Sadhukhan, M. Facile bulk production of highly blue fluorescent graphitic carbon nitride quantum dots and their application as highly selective and sensitive sensors for the detection of mercuric and iodide ions in aqueous media. *J. Mater. Chem.* **2012**, *22*, 21832–21837.

Barman, M. K.; Jana, B.; Bhattacharyya, S.; Patra, A. Photophysical properties of doped carbon dots (N, P, and B) and their influence on electron/hole transfer in carbon dots-nickel (II) phthalocyanine conjugates. *J. Phys. Chem. C* **2014**, *118*, 20034–20041.

Bhaisare, M. L.; Pandey, S.; Khan, M. S.; Talib, A.; Wu, H.-F. Fluorophotometric determination of critical micelle concentration (CMC) of ionic and non-ionic surfactants with carbon dots via Stokes shift. *Talanta* **2015**, *132*, 572–578.

Bourlinos, A. B.; Stassinopoulos, A.; Anglos, D.; Zboril, R.; Karakassides, M.; Giannelis, E. P. Surface functionalized carbogenic quantum dots. *Small* **2008**, *4*, 455–458.

Cai, Q.-Y.; Li, J.; Ge, J.; Zhang, L.; Hu, Y.-L.; Li, Z.-H.; Qu, L.-B. A rapid fluorescence “switch-on” assay for glutathione detection by using carbon dots-MnO_2 nanocomposites, *Biosens. Bioelectron.* **2015**, *72*, 31–36.

Cao, B.; Yuan, C.; Liu, B.; Jiang, C.; Guan, G.; Han, M.-Y. Ratiometric fluorescence detection of mercuric ion based on the nanohybrid of fluorescence carbon dots and quantum dots. *Anal. Chim. Acta* **2013**, *786*, 146–152.

Cayuela, A.; Soriano, M. L.; Valcárcel, M. Strong luminescence of carbon dots induced by acetone passivation: efficient sensor for a rapid analysis of two different pollutants. *Anal. Chim. Acta* **2013**, *804*, 246–251.

Chen, L.-Y.; Chen, C.-H.; Tseng, C.-H.; Lai, F.-L.; Hwang, B.-J. Synthesis $CdSe_xS_{1-x}$ core/shell type quantum dots via one injection method. *Chem. Commun.* **2011**, *47*, 1592–1594.

Chen, B.; Li, F.; Li, S.; Weng, W.; Guo, H.; Guo, T.; Zhang, X.; Chen, Y.; Huang, T.; Hong, X.; You, S.; Lin, Y.; Zeng, K.; Chen, S. Large scale synthesis of photoluminescent carbon nanodots and their application for bioimaging. *Nanoscale* **2013**, *5*, 1967–1971.

Costas-Mora, I.; Romero, V.; Lavilla, I.; Bendicho, C. In situ building of a nanoprobe based on fluorescent carbon dots for methylmercury detection. *Anal. Chem.* **2014a**, *86*, 4536–4543.

Costas-Mora, I.; Romero, V.; Lavilla, I.; Bendicho, C. An overview of recent advances in the application of quantum dots as luminescent probes to inorganic-trace analysis. *TrAC, Trends Anal. Chem.* **2014b**, *57*, 64–72.

Cui, X.; Zhu, L.; Wu, J.; Hou, Y.; Wang, P.; Wang, Z.; Yang, M. A fluorescent biosensor based on carbon dots-labeled oligodeoxyribonucleotide and graphene oxide for mercury(II) detection. *Biosens. Bioelectron.* **2015**, *63*, 506–512.

Deng, J.; Lu, Q.; Mi, N.; Li, H.; Liu, M.; Xu, M.; Tan, L.; Xie, Q.; Zhang, Y.; Yao, S. Electrochemical synthesis of carbon nanodots directly from alcohols. *Chem. Eur. J.* **2014**, *20*, 4993–4999.

Ding, H.; Wei, J.-S.; Xiong, H.-M. Nitrogen and sulfur co-doped carbon dots with strong blue luminescence. *Nanoscale* **2014**, *6*, 13817–13823.

Dong, Y.; Wang, R.; Li, G.; Chen, C.; Chi, Y.; Chen, G. Polyamine-functionalized carbon quantum dots as fluorescent probes for selective and sensitive detection of copper ions. *Anal. Chem.* **2012**, *84*, 6220–6224.

Dong, Y.; Pang, H.; Yang, H. B.; Guo, C.; Shao, J.; Chi, Y.; Li, C. M.; Yu, T. Carbon-based dots co-doped with nitrogen and sulfur for high quantum yield and excitation-independent emission. *Angew. Chem. Int. Ed.* **2013**, *52*, 7800–7804.

Du, F.; Zeng, F.; Ming, Y.; Wu, S. Carbon dots-based fluorescent probes for sensitive and selective detection of iodide. *Microchim. Acta* **2013**, *180*, 453–460.

Freeman, R.; Willner, I. Optical molecular sensing with semiconductor quantum dots (QDs). *Chem. Soc. Rev.* **2012**, *41*, 4067–4085.

Frigerio, C.; Ribeiro, D. S. M.; Rodrigues, S. S. M.; Abreu, V. L. R. G.; Barbosa, J. A. C.; Prior, J. A. V.; Marques, K. L.; Santos, J. L. M. Application of quantum dots as analytical tools in automated chemical analysis: a review. *Anal. Chim. Acta* **2012**, *735*, 9–22.

Gao, X.; Lu, Y.; Zhang, R.; He, S.; Ju, J.; Liu, M.; Li, L.; Chen, W. One-pot synthesis of carbon nanodots for fluorescence turn-on detection of Ag^+ based on the Ag^+-induced enhancement of fluorescence, *J. Mater. Chem. C* **2015**, *3*, 2302–2309.

Gogoi, N.; Barooah, M.; Majumdar, G.; Chowdhury, D. Carbon dots rooted agarose hydrogel hybrid platform for optical detection and separation of heavy metal ions. *ACS Appl. Mater. Interfaces* **2015**, *7*, 3058–3067.

Gong, X.; Lu, W.; Paau, M. C.; Hu, Q.; Wu, X.; Shuang, S.; Dong, C.; Choi, M. M. F. Facile synthesis of nitrogen-doped carbon dots for Fe^{3+} sensing and cellular imaging. *Anal. Chim. Acta* **2015**, *861*, 74–84.

Gu, J.; Hu, D.; Wang, W.; Zhang, Q.; Meng, Z.; Jia, X.; Xi, K. Carbon dot cluster as an efficient "off–on" fluorescent probe to detect Au(III) and glutathione. *Biosens. Bioelectron.* **2015**, *68*, 27–33.

Han, B.; Wang, W.; Wu, H.; Fang, F.; Wang, N.; Zhang, X.; Xu, S. Polyethyleneimine modified fluorescent carbon dots and their application in cell labeling. *Colloids Surf. A* **2012**, *100*, 209–214.

Han, T.; Yan, T.; Li, Y.; Cao, W.; Pang, X.; Huang, Q.; Wei, Q. Eco-friendly synthesis of electrochemiluminescent nitrogen-doped carbon quantum dots from diethylene triamine pentacetate and their application for protein detection. *Carbon* **2015**, *91*, 144–152.

Hou, X.; Zeng, F.; Du, F.; Wu, S. Carbon-dot-based fluorescent turn-on sensor for selectively detecting sulfide anions in totally aqueous media and imaging inside live cells. *Nanotechnol.* **2013**, *24*, 335502–335510.

Hu, S.-L.; Niu, K.-Y.; Sun, J.; Yang, J.; Zhao, N.-Q.; Du, X.-W. One-step synthesis of fluorescent carbon nanoparticles by laser irradiation. *J. Mater. Chem.* **2009**, *19*, 484–488.

Hu, S.; Huang, Q.; Lin, Y.; Wei, C.; Zhang, H.; Zhang, W.; Guo, Z.; Bao, X.; Shi, J.; Hao, A. Reduced graphene oxide-carbon dots composite as an enhanced material for electrochemical determination of dopamine. *Electrochim. Acta* **2014**, *130*, 805–809.

Huang, Q.; Hu, S.; Zhang, H.; Chen, J.; He, Y.; Li, F.; Weng, W.; Ni, J.; Bao, X.; Lin, Y. Carbon dots and chitosan composite film based biosensor for the sensitive and selective determination of dopamine. *Analyst* **2013**, *138*, 5417–5423.

Huang, Q.; Zhang, H.; Hu, S.; Li, F.; Weng, W.; Chen, J.; Wang, Q.; He, Y.; Zhang, W.; Bao, X. A sensitive and reliable dopamine biosensor was developed based on the Au@carbon dots–chitosan composite film. *Biosens. Bioelectron.* **2014a**, *52*, 277–280.

Huang, Z.; Lin, F.; Hu, M.; Li, C.; Xu, T.; Chen, C.; Guo, X. Carbon dots with tunable emission, controllable size and their application for sensing hypochlorous acid. *J. Lumin.* **2014b**, *151*, 100–105.

Jia, X.; Li, J.; Wang, E. One-pot green synthesis of optically pH-sensitive carbon dots with upconversion luminescence. *Nanoscale* **2012**, *4*, 5572–5575.

Jin, X.; Sun, X.; Chen, G.; Ding, L.; Li, Y.; Liu, Z.; Wang, Z.; Pan, W.; Hu, C.; Wang, J. pH-sensitive carbon dots for the visualization of regulation of intracellular pH inside living pathogenic fungal cells. *Carbon* **2015**, *81*, 388–395.

Kong, W.; Wu, H.; Ye, Z.; Li, R.; Xu, T.; Zhang, B. Optical properties of pH-sensitive carbon-dots with different modifications. *J. Lumin.* **2014**, *148*, 238–242.

Lai, C.-W.; Hsiao, Y.-H.; Peng, Y.-K.; Chou, P.-T. Facile synthesis of highly emissive carbon dots from pyrolysis of glycerol; gram scale production of carbon dots/$mSiO_2$ for cell imaging and drug release. *J. Mater. Chem.* **2012**, *22*, 14403–14409.

Li, H.; He, X.; Liu, Y.; Huang, H.; Lian, S.; Lee, S.-T.; Kang, Z. One-step ultrasonic synthesis of water-soluble carbon nanoparticles with excellent photoluminescent properties. *Carbon* **2011a**, *49*, 605–609.

Li, H.; He, X.; Liu, Y.; Yu, H.; Kang, Z.; Lee, S.-T. Synthesis of fluorescent carbon nanoparticles directly from active carbon via a one-step ultrasonic treatment. *Mater. Res. Bull.* **2011b**, *46*, 147–151.

Li, H.; Kang, Z.; Liu, Y.; Lee, S.-T. Carbon nanodots: synthesis, properties and applications. *J. Mater. Chem.* **2012**, *22*, 24230–24253.

Li, J.; Zhu, J.-J. Quantum dots for fluorescent biosensing and bioimaging applications. *Analyst* **2013**, *138*, 2506–2515.

Li, F.; Liu, C.; Yang, J.; Wang, Z.; Liu, W.; Tian, F. Mg/N double doping strategy to fabricate extremely high luminescent carbon dots for bioimaging. *RSC Adv.* **2014**, *4*, 3201–3205.

Li, C.-L.; Huang, C.-C.; Periasamy, A. P.; Roy, P.; Wu, W.-C.; Hsu, C.-L.; Chang, H.-T. Synthesis of photoluminescent carbon dots for the detection of cobalt ions. *RSC Adv.* **2015**, *5*, 2285–2291.

Lim, S. Y.; Shen, W.; Gao, Z. Carbon quantum dots and their applications. *Chem. Soc. Rev.* **2015**, *44*, 362–381.

Lin, Z.; Xue, W.; Chen, H.; Lin, J.-M. Peroxynitrous-acid-induced chemiluminescence of fluorescent carbon dots for nitrite sensing. *Anal. Chem.* **2011**, *83*, 8245–8251.

Lin, F.; Pei, D.; He, W.; Huang, Z.; Huang, Y.; Guo, X. Electron transfer quenching by nitroxide radicals of the fluorescence of carbon dots. *J. Mater. Chem.* **2012**, *22*, 11801–11807.

Lin, Z.; Dou, X.; Li, H.; Ma, Y.; Lin, J.-M. Nitrite sensing based on the carbon dots-enhanced chemiluminescence from peroxynitrous acid and carbonate. *Talanta* **2015**, *132*, 457–462.

Liu, C.; Zhang, P.; Tian, F.; Li, W.; Li, F.; Liu, W. One-step synthesis of surface passivated carbon nanodots by microwave assisted pyrolysis for enhanced multicolor photoluminescence and bioimaging. *J. Mater. Chem.* **2011**, *21*, 13163–13167.

Liu, C.; Zhang, P.; Zhai, X.; Tian, F.; Li, W.; Yang, J.; Liu, Y.; Wang, H.; Wang, W.; Liu, W. Nano-carrier for gene delivery and bioimaging based on carbon dots with PEI-passivation enhanced fluorescence. *Biomaterials* **2012a**, *33*, 3604–3613.

Liu, J.-M.; Lin, L.-p.; Wang, X.-X.; Lin, S.-Q.; Cai, W.-L.; Zhang, L.-H.; Zheng, Z.-Y. Highly selective and sensitive detection of Cu^{2+} with lysine enhancing bovine serum albumin modified-carbon dots fluorescent probe. *Analyst* **2012b**, *137*, 2637–2642.

Liu, Y.; Liu, C.-y.; Zhang, Z.-y. Synthesis of highly luminescent graphitized carbon dots and the application in the Hg^{2+} detection. *Appl. Surf. Sci.* **2012c**, *263*, 481–485.

Liu, J.-M.; Lin, L.-p.; Wang, X.-X.; Jiao, L.; Cui, M.-L.; Jiang, S.-L.; Cai, W.-L.; Zhang, L.-H.; Zheng, Z.-Y. $Zr(H_2O)_2EDTA$ modulated luminescent carbon dots as fluorescent probes for fluoride detection. *Analyst* **2013a**, *138*, 278–283.

Liu, R.; Li, H.; Kong, W.; Liu, J.; Liu, Y.; Tong, C.; Zhang, X.; Kang, Z. Ultra-sensitive and selective Hg^{2+} detection based on fluorescent carbon dots. *Mater. Res. Bull.* **2013b**, *48*, 2529–2534.

Liu, J.; Liu, X.; Luo, H.; Gao, Y. One-step preparation of nitrogen-doped and surface-passivated carbon quantum dots with high quantum yield and excellent optical properties. *RSC Adv.* **2014a**, *4*, 7648–7654.

Liu, X.; Zhang, N.; Bing, T.; Shangguan, D. Carbon dots based dual-emission silica nanoparticles as a ratiometric nanosensor for Cu^{2+}. *Anal. Chem.* **2014b**, *86*, 2289–2296.

Liu, Y.; Zhao, Y.; Zhang, Y. One-step green synthesized fluorescent carbon nanodots from bamboo leaves for copper(II) ion detection. *Sens. Actuators. B* **2014c**, *196*, 647–652.

Lu, J.; Yang, J.-x.; Wang, J.; Lim, A.; Wang, S.; Loh, K. P. One-pot synthesis of fluorescent carbon nanoribbons, nanoparticles, and graphene by the exfoliation of graphite in ionic liquids. *ACS Nano* **2009**, *3*, 2367–2375.

Ma, Z.; Ming, H.; Huang, H.; Liu, Y.; Kang, Z. One-step ultrasonic synthesis of fluorescent N-doped carbon dots from glucose and their visible-light sensitive photocatalytic ability. *New J. Chem.* **2012**, *36*, 861–864.

Ma, N.; Jiang, W.; Li, T.; Zhang, Z.; Qi, H.; Yang, M. Fluorescence aggregation assay for the protein biomarker mucin 1 using carbon dot-labeled antibodies and aptamers. *Microchim. Acta* **2015**, *182*, 443–447.

Mao, Y.; Bao, Y.; Yan, L.; Li, G.; Li, F.; Han, D.; Zhang, X.; Niu, L. pH-switched luminescence and sensing properties of a carbon dot–polyaniline composite. *RSC Adv.* **2013**, *3*, 5475–5482.

Mehta, V. N.; Jha, S.; Basu, H.; Singhal, R. K.; Kailasa, S. K. One-step hydrothermal approach to fabricate carbon dots from apple juice for imaging of mycobacterium and fungal cells. *Sens. Actuators. B* **2015**, *213*, 434–443.

Mohapatra, S.; Sahu, S.; Sinha, N.; Bhutia, S. K. Synthesis of a carbon-dot-based photoluminescent probe for selective and ultrasensitive detection of Hg^{2+} in water and living cells. *Analyst* **2015**, *140*, 1221–1228.

Nandi, S.; Ritenberg, M.; Jelinek, R. Bacterial detection with amphiphilic carbon dots. *Analyst* **2015**, *140*, 4232–4237.

Nie, H.; Li, M.; Li, Q.; Liang, S.; Tan, Y.; Sheng, L.; Shi, W.; Zhang, S. X.-A. Carbon dots with continuously tunable full-color emission and their application in ratiometric pH sensing. *Chem. Mater.* **2014**, *26*, 3104–3112.

Niu, W.-J.; Li, Y.; Zhu, R.-H.; Shan, D.; Fan, Y.-R.; Zhang, X.-J. Ethylenediamine-assisted hydrothermal synthesis of nitrogen-doped carbon quantum dots as fluorescent probes for sensitive biosensing and bioimaging. *Sens. Actuators. B* **2015**, *218*, 229–236.

Pedro, S. G.-d.; Salinas-Castillo, A.; Ariza-Avidad, M.; Lapresta-Fernández, A.; Sánchez-González, C.; Martínez-Cisneros, C. S.; Puyol, M.; Capitan-Vallvey, L. F.; Alonso-Chamarro, J. Microsystem-assisted synthesis of carbon dots with fluorescent and colorimetric properties for pH detection. *Nanoscale* **2014**, *6*, 6018–6024.

Peng, H.; Travas-Sejdic, J. Simple aqueous solution route to luminescent carbogenic dots from carbohydrates. *Chem. Mater.* **2009**, *21*, 5563–5565.

Qian, Z.; Ma, J.; Shan, X.; Feng, H.; Shao, L.; Chen, J. Highly luminescent N-doped carbon quantum dots as an effective multifunctional fluorescence sensing platform. *Chem. Eur. J.* **2014a**, *20*, 2254–2263.

Qian, Z.; Shan, X.; Chai, L.; Ma, J.; Chen, J.; Feng, H. Si-doped carbon quantum dots: a facile and general preparation strategy, bioimaging application, and multifunctional sensor. *ACS Appl. Mater. Interfaces* **2014b**, *6*, 6797–6805.

Qin, X.; Lu, W.; Asiri, A. M.; Al-Youbi, A. O.; Sun, X. Microwave-assisted rapid green synthesis of photoluminescent carbon nanodots from flour and their applications for sensitive and selective detection of mercury(II) ions. *Sens. Actuators. B* **2013**, *184*, 156–162.

Qu, Q.; Zhu, A.; Shao, X.; Shi, G.; Tian, Y. Development of a carbon quantum dots-based fluorescent Cu^{2+} probe suitable for living cell imaging. *Chem. Commun.* **2012**, *48*, 5473–5475.

Qu, K.; Wang, J.; Ren, J.; Qu, X. Carbon dots prepared by hydrothermal treatment of dopamine as an effective fluorescent sensing platform for the label-free detection of iron(III) ions and dopamine. *Chem. Eur. J.* **2013**, *19*, 7243–7249.

Salinas-Castillo, A.; Ariza-Avidad, M.; Pritz, C.; Camprubí-Robles, M.; Fernández, B.; Ruedas-Rama, M. J.; Megia-Fernández, A.; Lapresta-Fernández, A.; Santoyo-Gonzalez, F.; Schrott-Fischer, A.; Capitan-Vallvey, L. F. Carbon dots for copper detection with down and upconversion fluorescent properties as excitation sources. *Chem. Commun.* **2013**, *49*, 1103–1105.

Shan, X.; Chai, L.; Ma, J.; Qian, Z.; Chen, J.; Feng, H. B-doped carbon quantum dots as a sensitive fluorescence probe for hydrogen peroxide and glucose detection. *Analyst* **2014**, *139*, 2322–2325.

Shao, X.; Gu, H.; Wang, Z.; Chai, X.; Tian, Y.; Shi, G. Highly selective electrochemical strategy for monitoring of cerebral Cu^{2+} based on a carbon dot-TPEA hybridized surface. *Anal. Chem.* **2013**, *85*, 418–425.

Shen, Y.; Li, L.; Lu, Q.; Ji, J.; Fei, R.; Zhang, J.; Abdel-Halim, E. S.; Zhu, J.-J. Microwave-assisted synthesis of highly luminescent

CdSeTe@ZnS–SiO$_2$ quantum dots and their application in the detection of Cu(II). *Chem. Commun.* **2012**, *48*, 2222–2224.

Silva, J. C. G. E. d.; Gonçalves, H. M. R. Analytical and bioanalytical applications of carbon dots. *TrAC, Trends Anal. Chem.* **2011**, *30*, 1327–1336.

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.; Luo, P. G.; Yang, H.; Kose, M. E.; Chen, B.; Veca, L. M.; Xie, S.-Y. Quantum-sized carbon dots for bright and colorful photoluminescence. *J. Am. Chem. Soc.* **2006**, *128*, 7756–7757.

Sun, Y.-P.; Wang, X.; Lu, F.; Cao, L.; Meziani, M. J.; Luo, P. G.; Gu, L.; Veca, L. M. Doped carbon nanoparticles as a new platform for highly photoluminescent dots. *J. Phys. Chem. C* **2008**, *112*, 18295–18298.

Tang, Y.; Su, Y.; Yang, N.; Zhang, L.; Lv, Y. Carbon nitride quantum dots: a novel chemiluminescence system for selective detection of free chlorine in water. *Anal. Chem.* **2014**, *86*, 4528–4535.

Teng, X.; Ma, C.; Ge, C.; Yan, M.; Yang, J.; Zhang, Y.; Morais, P. C.; Bi, H. Green synthesis of nitrogen-doped carbon dots from konjac flour with “off–on” fluorescence by Fe^{3+} and L-lysine for bioimaging. *J. Mater. Chem. B* **2014**, *2*, 4631–4639.

Vedamalai, M.; Periasamy, A. P.; Wang, C.-W.; Tseng, Y.-T.; Ho, L.-C.; Shih, C.-C.; Chang, H.-T. Carbon nanodots prepared from o-phenylenediamine for sensing of Cu^{2+} ions in cells. *Nanoscale* **2014**, *6*, 13119–13125.

Vikneswaran, R.; Ramesh, S.; Yahya, R. Green synthesized carbon nanodots as a fluorescent probe for selective and sensitive detection of iron(III) ions. *Mater. Lett.* **2014**, *136*, 179–182.

Wang, X.; Cao, L.; Lu, F.; Meziani, M. J.; Li, H.; Qi, G.; Zhou, B.; Harru, B. A.; Kermarrec, F.; Sun, Y.-P. Photoinduced electron transfers with carbon dots. *Chem. Commun.* **2009**, 3774–3776.

Wang, C.-I.; Wu, W.-C.; Periasamy, A. P.; Chang, H.-T. Electrochemical synthesis of photoluminescent carbon nanodots from glycine for highly sensitive detection of hemoglobin. *Green Chem.* **2014a**, *16*, 2509–2514.

Wang, L.; Zhu, S.-J.; Wang, H.-Y.; Qu, S.-N.; Zhang, Y.-L.; Zhang, J.-H.; Chen, Q.-D.; Xu, H.-L.; Han, W.; Yang, B.; Sun, H.-B. Common origin of green luminescence in carbon nanodots and graphene quantum dots. *ACS Nano* **2014b**, *8*, 2541–2547.

Wang, Y.; Hu, A. Carbon quantum dots: synthesis, properties and applications. *J. Mater. Chem. C* **2014c**, *2*, 6921–6939.

Wang, Z.-X.; Zheng, C.-L.; Li, Q.-L.; Ding, S.-N. Electrochemiluminescence of a nanoAg–carbon nanodot composite and its application to detect sulfide ions. *Analyst* **2014d**, *139*, 1751–1755.

Wang, C.; Xu, Z.; Cheng, H.; Lin, H.; Humphrey, M. G.; Zhang, C. A hydrothermal route to water-stable luminescent carbon dots as nanosensors for pH and temperature. *Carbon* **2015a**, *82*, 87–95.

Wang, L.; Ruan, F.; Lv, T.; Liu, Y.; Deng, D.; Zhao, S.; Wang, H.; Xu, S. One step synthesis of Al/N co-doped carbon nanoparticles with enhanced photoluminescence. *J. Lumin.* **2015b**, *158*, 1–5.

Wang, W.; Kim, T.; Yan, Z.; Zhu, G.; Cole, I.; Nguyen, N.-T.; Li, Q. Carbon dots functionalized by organosilane with double-sided anchoring for nanomolar Hg^{2+} detection. *J. Colloids Surf. Sci.* **2015c**, *437*, 28–34.

Wang, X.; Zhang, J.; Zou, W.; Wang, R. Facile synthesis of polyaniline/carbon dot nanocomposites and their application as a fluorescent probe to detect mercury. *RSC Adv.* **2015d**, *5*, 41914–41919.

Wei, W.; Xu, C.; Ren, J.; Xu, B.; Qu, X. Sensing metal ions with ion selectivity of a crown ether and fluorescence resonance energy transfer between carbon dots and graphene. *Chem. Commun.* **2012**, *48*, 1284–1286.

Wei, C.; Huang, Q.; Hu, S.; Zhang, H.; Zhang, W.; Wang, Z.; Zhu, M.; Dai, P.; Huang, L. Simultaneous electrochemical determination of hydroquinone, catechol and resorcinol at Nafion/multi-walled carbon nanotubes/carbon dots/multi-walled carbon nanotubes modified glassy carbon electrode. *Electrochim. Acta* **2014**, *149*, 237–244.

Wu, G.; Zeng, F.; Yu, C.; Wu, S.; Li, W. A ratiometric fluorescent nanoprobe for H_2O_2 sensing and *in vivo* detection of drug-induced oxidative damage to the digestive system. *J. Mater. Chem. B* **2014a**, *2*, 8528–8537.

Wu, Z. L.; Gao, M. X.; Wang, T. T.; Wan, X. Y.; Zheng, L. L.; Huang, C. Z. A general quantitative pH sensor developed with dicyandiamide N-doped high quantum yield graphene quantum dots. *Nanoscale* **2014b**, *6*, 3868–3874.

Wu, L.; Ma, C.; Zheng, X.; Liu, H.; Yu, J. Paper-based electrochemiluminescence origami device for protein detection using assembled cascade DNA-carbon dots nanotags based on rolling circle amplification. *Biosens. Bioelectron.* **2015**, *68*, 413–420.

Xu, X.; Ray, R.; Gu, Y.; Ploehn, H. J.; Gearheart, L.; Raker, K.; Scrivens, W. A. Electrophoretic analysis and purification of fluorescent single-walled carbon nanotube fragments. *J. Am. Chem. Soc.* **2004**, *126*, 12736–12737.

Xu, Q.; Pu, P.; Zhao, J.; Dong, C.; Gao, C.; Chen, Y.; Chen, J.; Liu, Y.; Zhou, H. Preparation of highly photoluminescent sulfur-doped carbon dots for Fe(III) detection. *J. Mater. Chem. A* **2015a**, *3*, 542–546.

Xu, Q.; Zhao, J.; Liu, Y.; Pu, P.; Wang, X.; Chen, Y.; Gao, C.; Chen, J.; Zhou, H. Enhancing the luminescence of carbon dots by doping nitrogen element and its application in the detection of Fe(III). *J. Mater. Sci.* **2015b**, *50*, 2571–2576.

Yan, Y.; Sun, J.; Zhang, K.; Zhu, H.; Yu, H.; Sun, M.; Huang, D.; Wang, S. Visualizing gaseous nitrogen dioxide by ratiometric fluorescence of carbon nanodots–quantum dots hybrid. *Anal. Chem.* **2015**, *87*, 2087–2093.

Yang, Z.-C.; Wang, M.; Yong, A. M.; Wong, S. Y.; Zhang, X.-H.; Tan, H.; Chang, A. Y.; Li, X.; Wang, J. Intrinsically fluorescent carbon dots with tunable emission derived from hydrothermal treatment of glucose in the presence of monopotassium phosphate. *Chem. Commun.* **2011**, *47*, 11615–11617.

Yang, S.; Sun, J.; Li, X.; Zhou, W.; Wang, Z.; He, P.; Ding, G.; Xie, X.; Kang, Z.; Jianga, M. Large-scale fabrication of heavy doped carbon quantum dots with tunable-photoluminescence and sensitive fluorescence detection, *J. Mater. Chem. A*, **2014**, *2*, 8660–8667.

Yeh, T.-Y.; Wang, C.-I.; Chang, H.-T. Photoluminescent C-dots@RGO for sensitive detection of hydrogen peroxide and glucose. *Talanta* **2013**, *115*, 718–723.

Yin, B.; Deng, J.; Peng, X.; Long, Q.; Zhao, J.; Lu, Q.; Chen, Q.; Li, H.; Tang, H.; Zhang, Y.; Yao, S. Green synthesis of carbon dots with down- and up-conversion fluorescent properties for sensitive detection of hypochlorite with a dual-readout assay. *Analyst* **2013**, *138*, 6551–6557.

Yu, J.; Song, N.; Zhang, Y.-K.; Zhong, S.-X.; Wang, A.-J.; Chen, J. Green preparation of carbon dots by Jinhua bergamot for sensitive and selective fluorescent detection of Hg^{2+} and Fe^{3+}. *Sens. Actuators. B* **2015**, *214*, 29–35.

Zhai, X.; Zhang, P.; Changjun Liu, T. B.; Li, W.; Dai, L.; Liu, W. Highly luminescent carbon nanodots by microwave-assisted pyrolysis. *Chem. Commun.* **2012**, *48*, 7955–7957.

Zhang, Y.-Y.; Wu, M.; Wang, Y.-Q.; He, X.-W.; Li, W.-Y.; Feng, X.-Z. A new hydrothermal refluxing route to strong fluorescent carbon dots and its application as fluorescent imaging agent. *Talanta* **2013**, *117*, 196–202.

Zhang, H.; Dai, P.; Huang, L.; Huang, Y.; Huang, Q.; Zhang, W.; Weia, C.; Hu, S. A nitrogen-doped carbon dot/ferrocene@bcyclodextrin composite as an enhanced material for sensitive and selective determination of uric acid. *Anal. Methods* **2014a**, *6*, 2687–2691.

Zhang, P.; Xue, Z.; Luo, D.; Yu, W.; Guo, Z.; Wang, T. Dual-peak electrogenerated chemiluminescence of carbon dots for iron ions detection. *Anal. Chem.* **2014b**, *86*, 5620–5623.

Zhang, R.; Chen, W. Nitrogen-doped carbon quantum dots: Facile synthesis and application as a “turn-off” fluorescent probe for detection of Hg^{2+} ions. *Biosens. Bioelectron.* **2014c**, *55*, 83–90.

Zhang, L.; Han, Y.; Zhu, J.; Zhai, Y.; Dong, S. Simple and sensitive fluorescent and electrochemical trinitrotoluene sensors based on aqueous carbon dots. *Anal. Chem.* **2015**, *87*, 2033–2036.

Zhao, A.; Zhao, C.; Li, M.; Ren, J.; Qu, X. Ionic liquids as precursors for highly luminescent, surface-different nitrogen-doped carbon dots used for label-free detection of Cu^{2+}/Fe^{3+} and cell imaging. *Anal. Chim. Acta* **2014a**, *809*, 128–133.

Zhao, L.; Geng, F.; Di, F.; Guo, L.-H.; Wan, B.; Yang, Y.; Zhang, H.; Sun, G. Polyamine-functionalized carbon nanodots: a novel chemiluminescence probe for selective detection of iron(III) ions. *RSC Adv.* **2014b**, *4*, 45768–45771.

Zheng, A.-X.; Cong, Z.-X.; Wang, J.-R.; Li, J.; Yang, H.-H.; Chen, G.-N. Highly-efficient peroxidase-like catalytic activity of graphene dots for biosensing. *Biosens. Bioelectron.* **2013**, *49*, 519–524.

Zhou, J.; Booker, C.; Li, R.; Zhou, X.; Sham, T.-K.; Sun, X.; Ding, Z. An electrochemical avenue to blue luminescent nanocrystals from multiwalled carbon nanotubes (MWCNTs). *J. Am. Chem. Soc.* **2007**, *129*, 744–745.

Zhou, L.; Lin, Y.; Huang, Z.; Ren, J.; Qu, X. Carbon nanodots as fluorescence probes for rapid, sensitive, and label-free detection of Hg^{2+} and biothiols in complex matrices. *Chem. Commun.* **2012**, *48*, 1147–1149.

Zhou, J.; Shan, X.; Ma, J.; Gu, Y.; Qian, Z.; Chen, J.; Feng, H. Facile synthesis of P-doped carbon quantum dots with highly efficient photoluminescence. *RSC Adv.* **2014**, *4*, 5465–5468.

Zhou, Z.; Zhou, M.; Gong, A.; Zhang, Y.; Li, Q. Synthesis of highly photoluminescent carbon dots via citric acid and Tris for iron (III) ions sensors and bioimaging. *Talanta* **2015**, *143*, 107–113.

Zhu, H.; Wang, X.; Li, Y.; Wang, Z.; Yang, F.; Yang, X. Microwave synthesis of fluorescent carbon nanoparticles with electrochemiluminescence properties. *Chem. Commun.* **2009**, 5118–5120.

Zong, J.; Yang, X.; Trinchi, A.; Hardin, S.; Cole, I.; Zhu, Y.; Li, C.; Muster, T.; Wei, G. Carbon dots as fluorescent probes for “off-on” detection of Cu^{2+} and L-cysteine in aqueous solution. *Biosens. Bioelectron.* **2014**, *51*, 330–335.

Bionotes

Isabel Costas-Mora
Facultad de Química, Departamento de Química Analítica y Alimentaria, Área de Química Analítica, Universidad de Vigo, Campus As Lagoas-Marcosende s/n, 36310 Vigo, Spain

Isabel Costas-Mora graduated from the University of Vigo in 2009. She was a research fellow in the Department of Analytical Chemistry and Food from 2009 to 2013. She obtained her PhD from the University of Vigo in 2015. Her research interest is focused on the development of new miniaturized methodologies based on the use of fluorescent nanoparticles for sensing chemical species.

Vanesa Romero
Facultad de Química, Departamento de Química Analítica y Alimentaria, Área de Química Analítica, Universidad de Vigo, Campus As Lagoas-Marcosende s/n, 36310 Vigo, Spain

Vanesa Romero is a current PhD student at the Department of Analytical Chemistry and Food of Vigo University. In 2009, she finished her BS in Chemistry, and in 2010, she obtained her MS in Advanced Chemistry from the same university. In 2011, she obtained a national research grant (FPU) to develop her PhD thesis. Her research interest is focused on the development of solid substrates through the incorporation of nanomaterials for their use as selective sorbents for trace metal analysis and speciation.

Isela Lavilla
Facultad de Química, Departamento de Química Analítica y Alimentaria, Área de Química Analítica, Universidad de Vigo, Campus As Lagoas-Marcosende s/n, 36310 Vigo, Spain

Isela Lavilla obtained her PhD degree from the University of Zaragoza. She became associate professor of analytical chemistry in the University of Vigo in 2002. Her research interests include sample preparation, green analytical chemistry, and miniaturization. She is coauthor of about 130 papers and book chapters. Her Hirsch index is 30.

Carlos Bendicho
Facultad de Química, Departamento de Química Analítica y Alimentaria, Área de Química Analítica, Universidad de Vigo, Campus As Lagoas-Marcosende s/n, 36310 Vigo, Spain
bendicho@uvigo.es

Carlos Bendicho is an Associate Professor at the Department of Analytical Chemistry and Food in Vigo University, Spain. His current research focuses on green analytical chemistry, miniaturization, analytical nanoscience and nanotechnology, and atomic and molecular spectroscopy methods for trace metal analysis and speciation. He is author or coauthor of about 160 scientific papers. He has supervised 12 PhD theses and 40 master's theses. His Hirsch index is 35.