Sensitivity limits of biosensors used for the detection of metals in drinking water

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Abstract

Even when present in very low concentrations, certain metal ions can have significant health impacts depending on their concentration when present in drinking water. In an effort to detect and identify trace amounts of such metals, environmental monitoring has created a demand for new and improved methods that have ever-increasing sensitivities and selectivity. This paper reviews the sensitivities of over 100 recently published biosensors using various analytical techniques such as fluorescence, voltammetry, inductively coupled plasma techniques, spectrophotometry and visual colorimetric detection that display selectivity for copper, cadmium, lead, mercury and/or aluminium in aqueous solutions.

Keywords Heavy metals · Biosensors · Sensitivity · Water · Toxicity · Detection limits

Introduction

Toxicity is typically measured by the amount of harm or ill health caused by exposure to toxicants. In general, there is an inverse relationship between the environmental abundance of metals and their toxicity (Lithner 1989). Some metals bioaccumulate after consumption of contaminated drinking water and/or seafood with varying degrees of toxicity (Gruber 1989). Various human activities contribute to the pollution of ground, drinking and wastewater with toxic metals (Chowdhury et al. 2016).

Previous biosensors have relied on bioassays using animal models such as *Salmo gairdneri* fish (Lanno et al. 1985), cladocerans (*Ceriodaphnia dubia*) (Hyne et al. 2005) or *Daphnia magna* (Bang et al. 2011) and *Vibrio fischeri* (commercialised by Microtox®). The widespread industrial and domestic uses of these bioassays are typically limited by high costs, long assay times, the requirement for specialised infrastructure, ethical considerations, significant data variability and low specificity towards specific metals. Recently, SYBR Green I-based sensors such as HazardScreen® (HS®) assay have been used to assess additive, synergistic

or antagonistic toxicity effects of heavy metals in water (Foreman et al. 2011). Strong correlations of results have been shown between the Microtox® sensor, the *Ceriodaphnia dubia* bioassays and the HazardScreen DNA-based sensor. Until recently, bioassays have been unable to identify the individual toxicants that contribute to the overall toxicity of complex aqueous solutions (Chang et al. 1981; Foreman et al. 2011). Recently developed sensors use a variety of methods of quantifying the toxicity of trace quantities of metals in drinking water. These new biosensors are becoming increasing cost-effective and in delivering fast in situ and real-time results. The sensitivities and overall mechanisms of actions of newly published biosensors for copper, cadmium, lead, mercury and aluminium are compiled in Tables 1, 2, 3, 4 and 5, respectively.

The author of this review presents a compilation of various published sensor mechanisms and the molecular basis for their high degree of selectivity for either copper, cadmium, lead, mercury and/or aluminium. All techniques are listed in order of their sensitivities in aqueous solutions. Analytical techniques presented here include fluorescence, voltammetry, inductively coupled plasma techniques, spectrophotometry and colorimetry. The aim of this review is to identify which techniques display the highest degree of sensitivity for the selected heavy metals. Furthermore, the author is happy to discuss any areas of further optimisation and provide helpful suggestions to developers of sensors for the selected heavy metals.

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Table 1 Copper biosensors. Copper detection limits of each sensor with the linear range in parenthesis (if reported) are listed in column two

Ion-selective receptor molecule	Detection limit (linear range)	Sensor mechanism	References
Au NPs	~ 1 nM	Functionalized cysteine-Au NPs	Gooding et al. 2009
6-Acetyl-2-hydroxynaphthalene	8.5 nM	Using a reaction-based fluorescent probe	Ren et al. 2018
2-Dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran	13 nM	Colorimetric fluorescent probe based on dihydrofuran with a picolinate moiety	Xu et al. 2018a, b
DsRed protein	< 15.7 nM	Fluorescence utilising the wild-type red fluorescent protein, DsRed	Sumner et al. 2006
Neoprene	15.7 nM	Voltammetry screen-printed thick-film neoprene	Malzahn et al. 2011
Transgenic zebrafish	15.7 nM	Fluorescence using a metal-responsive promoter linked to a fluorescent reporter gene (DsRed2)	Pawar et al. 2016
cDNA of drFP583	100 nM	Fluorescence assays utilising drFP583-pRSETB expression plasmids in <i>Escherichia coli</i>	Bereza-Malcolm et al. 2016
Yeast	110 nM	Amperometry	Jarque et al. 2016
Bismuth nanoparticles	0.4 µM	Nano composite of reduced graphene oxide–bismuth nanoparticles	Sahoo et al. 2013
Natural tripeptide GGH (Gly-Gly-His) moiety	0.44 µM	Fluorescence using a fluorophore-tripeptide probe (C-Gly-Gly-His)	Hao et al. 2015
<i>Saccharomyces cerevisiae</i>	0.5 µM	<i>S. cerevisiae</i> cells harbouring plasmid pYEX-GFPuv with a cup::gfp construct	Shetty et al. 2004
Coumarin	0.64 µM	Fluorescence utilising N'-acetyl-2-((4-methyl-2-oxo-2H-chromen-7-yl)oxy)acetohydrazide (HMC1)	Warrier and Kharkar 2018
Au NPs	1 µM	Au NPs bound to N,N'-2,6-diisopropylphenyl-1,7-bis(4-hydroxypyridine) perylene-3,4,9,10-tetracarboxylic acid bisimide	He et al. 2005
<i>Alcaligenes eutrophus</i> (AE1239)	1 µM (0–25 µM)	Fluorescence utilising optical bioluminescent of <i>Alcaligenes eutrophus</i> (AE1239) with <i>Vibrio fischeri</i> luxCDABE operon under the influence of a copper-induced promoter	Suzanne et al. 2002
<i>Anabaena torulosa</i>	1.2 µM (2.5–10 µM)	Fluorescence utilising cyanobacteria via whole-cell entrapment on cellulose membranes	Wong et al. 2013
Graphene QDs	2 µM (1–50 µM)	Fluorescent utilising the unfolding of C60 Buckminsterfullerene-derived graphene QDs	Ciotta et al. 2017
Naphthalene diimide	4.0 µM	Fluorescence utilising the “turn-on” luminescence of an azathiacrown ether-substituted naphthalene diimide	Zong et al. 2016
DNAzymes	6.5 µM (6.5–40 µM)	Electrode surface modification by DNAzyme-catalysed oxidation of ascorbic acid	Ocaña et al. 2013
Au NPs	10 µM	L-cysteine-functionalized Au NPs	Yang et al. 2007
Calix[4]arene	14 µM (19–115 µM)	Colorimetry using functionalized calix[4]arene	Bhatt et al. 2017
Macro-metallocycle	15 µM	Fluorescence and UV spectroscopy using macro-metallocycle	Liu et al. 2018

Au NPs gold nanoparticles, QDs quantum dots

Discussion and concluding remarks

This review gives a brief overview of the current mechanisms used to construct biosensors and their detection limits. There are a few clear trends from this review. Firstly, nanoparticles (NPs) are becoming increasingly used in the construction of the most sensitive biosensors. Secondly, simple NP receptor molecules are insufficient and require continual optimisation. Surface modifications and/or forming complex structures

greatly improve sensitivities. Thirdly, more work is needed to verify not just the detection limits, but also the sensitivities of these biosensors to their target analytes. For example, authors should test the robust nature of their biosensors by adding trace amounts of metal to samples of river and sea water once they have optimised their techniques. The clear contribution of nanotechnology and biotechnology to the performance of the reviewed biosensors suggests that rapid performance improvements are in progress to develop

Table 2 Cadmium biosensors. Receptor molecules are listed in column one. Cadmium detection limits of each sensor with the linear range in parenthesis (if known) are listed in column two

Ion-selective receptor molecule	Detection limit (linear range)	Sensor mechanism	References
CNTs	2.2 pM	Colorimetric and electrochemical microfluidic paper-based analytical devices using screen-printing multi-walled CNTs	Rattanarat et al. 2014
Porous magnesium oxide nano-flowers	81 pM (40–140 nM)	Porous magnesium oxide nano-flowers sensitive electrode monitoring using square-wave anodic stripping voltammetry	Wei et al. 2012
Yeast	0.2 nM	Amperometry	Jarque et al. 2016
CNTs	0.27 nM (0.44–178 nM)	Differential pulse anodic stripping voltammetry using glassy carbon electrode modified with Nafion, poly(2,5-dimercapto-1,3,4-thiadiazole) and multi-walled CNTs	He et al. 2011
Polyaniline nanofibers	0.7 nM (5–80 nM)	Square-wave anodic stripping voltammetry using glassy carbon electrode modified with self-doped polyaniline nanofibers/mesoporous carbon nitride and bismuth	Zhang et al. 2016a, b, c
C18 silica monolith column	0.8 nM (0.44–44 µM)	Reversed-phase high-performance liquid chromatography	Thirumalai et al. 2018
Au NPs	3.5 nM (10–30 µM)	Colorimetric assay using trithiocyanuric acid-functionalized Au NPs and ascorbic acid	Wang et al. 2018
Screen-printed thick-film electrodes	4.4 nM (0–1.3 µM)	Standard electrochemical couple of potassium ferrocyanide-ferricyanide and solid thick-film electrodes	Prášek et al. 2006
Glutathione	5 nM	Voltammetry using glutathione as a selective ligand immobilised on a gold electrode modified with a self-assembled monolayer of 3-mercaptopropionic acid	Chow et al. 2005
Transgenic zebrafish	8.9 nM	Metal-responsive promoter linked to a fluorescent reporter gene (DsRed2)	Pawar et al. 2016
Whole-cell bacterial fluorescence	10 nM	<i>Staphylococcus aureus</i> strain RN4220 and <i>Bacillus subtilis</i> strain BR151 using the regulatory sequence from the cadA gene of plasmid p1258	Tauriainen et al. 1998
Bismuth nanoparticles	20 nM	Nano composite of reduced graphene oxide–bismuth nanoparticles	Sahoo et al. 2013
<i>Anabaena torulosa</i>	27 nM (0.5–10 µM)	Optical transduction using whole-cell entrapment on cellulose membrane	Wong et al. 2013
CNTs	0.4 µM (0.4–71 µM)	CNTs nanoelectrode array/epoxy voltammetry	Liu et al. 2005
CNTs carbon nanotubes, Au NPs gold nanoparticles			

Table 3 Lead biosensors. Receptor molecules are listed in column one. Lead detection limits of each sensor with the linear range in parenthesis (if known) are listed in column two

Ion-selective receptor molecule	Detection limit (linear range)	Sensor mechanism	References
GR-5 DNAAzyme CNTs	0.9 pM (2–1000 pM) 1.2 pM	Electrochemiluminescence using the GR-5 lead-dependent DNAAzyme and Pb-induced release of ruthenium tris (1,10-phenanthroline) (Ru(phen) ₃) ₂ ⁺	Gao et al. 2013
		Colorimetric and electrochemical microfluidic paper-based analytical devices using screen-printing multi-walled CNTs	Rattanaat et al. 2014
Porous magnesium oxide nano-flowers	2.1 pM (3.3–22 nM)	Porous magnesium oxide nano-flowers sensitive electrode monitoring using square-wave anodic stripping voltammetry	Wei et al. 2012
DNAzymes and Cds QDs modified ssDNA	7.8 pM	Biosensor based on DNAAzyme, rolling circle amplification (RCA) and Cds QDs modified ssDNA	Tang et al. 2013
Self-doped polyaniline nanofibers	0.2 nM (5–80 nM)	Square-wave anodic stripping voltammetry using glassy carbon electrode modified with self-doped polyaniline nanofibers/mesoporous carbon nitride (and bismuth)	Zhang et al. 2016a, b, c
CNTs	0.24 nM (0.48–106 nM)	Differential pulse anodic stripping voltammetry using glassy carbon electrode modified with Nafion, poly(2,5-dimercapto-1,3,4-thiadiazole) and multi-walled carbon nanotubes	He et al. 2011
C18 silica monolith column	0.36 nM (0.24–24 µM)	Reversed-phase high-performance liquid chromatography	Thirumalai et al. 2018
G-rich DNA	0.4 nM (1 nM–1 mM)	Pb ²⁺ -induced G-rich DNA conformational switch from a random-coil to G-quadruplex (G4) with crystal violet as the G4-binding indicator	Li et al. 2011a, b
Silica nanoparticles	0.48 nM (4.8–145 nM)	Screen-printed carbon electrode modified with functionalized mesoporous silica nanoparticles	Sánchez et al. 2010
Nano-structured polymer nanoparticles	0.6 nM (1.0 to 0.08 nM)	Voltammetry using carbon-paste electrodes modified with nano-structured ion-imprinted polymer nanoparticles	Alizadeh and Amjadi 2011
DNAzyme	0.5 nM (1 nM–1 µM)	Amperometric sensing platform for detection of Pb-based on horseradish peroxidase (HRP)-mimicking DNAAzyme-catalysed template-guided deposition of polyaniline (PANI) that catalysed the oxidation of anilino PANI with H ₂ O ₂	Li et al. 2013a, b
G-rich DNA with redox probe	0.5 nM	Conformational switch from hairpin DNA to G-quadruplex induced by Pb ²⁺ by electrochemical impedance spectroscopy (EIS) in the presence of [Fe(CN) ₆] ^{3-/4-} as the redox probe	Lin et al. 2011
Nano hydroxyapatite	1 nM	Voltammetry using a nafion conductive matrix and a modified glassy carbon electrode for composed of nanosized hydroxyapatite coupled to an ionophore	Pan et al. 2009
Bismuth nanoparticles	2.7 nM	Nano composite of reduced graphene oxide–bismuth nanoparticles	Sahoo et al. 2013
DNAzymes and SYBER Green I	5 nM (0–50 nM)	Fluorescence based on DNAAzyme activation and cDNA strand cleavage via an RNA site	Ravikumar et al. 2017
Au NP-functionalized graphene	10 nM (50–1000 nM)	Fluorescence using Au NP-functionalized graphene in the presence of both thiosulfate and 2-mercaptoethanol	Fu et al. 2012
Graphene QDs and Au NPs	16.7 nM (50 nM–4 µM)	Fluorescence using graphene QDs and Au NPs	Niu et al. 2018
<i>Phormidium</i> sp.	25 nM (50 nM–20 µM)	Voltammetry using non-immobilised whole cells	Yüce et al. 2010
Whole-cell bacterial fluorescence	33 nM	<i>Staphylococcus aureus</i> strain RN4220 and <i>Bacillus subtilis</i> strain BR151 employing the regulatory sequence from the <i>cadA</i> gene of plasmid p1258	Taurainen et al. 1998
Fluorescence-labelled oligonucleotides	61 nM (0.1–1 µM)	Fluorescence using a fluorescence-labelled aptamer from complex with a quencher-labelled short complementary sequence	Chen et al. 2018
Gram-negative whole-cell bacteria	0.97 µM	Plasmid-based whole-cell <i>Pseudomonas aeruginosa</i> bacterial biosensors using the PAO1 (pBBpBrGfp) genetic element	Bereza-Malcolm et al. 2016
<i>Anabaena torulosa</i> Au NPs	0.1 µM (0.5–5 µM) 0.1 µM	Whole-cell entrapment on cellulose membrane Surface-enhanced resonance Raman scattering (SERS) utilising 2-mercaptoisonicotinic acid-modified Au NPs	Wong et al. 2013 Zamarian et al. 2008
DNAzyme	0.3 µM	Electrochemical sensor based on 8–17 lead-dependent DNAAzyme immobilised on a gold electrode	Xiao et al. 2007
6-Carboxyfluorescein and Cy5	1 µM	Visual detection using Au NPs, DNAAzyme microparticles and 6-carboxyfluorescein and Cy5	Kim and Lee 2016
Graphene QDs	2 µM (30–100 µM)	Fluorescent using unfolded fullerene QDs	Ciotta et al. 2017

CNTs carbon nanotubes, Au NPs gold nanoparticles, ssDNA single-stranded DNA, QDs quantum dots

Table 4 Mercury sensors. Receptor molecules are listed in column one. Mercury detection limits of each sensor with the linear range in parenthesis (if reported) are listed in column two

Ion-selective receptor molecule	Detection limit (linear range)	Sensor mechanism	References
Au NPs	2.5 fM	Surface enhancement Raman spectrum (SERS) spot tests using Au NPs and dithizone	Grasseschi et al. 2010
Single-walled carbon nanotubes	3 fM (10 fM–1 μ M)	Voltammetry using a gold substrate with tunable vertically aligned single-walled carbon nanotubes and a target recycling strategy	Shi et al. 2017
<i>Chlorella vulgaris</i>	10 fM	Electrochemical amperometry using algae-bovine serum albumin cross-linked with glutaraldehyde	Singh and Mittal 2012
Silver-coated Au NPs	10 fM	SERS silicon wafer modified with 4,4'-dipyridyl (DPy)	Du et al. 2013
Magnetic substrate CoFe ₂ O ₄ /Ag and single-walled carbon nanotubes	0.84 pM (1 pM–100 nM)	SERS optometry utilising a stable thymine-Hg ²⁺ -thymine structure and the π - π interaction between single-stranded DNA and single-walled carbon nanotubes	Yang et al. 2017
Au NPs	1 pM	SERS sensor for Hg ²⁺ detection by using nanoporous gold as a substrate and Cy5-labelled aptamer as optical tags	Zhang et al. 2013
Ag NPs	1 pM	SERS using a L-cysteine-functionalized AgNP attached with Raman-labelling molecules 3,5-dimethoxy-4-(60--azobenzotriazolyl)phenol	Li et al. 2013a, b
Lysozyme type VI-stabilised gold nanoclusters (Lys VI-Au NCs)	3 pM	Fluorescence quenching using lysozyme type VI-stabilised Lys VI-Au NCs of methyl mercury. Detection limit of 4 nM reported for methyl mercury	Lin and Tseng 2010
Self-assembled gold nanostar dimer QDs	4 pM	SERS using self-assembled gold nanostar dimers	Ma et al. 2013
Au NPs	4.6 pM	Fluorescence based on QDs and oligonucleotides	Gao et al. 2018
Au/polyaniline composite nanospheres	10 pM	Rhodamine B (RB) protected Au NPs in soil, water and fish	Darbha et al. 2007
Au NPs	10 pM	Dandelion-like Au/polyaniline composite nanospheres used as SERS sensors	Wang et al. 2011
Bimetallic Au–Pt nanoparticles	25 pM	SERS utilising Au NPs functionalized with 4-mercaptopbenzoic acid in the presence of 2,6-pyridinedicarboxylic acid	Peng et al. 2017
Rhodamine 6G dye	38.9 pM	Anodic stripping voltammetry using bimetallic Au–Pt nanoparticles/organic nanofiber glassy carbon electrodes	Gong et al. 2010
Au nanowire	0.06 nM	Au NP-(rhodamine 6G dye)-based fluorescent sensor	Chen et al. 2007
Droplet-based microfluidic system	0.1 nM	Au nanowire on-film surface-enhanced resonance Raman scattering (SERS) sensor for Hg ²⁺ based on Hg ²⁺ -T coordination	Taejoon et al. 2011
Semiconductor QDs and Au NPs	0.1–2.5 nM	Quantification achieved using a droplet-based microfluidic system	Li et al. 2012
Transgenic zebrafish Ag nanoclusters (Ag Cs)	0.49–0.87 nM	Time-gated fluorescence resonance energy transfer (TGFRET) sensing strategy using DNA-functionalized Mn-doped CdS/ZnS QDs and Au NPs	Huang et al. 2013
	0.1 nM	Metal-responsive promoter linked to a fluorescent reporter gene (DsRed2)	Pavar et al. 2016
	0.1 nM	“Turn-off” Hg ²⁺ sensors using Ag NCs stabilised with glutathione	Wang et al. 2012a, b, c
ZnSe/ZnS colloidal nanoparticles	(0.1 nM–10 μ M)	Fluorescence based on mercaptopropionic acid-coated Mn-doped ZnSe/ZnS colloidal nanoparticles	Ke et al. 2014
Mn:CdS/ZnS QDs and Au NPs	0.1 nM (0–20 nM)	Enhanced signal enhancement achieved with resonance energy transfer (FRET) via Au NPs functionalized with 10-mer DNA (strand B) that quench the fluorescence of Mn:CdS/ZnS QDs functionalized with 33-mer thymine-rich DNA (strand A)	Changqing et al. 2005
Au nanoclusters	0.18 nM	Fluorescence using gold nanoclusters tuned with bovine serum albumin and bromelain	Bhamore et al. 2018
Au/graphene electrode	0.3 nM (0.75 nM–5 μ M)	Mercury-induced charge transfer resistance of oligonucleotide-gold electrodes	Wang et al. 2012a, b, c
ZnO nanorods	0.5 nM	Potentiometry using glucose oxidase immobilised on Zinc oxide nanorods and gold-coated glass electrodes	Chey et al. 2012
C18 silica monolith column	0.5 nM, (0.5 nM–20 mM)	Reversed-phase high-performance liquid chromatography	

Table 4 (continued)

Ion-selective receptor molecule	Detection limit (linear range)	Sensor mechanism	References
Ag NPs	0.6 nM (0.25–25 μ M)	Colorimetric and a “turn-on” fluorescent sensor using folic acid-functionalized Ag NPs	Thirumalai et al. 2018
Au NPs	1 nM	Para-aminothiophenol coupled Au NPs (PATP-Au) multilayer as SERS probes	Dongyue et al. 2014
Fluorescently labelled DNA oligonucleotides	1.2 nM	Evanescent-wave optical fibres using structure-switching DNA and a fluorescence-labelled complementary DNA oligonucleotide	Ma et al. 2012
Carbonothioate	1.4 nM (0–1 μ M)	Rhodol-derived colorimetric and fluorescent with a recognition receptor of carbonothioate	Long et al. 2013
DNA-conjugated QDs	6 nM (0–0.8 μ M)	Fluorescence using nanometal surface energy transfer in DNA-conjugated QDs and Au nanoparticles as part of a QDs/DNA/Au NPs ensemble	Duan et al. 2017
Au NPs	2.8 nM (5 nM–1 μ M)	Colorimetric assay using trithiocyanuric acid-functionalized Au NPs and ascorbic acid	Li et al. 2011a, b
Ag NP	3.3 nM	Colorimetry based on an Ag NP paper-based device utilising the morphology transition of 1-dodecane-thiol (C12H25SH)-capped Ag nano prisms in the presence of excess iodide	Wang et al. 2018
Ag NCs	2 nM	Poly(acrylic acid)-templated Ag NCs as a platform for fluorescence “turn-on” detection	Chen et al. 2013
Ag NCs	4 nM	Ratiometric fluorescent probe using DNA-stabilised Ag NCs	Tao et al. 2012
Denatured ovalbumin-coated CdTe QDs	4.2 nM	3-Mercaptopropionic acid-stabilised CdTe QDs coated with chemically denatured ovalbumin	Maclean et al. 2013
CdS NPs	4.5 nM	Synchronous fluorescence based on glutathione-capped CdS NPs	Wang et al. 2012a, b, c
Ag NP	5 nM	Ag NP-embedded poly(vinyl alcohol) (Ag-PVA) thin film	Liang et al. 2010
ZnS QDs	5 nM	Water-soluble ZnS QDs capped with N-acetyl-L-cysteine	Ramesh and Radhakrishnan 2011
Au NPs	5 nM	Fluorescence quenching of 11-mercapto-undecanoic acid-protected gold nanoparticles in the presence of 2,6-pyridine dicarboxylic acid	Duan et al. 2011
Au NPs	6 nM	Photoluminescence quenching of perylene bisimide chromophores by Au NPs	Chih-Ching et al. 2007
Au NPs	9.93 nM	Photoluminescence quenching of rhodamine-Au NPs complexes	He et al. 2007
Ag NCs	10 nM	“Turn-on” fluorescence sensor based on DN duplexes and Ag NCs	Huang and Chang 2006
Oligothiophene	10.3 nM	Colorimetry and ratiometric fluorescence using the probe 5-(1,3-dithiolan-2-yl)-2,2':5',2''-terthiophene	Deng et al. 2011
Au NPs	14.9 nM	Colorimetry using Au NPs tethered by a linker oligonucleotide with thymine–thymine mismatches	Lan et al. 2018
UfO-66-NH ₂ and a T-rich FAM-labelled ssDNA	17.6 nM (0.14 μ M)	Fluorescence using a Metal–Organic Framework/DNA Hybrid System (UfO-66-NH ₂) sensing material	Xue et al. 2008
Au NPs	25 nM	Tryptophan-protected popcorn-shaped Au NPs-based SERS probe	Lan-Lan et al. 2016
Au NPs	25 nM	Hyper-Rayleigh scattering of Au NPs	Senapati et al. 2011
Ag NPs	25 nM	Starch-stabilised Ag NPs colorimetry	Darbha et al. 2008
Au NPs	34 nM	2-Mercaptoisonicotinic acid-modified Au NPs	Fan et al. 2009
New rhodamine-based fluorescent probe	38 nM	Fluorescence based on a new rhodamine-based fluorescent probe	Zamarion et al. 2008
Au NPs	40 nM		Zhang et al. 2016a, b, c
			Wang et al. 2008

Table 4 (continued)

Ion-selective receptor molecule	Detection limit (linear range)	Sensor mechanism	References
Ag NPs	45 nM	Colorimetric and fluorescent dual sensor using Au NPs and fluorescein (FAM)-tagged ssDNA with mismatched T-T sequences	Bera et al. 2010
2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)diammonium salt	50 nM	Polyhedral Ag NPs colorimetry	Li et al. 2009
PVA-Ag-NPs	50 nM (50 nM–25 μ -M)	Colorimetry utilising G-quadruplex-based DNAzymes and H ₂ O ₂ -mediated oxidation of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)diammonium salt	Sarkar et al. 2017
Condensed fluorophore of Changsha dye and 4-Phenyl-3-thiosemicarbazide	58 nM (0.5–5 μ M)	PVA-Ag-NPs nanocomposite thin film	Jiaoliang et al. 2017
Carbonothioate	55 nM (0–16 μ M)	Near-infrared fluorescence via an irreversible spiro lactam ring-opening process and a condensed probe of Changsha dye and 4-Phenyl-3-thiosemicarbazide	Xu et al. 2018a, b
Au NPs	100 nM	Carbonothioate-based fluorescent probe using 2-(2'-hydroxyphenyl)benzothiazole as the fluorophore	Fang et al. 2010
Benzothiazole-derived chemosensor "L"	0.11 μ M	Colorimetry using L-cysteine-functionalized Au NPs	Sahana et al. 2015
Metallothioneins	225 nM	Excited-state intramolecular proton transfer mechanism using a benzothiazole-derived chemosensor "L"	Irvine et al. 2017
Carbon NDs	0.23 μ M	Metallothionein-impregnated paper discs on screen-printed carbon electrodes	Zhang and Chen 2014
Dendritic compounds RhB-BODIPY	334 nM	Fluorescent using nitrogen-doped carbon QDs	Shen and Qian 2017
Carbon dots	0.47 μ M (1–100 μ M)	Intramolecular fluorescence resonance energy transfer (FRET) using rhodamine coupled with the dendritic compound RhB-BODIPY	Yusha et al. 2018
Micro-electro-mechanical sensors	0.5 μ M	Ratiometric fluorescence using rhodamine B hydrazide and carbon dots	Ham and Popovics 2015
Naphthalene diimide	1.3 μ M	Concrete non-destructive air-coupled micro-electro-mechanical sensors	Zong et al. 2017
Ag NPs	2.2 μ M	Fluorescence using a naphthalene diimide-based probe (NDI-5)	Farhadi et al. 2012
NBD-Cl	23 μ M (0–20 μ M)	Unmodified Ag NPs colorimetry	Zhang et al. 2016a, b, c
Ag NPs	~60 μ M	Colorimetry and ratiometric fluorescence NBD-Cl	Karthiga and Anthony 2013
		Green-synthesised Ag NPs using plant extracts	

Au NPs gold nanoparticles, *Pd NPs* palladium nanoparticles, *NDs* nano dots, *Ag NPs* silver nanoparticles, *Ag NCs* silver nanoclusters, *PVA-Ag-NPs* silver nanoparticle-impregnated poly(vinyl alcohol), *SERS* surface enhancement Raman spectrum, *QDs* quantum dots, *NBD-Cl* 4-chloro-7-nitrobenzo-2,1,3-oxadiazole

Table 5 Aluminium sensors. Receptor molecules are listed in column one. Aluminium detection limits of each sensor with the linear range in parenthesis (if known) are listed in column two

Ion-selective receptor molecule	Detection limit (linear range)	Sensor mechanism	Reference
Methylene blue	0.2 nM	Exonuclease III activity of DNA oligonucleotides and methylene blue-labelled T-rich probes	Xuan et al. 2013
Au NPs	0.5 nM	Au NP-functionalized DNA	Kong et al. 2009
Au NPs	2.3 nM	Electrochemical stripping assay using thiolated amino acid-capped Au NPs in a carbon ionic liquid electrode	Safavi and Farjami 2011
Pd NPs	2 µM	Amperometry using superoxide dismutase and glutaraldehyde on screen-printed carbon electrodes modified with tetrathiofulvalene and Pd NPs	Barquero-Quirós and Arcos-Martínez 2016
Au NPs	3.6 µM (2–18 µM)	Colorimetry using ethylenediaminetetraacetic acid (EDTA)-capped Au NPs	Siewdorlang and Devendra 2016

commercial tests in real-time systems. It is crucial that testing technology move away from infrastructure-intensive sensors such as atomic absorption spectroscopy (Vil'pan et al. 2005), cold vapour atomic fluorescence spectrometry (Yan et al. 2002), inductively coupled plasma mass spectrometry (Moreton and Delves 1998), electrochemical methods (Liu et al. 2009), gas chromatography (Fitzgerald and Gill 1979) and high-performance liquid chromatography (Balarama Krishna et al. 2007). There is a need to develop new portable and rapid biosensors that can be used even by school children with minimal training (Foreman et al. 2011). However, important considerations of biosensors designed for use in rural areas of developing countries are low cost, and a long shelf half-life of certain reagents (e.g., enzymes and oligonucleotides) (Fernandez-Lafuente 2009; Gibson et al. 1992; Panjan et al. 2017).

Author contributions All authors wrote, revised and approved the final manuscript.

Compliance with ethical standards

Conflict of interest Vangelis George Kanellis declares that he has no conflicts of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by the author.

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