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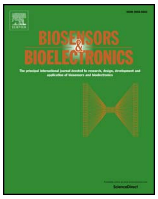

SERS and fluorescence-based ultrasensitive detection of mercury in water

Pandeeswar Makam[a], Rohilla Shilpa[a], Ahmad Esmaielzadeh Kandjani[b], Selvakannan R. Periasamy[b], Ylias Mohammad Sabri[b], Chilakapati Madhu[a], Suresh Kumar Bhargava[b,*], Thimmaiah Govindaraju[a,*]

[a] Bioorganic Chemistry Laboratory, New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bengaluru 560064, India
[b] Centre for Advanced Materials and Industrial Chemistry (CAMIC), School of Applied Sciences, RMIT University, GPO Box 2476 V, Melbourne, Victoria 3001, Australia

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ABSTRACT

The development of reliable and ultrasensitive detection marker for mercury ions (Hg^{2+}) in drinking water is of great interest for toxicology assessment, environmental protection and human health. Although many Hg^{2+} detection methods have been developed, only few offer sensitivities below 1 pM. Herein, we describe a simple histidine (H) conjugated perylene diimide (PDI) bolaamphiphile (HPH) as a dual-responsive optical marker to develop highly selective and sensitive probe as visible (sol-to-gel transformation), fluorescence and SERS-based Hg^{2+} sensor platform in the water. Remarkably, HPH as a SERS marker supported on Au deposited mono-dispersed nanospheres monolayers (Au-MNM) of polystyrene offers an unprecedented selectivity and the best ever reported detection limit (LOD) of 60 attomolar (aM, 0.01 parts-per-quadrillion (ppq)) for Hg^{2+} in water. This is ten orders of magnitude lower than the United States Environmental Protection Agency (USEPA) tolerance limit of Hg^{2+} in drinking water (10 nM, 2 ppb). This simple and effective design principle of host-guest interactions driven fluorescence and SERS-based detection may inspire the future molecular engineering strategies for the development of ultrasensitive toxic analyte sensor platforms.

1. Introduction

Mercury is one of the top ten globally widespread hazardous environmental pollutants and recognized as a major public health concern by the World Health Organization (WHO) (Qiu, 2013; Schrope, 2001). Even at very low concentrations (> 2 mg/Kg body weight per day) of mercury exposure is responsible for many fatal diseases like Minamata disease, pulmonary edema, cyanosis, loss of intelligence quotient (IQ) and nephritic syndrome, respectively (Jensen and Jernelov, 1969; Nolan and Lippard, 2008). Although few conventional analytical methods permit ultrasensitive detection of Hg^{2+} in water, the expensive experimental setup, long response time and complex sample preparation make them unsuitable for routine monitoring (Esmaielzadeh Kandjani et al., 2015). Consequently, conductometric and optical Hg^{2+} readout methods in water are emerging as potential alternatives (Duan and Zhan, 2015; Kim et al., 2012; Nolan and Lippard, 2008; Pandeeswar et al., 2016a). Diverse colorimetric and fluorometric Hg^{2+} detection systems in water using organic chromophores, fluorophores (Areti et al., 2014; Dessingou et al., 2012; Harano et al., 2007; Hatai et al., 2012; Joseph et al., 2008; Nolan and Lippard, 2008; Pal et al., 2014; Shiraishi et al., 2007; Yoon et al., 2005), conjugated polymers (Liu et al., 2007), DNAzymes (Liu and Lu, 2007), proteins (Wegner et al., 2007), oligonucleotides and nanoparticles (NPs) (Jiang et al., 2011; Lee et al., 2007; Lin et al., 2013; Miyake et al., 2006; Wen et al., 2011) have been developed. However, the concerns related interference of other metal ions, low sensitivity, complexity and poor water solubility are yet be addressed. In this regard, surface enhanced Raman spectroscopy (SERS) found to be promising analytical tool owing to its unique capabilities, such as high sensitivity reaching up to single molecule detection, ease of sample treatment, robust and ambient operational processability (Nie and Emory, 1997). Recently, a wide range of Au-nanomaterials based SERS sensors for detection of Hg^{2+} has been developed (Table 1) (Esmaielzadeh Kandjani et al., 2015; Song et al., 2016; Sun et al., 2015b; Zhang et al., 2013). Among them, oligonucleotides functionalized Au-SERS markers provide the highest selectivity and sensitivity (ppb to ppt) at controlled environmental (viz, pH, temperature etc.) conditions. Therefore, development of simple, cost-effective, rapid, high-throughput, selective and sensitive (concentration less than a few picomolar or sub-ppq level) detection of Hg^{2+} in water at ambient conditions remains a formidable challenge. Considering the advantages and merits of both fluorescence and SERS methods, herein we describe the histidine (H) conjugated perylene

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* Corresponding authors.
E-mail addresses: suresh.bhargava@rmit.edu.au (S.K. Bhargava), tgraju@jncasr.ac.in (T. Govindaraju).

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Table 1
List of few ultrasensitive Au-nanomaterials based signal turn-on mode SERS Hg^{2+} sensors.

SERS substrate	Raman dye	LOD	Working principle of SERS sensor	Ref.
Au-MNM	HPH	60 attomol/L	Synergy between ordered alignment, small pores of Au-MNM surface and smaller size, high affinity of HPH toward Hg^{2+} ions	This work
AuNPs/SiNWAr[a]	Cy5	0.73 pmol/L	Cy5-labelled-ssDNA[b] structure converts to the hairpin structure to push Cy5 closer to the SERS substrate	(Sun et al., 2015a)
AuNPs	VBB[c]	0.8 nmol/L	Hg^{2+} first reduced by NaH_2PO_2 to form nano-mercury that could catalyze the reduction reaction between NaH_2PO_2 and $HAuCl_4$ producing AuNPs	(Liang et al., 2015)
AuNPs	ATP/MATT/NTP[d]	12.2 pmol/L	T-Hg^{2+}-T mediated duplex DNA to assemble special dimer or trimer nanostructures	(Li et al., 2015)
MSS@Au; AuNPs[e]	DTNB[f]	0.1 nmol/L	T-Hg^{2+}-T mediated duplex DNA to combine MSS@AuNPs and AuNPs	(Liu et al., 2014)
AuNPs	4-NTP	2.24 pmol/L	T-Hg^{2+}-T mediated duplex DNA to trigger the assembling of the DNA modified-AuNPs into nanochains	(Xu et al., 2015)
AgNPs[g]	DEB[h]	0.8 nmol/L	Hg^{2+} linked to DEB to trigger the aggregation of DEB-labelled AgNPs	(Kang et al., 2014)
Metal SRRs[i]	G-tetrad	1 pmol/L	AND, INHIBIT and OR logic gate operations based upon the metallophilic properties of a guanine- and thymine-rich oligonucleotide sequence to K^+ and Hg^{2+}	(Cao et al., 2014)
Au flower particle	PANI[j]	10 pmol/L	Hg^{2+} bond to nitrogen atoms of PANI on Au flower particle, causing the particle aggregation	(Wang et al., 2011)
AgNPs	PANI	1 pmol/L	The same principles as above	(Wang et al., 2013)
Ag@AuNPs	TAMRA[k]	50 nmol/L	Hg^{2+} introduced transformation of DNA single strain to hairpin structure through T-Hg^{2+}-T pairs to let Cy5 at the end of the ssDNA get closer to the SERS substrate	(Han et al., 2010)
Au Nanostars	4-ATP	3.99 pmol/L	T-Hg^{2+}-T mediated duplex DNA to assemble special dimer structure of nanostars	(Ma et al., 2013)
AgNPs	3,5-dimethoxy-4-(6′- azobenzotriazolyl) phenol	1 pmol/L	Hg^{2+} linked to cysteine to trigger the aggregation of cysteine-labelled AuNPs	(Li et al., 2013)
Au SNOF[l]	Cy5	100 pmol/L	T-Hg^{2+}-T pairs induced conformational changes of the ssDNA1 and let DNA1' Raman-labelled complementary match with DNA2 on the SNOF structure	(Kang et al., 2011)
AuNPs	PAL[m]	10 pmol/L	Hg^{2+} linked to PAL to trigger the aggregation of AuNPs	(Cecchini et al., 2014)
AuNPs/rGO/SiO2/Si[n]	TAMRA	0.1 nmol/L	T-Hg^{2+}-T pairs induced the formation of dsDNAs and let the Raman reporter get close to the SNOF substrate	(Ding et al., 2013)

[a] AuNPs, gold nanoparticles; SiNWAr, Si nanowire array.

[b] ssDNA, single-stranded DNA.

[c] VBB, Vitoria blue B.

[d] ATP, aminothiophenol; NTP, nitrothiophenol; MATT, 4-methoxy-α-toluenethiol.

[e] MSS, magnetic silica sphere.

[f] DTNB, 5,5′-dithiobis-(2-nitrobenzoic acid).

[g] AgNPs, silver nanoparticles.

[h] DEB, dialkyne 1,4-diethynylbenzene.

[i] SRRs, artificial split-ring resonators.

[j] PANI, polyaniline.

[k] TAMRA, tetramethyl-rhodamine.

[l] SNOF, single nanowire-on-film.

[m] PAL, polyaromantic ligands.

[n] rGO, reduced graphene oxide. LOD: Limit of detection.