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# Upcycling waste zirconia block dental powders: towards a facile and highly selective on-off optical probe for sensing Zn<sup>2+</sup> and Hg<sup>2+</sup> in aqueous media†

Amin Moghaddasfar, Da Ghodsi Mohammadi Ziarani Db and Alireza Badiei D\*\*

Upcycling waste materials to produce high-value-added substances can pave the way for sustainable development. Waste block dental powders (WBDPs), a valuable source of zirconia, represent a significant portion of dentistry wastage and are valuable candidates for upcycling. Herein, a highly selective and facile optical probe based on upcycled WBDPs with surface interaction of 8-hydroxyquinoline-5-sulfonate (8-HQS) was developed to produce a powerful solid-state optical chemoprobe for sensing  $\rm Zn^{2+}$  and  $\rm Hg^{2+}$  in aqueous media.  $\rm ZrO_2$ -8-HQS provided high selectivity for sensing  $\rm Zn^{2+}$  over a wide range of cations and anions, with a remarkable fluorescence intensity enhancement ( $\rm \lambda_{em}=517~nm$ ) over a wide pH range (4–10). The as-prepared optical probe had a remarkable sensitivity, with a limit of detection (LoD) of 5.2  $\rm \mu M$  for  $\rm Zn^{2+}$ . The fluorescence of the  $\rm Zn^{2+}$  probe complex was quenched in the presence of aqueous solutions of  $\rm Hg^{2+}$ , allowing the as-prepared chemo-probe to sense  $\rm Hg^{2+}$  in aqueous media (LoD of 0.8  $\rm \mu M$  for  $\rm Hg^{2+}$ ). The Stern–Volmer equation revealed static and dynamic mechanisms in the quenching process, and the ( $\rm K_S \times \rm K_D$ ) and ( $\rm K_S + \rm K_D$ ) values were 0.0012 and 0.0076, respectively.

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#### 1. Introduction

Upcycling of waste materials is a promising method to convert them into high-value-added substances in their second life. 1,2 In the past few decades, with the development of industries, a wide range of high-value inorganic solids have been produced for use in various sectors. However, significant amounts of these materials have been wasted and have not been recycled or upcycled. The development of a recycling or upcycling system for inorganic solid wastes is one of the important issues that help to continue environmentally sustainable development in the future. For instance, Badiei's group recycled e-waste tantalum and PET waste to synthesize an upcycled metalorganic framework as an optical chemo-sensor for the detection of chloroacetaldehyde.

One of the inorganic solids is yttria tetragonal zirconia (YTZ), which has attracted attention as a promising material for dentistry. It is mainly used for building prosthodontics due to its biocompatibility, mechanical strength, and excellent esthetic properties.<sup>5</sup> The utilization of computer-aided design/computer-aided manufacturing (CAD/CAM) technology allows dental laboratories and clinicians to manufacture dental

restorations with precision and efficiency. However, the CAD/ CAM milling process results in up to 80% of waste from the original disc's or block's bulk due to indirect milling of restoration. During this process, 30% of the waste becomes powder, while up to 50% remains unused, leading to noticeable environmental and economic losses.<sup>6</sup> Nowadays, residual dental YTZ has been recycled by some companies. Unfortunately, the recycled YTZ has an irregular shape and a larger particle size, which can negatively impact its molding and sintering kinetics.<sup>7</sup>

In the last decade, human civilization development has rapidly increased water pollution.8,9 Conventional detection techniques such as GC, LC, and HPLC are limited by some shortcomings. The drawbacks of traditional methods are that some cannot detect low levels of harmful pollutants in water, especially free metal ions, and are costly, inaccessible, and complicated.10,11 Recently, fluorescence chemo-probes have been developed as a powerful method for sensing a wide range of metal ions, due to their high sensitivity, simplicity, selectivity, and on-site detection. Among the chemo-probes, some normally have a receptor that selectively interacts with the specific contaminant and a fluorophore that translates the molecular recognition into a fluorescence signal.12-14 Selective detection of transition metal ions has attracted the attention of researchers due to their fundamental effects on environmental, medical, and biological processes. Among metal ions, zinc ion (as a d<sup>10</sup> metal ion) cannot effectively be detected by conventional methods such as absorption spectroscopy. 15,16 Behind iron, zinc (Zn2+), the second most essential and abundant

<sup>&</sup>quot;School of Chemistry, College of Sciences, University of Tehran, Iran. E-mail: abadiei@ ut.ac.ir

<sup>\*</sup>Department of Organic Chemistry, Faculty of Chemistry, Alzahra University, Iran
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transition element in the human body, plays a crucial role in biological processes, including gene transcription, brain function, signal transmission, and mammalian reproduction. <sup>17,18</sup> A wide range of Zn<sup>2+</sup> fluorescence sensors have been developed based on various mechanisms including internal charge transfer (ICT), <sup>19</sup> excimer/exciplex formation and extinction, <sup>20</sup> photoinduced electron transfer (PET), <sup>21</sup> and fluorescence resonance energy transfer (FRET). <sup>22</sup> However, some of them also respond to other metal ions such as Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, and Co<sup>2+</sup>. Therefore, researchers still desire to develop novel optical chemo-probes with selective high affinity for Zn<sup>2+</sup> over other

relevant metal ions. Mercury (Hg<sup>2+</sup>) is also a hazardous heavy

metal ion that is discharged into water because of human

industrial activity developments, leading to environmental

pollution that can adversely affect human health.<sup>23–25</sup> Therefore, the development of a facile and selective optical probe for

sensing Zn<sup>2+</sup> and Hg<sup>2+</sup> in aqueous media is very essential for the

development of human civilization.26,27

One of the most promising compounds for this purpose is the use of 8-hydroxyguinoline-5-sulfonate (8-HOS) and its derivatives due to their affinity and chelating interaction towards a wide range of metal ions and the high luminescence efficiency of the resulting metal complexes.28,29 As a ligand, it exhibits weak fluorescence activity primarily due to an intramolecular proton (H<sup>+</sup>) transfer from oxygen to nitrogen in the excited state, leading to a non-radiative relaxation pathway. The interaction of 8-HQS with a wide range of metal ions can result in hydroxyl H<sup>+</sup> replacement with metal ions and consequently suppress the intramolecular H<sup>+</sup> transfer.<sup>30</sup> Therefore, the chelation of metal ions to 8-HQS produces a solid-state probe, bestowing it with significant enhancement in the emission intensity. According to research, zirconia (ZrO2) presumably interacts with the sulfonic acid head of 8-HQS, for which two scenarios are possible: tripodal and chelating configuration.31

Furthermore, Zn<sup>2+</sup> presumably bonds to 8-HQS through the nitrogen and oxygen donor atoms.<sup>32-34</sup>

This study, to the best of our knowledge, is the first attempt to upcycle WBDPs with 8-HQS as a powerful solid-state optical chemo-probe. The result revealed that  $\rm ZrO_2$  nanoparticles (NPs) could successfully enhance the PL properties of 8-HQS for the sensing of  $\rm Zn^{2+}$  ions. The PL properties, stability in a wide pH range, particle size distribution, and zeta potential of the asprepared solid-state optical probe were investigated. The quenching of emission intensity in the presence of  $\rm Hg^{2+}$  allows the  $\rm Zn^{2+}$  optical probe complex to sense  $\rm Hg^{2+}$  in aqueous media. The quenching mechanism was evaluated by the Stern–Volmer equation and illustrated static and dynamic mechanisms in the quenching process.

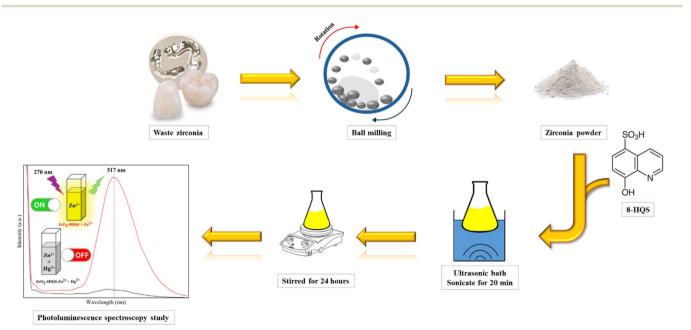
# 2. Experimental section

#### 2.1. Chemicals

The chemicals used in this study are waste zirconia block, 8-HQS (Merck), sodium hydroxide (NaOH, Sigma), hydrochloric acid (HCl, Sigma), nitrate salts of the metal cations (K<sup>+</sup>, Ag<sup>+</sup>, Hg<sup>+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup>, Ca<sup>2+</sup>, Pb<sup>2+</sup>, Fe<sup>2+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Hg<sup>2+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, and Al<sup>3+</sup>) and sodium salts of anions (I<sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, MoO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup> and SCN<sup>-</sup>). All the above-mentioned compounds were of HPLC-reagent grade and used without any further purification.

#### 2.2. Characterization techniques

For Fourier-transform infrared (FTIR) spectroscopy measurement of ZrO<sub>2</sub> NPs, Rayleigh WQF-510A (China) was used. A tablet mixture of ZrO<sub>2</sub> NPs and potassium bromide (KBr) was scanned in the range of 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> with 9 scans. The X-ray diffraction (XRD) pattern to determine the



Scheme 1 Schematic of the preparation of ZrO<sub>2</sub>-8-HQS as an on-off optical chemo-probe for sensing Zn<sup>2+</sup> and Hq<sup>2+</sup>.

crystallinity and phase of the  $ZrO_2$  NPs was recorded using a Rigaku Ultima IV (Belgium) instrument (the characterization was done at ambient temperature (K $\alpha$  X-ray of Cu was used)). Scanning electron microscopy (SEM) was performed using a MIRA3-Tescan for morphology investigation. The Raman spectrum was studied using a Teksan N1-541 instrument (Nd:YAG laser source,  $\lambda=785$  nm/Iran). To find the optical properties of the as-prepared chemo probe, a UV-vis spectrophotometer (Raleigh UV-1600/China) and a PL spectrometer (Agilent-G980A/USA) were used. Horiba SZ-100 was used for dynamic light scattering (DLS) and zeta potential to estimate

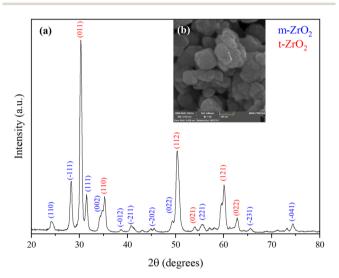


Fig. 1 (a) XRD pattern and (b) SEM image of  $\rm ZrO_2$  NPs prepared from WBDPs.

the particle size of ZrO<sub>2</sub>-8-HQS and ZrO<sub>2</sub> and to confirm the interaction between HQS and ZrO<sub>2</sub> in the liquid phase, respectively.

# 2.3. Suspension preparation and photoluminescence property examination

The WBDP ball milling was used to achieve a fine  $ZrO_2$  NPs powder. To activate the  $ZrO_2$  NP surface, 0.03 g of the obtained  $ZrO_2$  NPs were dispersed in 50 mL of distilled water and sonicated in an ultrasonic bath for 20 min. Then, 0.01 g of 8-HQS was dissolved in 50 mL of water and poured into the  $ZrO_2$ -activated suspension. The obtained suspension was sonicated for 20 min and then stirred for 24 hours (Scheme 1). For PL studies, 2 mL of prepared suspension was poured into a cuvette. Subsequently, 5  $\mu$ L of different cations and anions ( $10^{-2}$  M) was added to examine the chemo-sensitivity of the as-prepared probe. The pH of the solution was adjusted by utilizing the desired volumes of HCl and NaOH solutions.

## 3. Results and discussion

#### 3.1. Characterization of ZrO<sub>2</sub> NPs and ZrO<sub>2</sub>-8-HQS

The XRD analysis obtained from  $ZrO_2$  NPs revealed that the particles are highly pure and crystalline (Fig. 1a). The deflection peaks revealed sharp and high intensity. The XRD obtained result confirms the dominance of the tetragonal phase of  $ZrO_2$  NPs over the monoclinic phase (JCPDS cards no. 17-0923 and 37-1484). The positions of the deflections corresponding to the monoclinic phase were (110), (-111), (111), (002), (-012), (-211), (-202), (022), (221), (-231), and (-041), while the

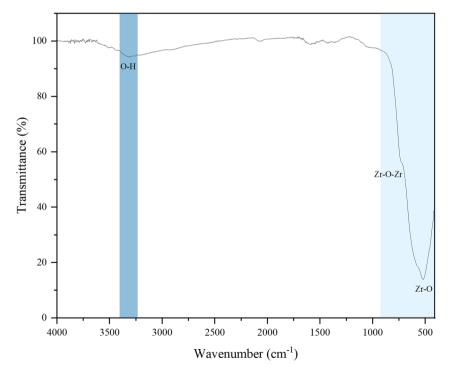


Fig. 2 FTIR spectrum of ZrO<sub>2</sub> NPs prepared from WBDPs.

positions corresponding to the tetragonal phase were (011), (110), (112), (021), (121), and (022). Furthermore, the crystallite size of the  $\rm ZrO_2$  NPs was estimated from the XRD data using the Scherrer equation given in eqn (1):

$$D = \frac{k\lambda}{\beta\cos\theta} \tag{1}$$

In this context, the size of the crystallite is represented as D, where k = 0.89 denotes a correction particle shape factor. The full width at half maximum (FWHM) is represented as  $\beta$ , the

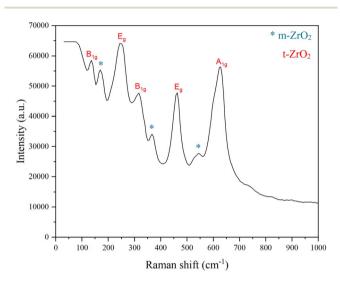


Fig. 3 Raman spectrum of ZrO<sub>2</sub> NPs prepared from WBDPs.

Table 1 DLS results of ZrO<sub>2</sub> NPs and ZrO<sub>2</sub>-8-HQS

Sample	Hydrodynamic radius (nm)	PL
$ m ZrO_2$ $ m ZrO_2$ -8-HQS	16.1 23.1	0.076 0.230

wavelength of the Cu target is 1.54 Å and is represented as  $\lambda$ , and the Bragg angle is represented as  $\theta$ . The average crystallite size was calculated to be 16.55 nm using the Debye–Scherrer equation.

The SEM characterization of the as-prepared ZrO<sub>2</sub> NPs is illustrated in Fig. 1b. The SEM result reveals the aggregation of NPs. Furthermore, it confirmed a uniform morphology of the as-prepared NPs, and the particle size was estimated using the Digimizer software and obtained as about 14 nm. The Fourier transform infrared (FTIR) spectra recorded in the range of 4000–400 cm<sup>-1</sup> are presented in Fig. 2. In the fingerprint region at 900–500 cm<sup>-1</sup>, the transmittance peak at 733 cm<sup>-1</sup> corresponds to the Zr–O–Zr vibration bond. The peak at 523 cm<sup>-1</sup> exhibits a Zr–O peak. To distinguish the structure of ZrO<sub>2</sub>, the Raman spectra of ZrO<sub>2</sub> are displayed in Fig. 3. The vibration bonds of m-ZrO<sub>2</sub> appeared at 170, 366, and 544 cm<sup>-1</sup>. Meanwhile, the vibration bonds of t-ZrO<sub>2</sub> appeared at 135, 247, 316, 461, and 625 cm<sup>-1</sup>.<sup>35</sup>

The DLS results of ZrO<sub>2</sub>-8-HQS are shown in Fig. S1.† According to these results, some NPs successfully interacted with 8-HQS, forming complexes of 23.1 nm, while others remain dispersed as ZrO<sub>2</sub> NPs in water, measuring 16.1 nm. This behavior can be clarified by the formation of coordination complexes between the ZrO2 NPs and 8-HQS. It is pertinent to mention that the PL properties obtained from DLS analysis confirm this interaction. As indicated in Table 1, the PL properties of ZrO2 NPs interacting with 8-HQS show a remarkable increase in emission intensity compared to ZrO<sub>2</sub> NPs alone. Additionally, the DLS peak of ZrO2 NPs is sharp, whereas the DLS peak of ZrO<sub>2</sub>-8-HQS is broader. This phenomenon is attributed to the uniform hydrodynamic radius around ZrO<sub>2</sub> NPs. However, the interaction between 8-HQS and the ZrO<sub>2</sub> network is not uniform, resulting in a non-uniform hydrodynamic radius and a broad non-uniform DLS peak for ZrO2-8-HOS.

The zeta potential of  $ZrO_2$ -8-HQS, as shown in Fig. S2,† revealed a negative charge of -0.3 mV, indicating the successful interaction of 8-HQS with  $ZrO_2$  NPs.

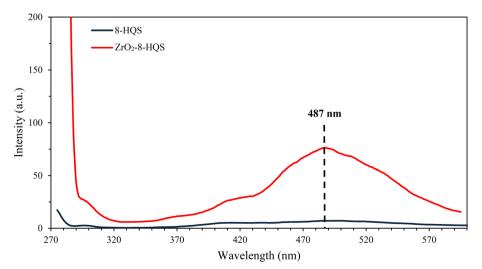


Fig. 4 Fluorescence emission comparison of 8-HQS (dark blue line) and  $ZrO_2$ -8-HQS (red line) ( $\lambda_{PX} = 270$  nm).

#### 3.2. Photoluminescence examination

3.2.1. ZrO<sub>2</sub>-8-HQS as a sensory probe for Zn<sup>2+</sup>. Optical chemo-probe gained scientific attention due to their promising advantages compared to the conventional methods. To visualize the performance of ZrO<sub>2</sub>-8-HQS as the optical chemo-probe, a wide range of anions and cations were used to estimate its selectivity and sensitivity. For all PL analyses, 2 mL of ZrO<sub>2</sub>-8-HQS was poured into the cuvette, and the excitation wavelength

was adjusted at 270 nm ( $\lambda_{ex}=270$  nm). The PL studies of 8-HQS and  $ZrO_2$  bonded to 8-HQS ( $ZrO_2$ -8-HQS) are illustrated in Fig. 4. The PL results showed an enhancement in the emission intensity of  $ZrO_2$ -8-HQS at 487.01 nm. According to research, zirconia bonded with the sulfuric acid head of 8-HQS. $^{36}$ 

To evaluate the selectivity of the as-prepared chemo-probe for sensing ions in water, 2 mL of  $ZrO_2$ -8-HQS was poured into the cuvette, followed by the addition of 5  $\mu$ L of various

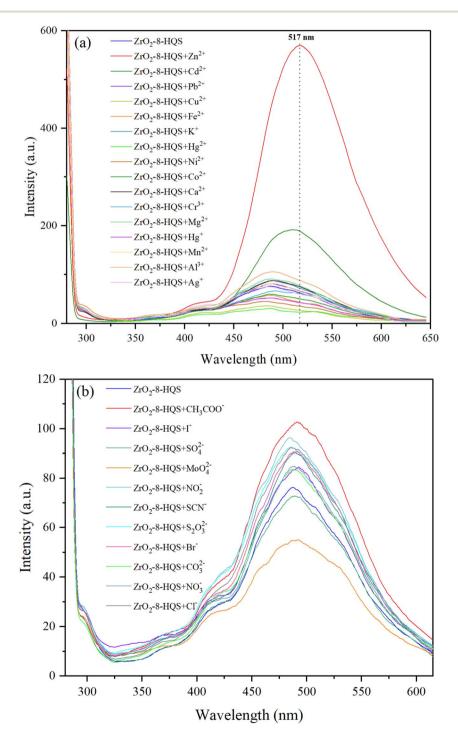
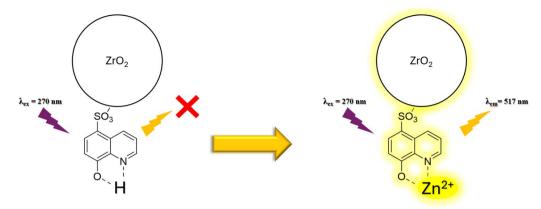


Fig. 5 Fluorescence emission of ZrO<sub>2</sub>-8-HQS in the presence of a wide range of (a) metal ions including K<sup>+</sup>, Ag<sup>+</sup>, Ni<sup>2+</sup>, Cm<sup>2+</sup>, Cd<sup>2+</sup>, Ca<sup>2+</sup>, Pb<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Hg<sup>2+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, and Al<sup>3+</sup> and (b) anions including I<sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, MoO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup> and SCN<sup>-</sup> ( $\lambda_{ex} = 270$  nm).



Scheme 2 Mechanistic pathway of the ZrO<sub>2</sub>-8-HQS for the sensing of Zn<sup>2+</sup>.

Table 2 Compression of different studies to detect  $Zn^{2+}$ 

Sensor	LoD (M)	Measured signal	Reference
4-Methyl-2,6-bis((E)-(2-(phthalazin-1-yl)hydrazono)methyl)phenol	$2.3\times10^{-6}$	Fluorescence	38
(E)-1-((2-(9-(Naphthalen-1-yl)-8-(thiophen-2-yl)-9H-purin-6-yl)hydrazono)methyl)naphthalen 2-ol	$6.1\times10^{-8}$	Fluorescence	39
2-(Pyridin-2-yl)-4,7-di(thiophen-2-yl)-3 <i>H</i> -benzo[ <i>d</i> ]imidazole	$1.6\times10^{-8}$	Fluorescence	40
3-[1-(4 Dimethylamino)phenylimino]ethyl 4-hydroxy-2 <i>H</i> -chromen-2-one	$6.5  imes 10^{-5}$	Fluorescence	41
7-(2',4'-Dihydroxy benzylidene amino)-4-methylcoumarin	$3.8 \times 10^{-6}$	Fluorescence	42
Dipicolinohydrazonamide	$24\times 10^{-6}$	Fluorescence	43
4,4'-(Propane-2,2-diyl)bis(2-(((2morpholinoethyl)imino)methyl)phenol)	$7.05 \times 10^{-8}$	Fluorescence	44
(E)-2-((2-(2,4-Dinitrophenyl)hydrazineylidene) methyl)phenol	$1.1\times10^{-8}$	Fluorescence	45
(E)-3,5-Di- <i>tert</i> -butyl-2-hydroxy-N'-((1-hydroxynaphthalen-2-yl)methylene)benzohydrazide	$2.2  imes 10^{-9}$	Fluorescence	46
2-(Benzo[d]thiazol-2-yl)-6-(1-(pyridin-2-yl)imidazo[1,5-a] pyridin-3-yl) phenol	$2.36 \times 10^{-8}$	Fluorescence	47
$ m ZrO_2 ext{-}8 ext{-}HQS$	$5.2\times10^{-6}$	Fluorescence	This study

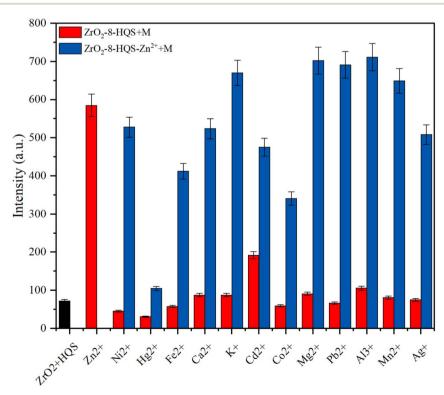


Fig. 6 Effect of various metal ions on the  $ZrO_2$ -8-HQS +  $Zn^{2+}$  emission intensity.

metal ions and anions (the concentration of all metal ions and anions adjusted at  $10^{-2}$  M). Fig. 5 reveals the response of the chemo-probe to different metal ions and anions. Compared to other metal ions, the emission intensity was enhanced for  $Al^{3+}$ ,  $Cd^{2+}$ , and  $Ag^+$ , while other ions caused quenching. Upon the addition of  $Zn^{2+}$ , the emission intensity was remarkably enhanced and showed a red shift from 487.01 nm to

517.951 nm. Jianbo and co-workers<sup>34</sup> reported that Zn<sup>2+</sup> interacts with oxygen and nitrogen groups of 8-HQ and produces 8-HQ zinc complexes that suppress the intramolecular H<sup>+</sup> transfer (Scheme 2). The absorption spectroscopy results (Fig. S3†) clearly indicated a blue shift after the interaction of Zn<sup>2+</sup> with the as-prepared solid-state optical probe, leading to an ICT mechanism.<sup>37</sup> According to Fig. S4,† the LoD of sensing Zn<sup>2+</sup>

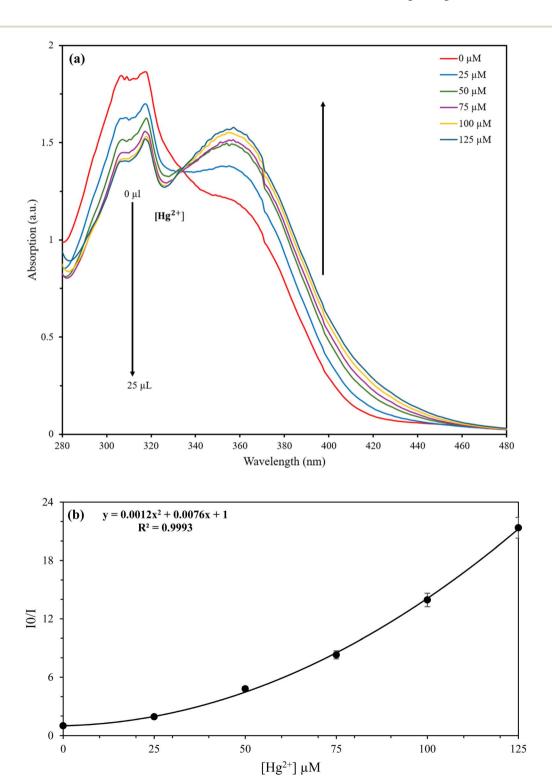


Fig. 7 (a) Titration plot of ZrO<sub>2</sub>-8-HQS-Zn<sup>2+</sup> through the addition of Hg<sup>2+</sup>. (b) Non-linear modified Stern-Volmer quenching plot.

Table 3 Comparison of different studies to detect Hg<sup>2+</sup>

Sensor	LoD (M)	Measured signal	Reference	
rGO@MoS <sub>2</sub>	$2.3 \times 10^{-9}$	Fluorescence	49	
S,N-GQDs	$9.1 \times 10^{-6}$	Fluorescence	50	
Tetra(p-dimethylaminophenyl)porphyrin	$8.0 \times 10^{-9}$	Fluorescence	51	
CNPs-RhB nanohybrid	$4.2\times10^{-8}$	Fluorescence	52	
PET-CHEF-FRET	$1.5  imes 10^{-10}$	Fluorescence	53	
Rhodamine pyrene conjugate	$1.9\times10^{-5}$	Fluorescence	54	
2-(Rhodamine- <i>b</i> -hydrazido)- <i>N</i> -(quinolin-8-yl)acetamide	$4.5 \times 10^{-7}$	Fluorescence	55	
NETBZ	$1.4  imes 10^{-8}$	Fluorescence	56	
ZrO <sub>2</sub> -8-HQS-Zn	$8.04\times10^{-7}$	Fluorescence	This study	

was calculated as  $5.2~\mu M$ . The response time of the as-prepared chemo probe interacting with  $Zn^{2+}$  was evaluated, and is shown in Fig. S5.† The results indicated that the interaction of  $ZrO_2$ -8-HQS occurred rapidly within the first 10 seconds, and no noticeable change in emission intensity was observed afterward, even when the duration was extended to 300 seconds. Table 2 demonstrates the compression of various studies to detect  $Zn^{2+}$  with this work.

**3.2.2. Effects of competitive metal ions.** The presence of a wide range of interfering ions in environments can affect chemo-probe response. In this regard, metal ions including  $\operatorname{Ni}^{2+}$ ,  $\operatorname{Hg}^{2+}$ ,  $\operatorname{Fe}^{2+}$ ,  $\operatorname{Ca}^{2+}$ ,  $\operatorname{K}^+$ ,  $\operatorname{Cd}^{2+}$ ,  $\operatorname{Co}^{2+}$ ,  $\operatorname{Mg}^{2+}$ ,  $\operatorname{Pb}^{2+}$ ,  $\operatorname{Al}^{3+}$ ,  $\operatorname{Mn}^{2+}$ , and  $\operatorname{Ag}^+$  were added to the mixture of  $\operatorname{ZrO}_2$ -8-HQS +  $\operatorname{Zn}^{2+}$  for competitive study examination (Fig. 6). The results indicated that  $\operatorname{ZrO}_2$ -8-HQS +  $\operatorname{Zn}^{2+}$  showed no significant change in emission intensity in the presence of  $\operatorname{Ni}^{2+}$ ,  $\operatorname{Ca}^{2+}$ ,  $\operatorname{Cd}^{2+}$ ,  $\operatorname{Mn}^{2+}$ , and  $\operatorname{Ag}^+$ . However, the emission intensity was slightly enhanced by the presence of  $\operatorname{K}^+$ ,  $\operatorname{Mg}^{2+}$ ,  $\operatorname{Pb}^{2+}$ , and  $\operatorname{Al}^{3+}$ . In contrast, the addition of  $\operatorname{Co}^{2+}$  and  $\operatorname{Fe}^{2+}$  caused a negligible quenching of the emission intensity of  $\operatorname{ZrO}_2$ -8-HQS +  $\operatorname{Zn}^{2+}$ . Notably, the addition of  $\operatorname{Hg}^{2+}$  completely quenched the emission intensity.

3.2.3.  $ZrO_2$ -8-HQS +  $Zn^{2+}$  as a sensory probe for  $Hg^{2+}$ . Through the competitive investigation,  $Hg^{2+}$  remarkably quenched the emission intensity of  $ZrO_2$ -8-HQS +  $Zn^{2+}$ . To find the quenching mechanism, the Stern–Volmer (SV) equation was used. The emission intensity quenches are related to the quencher concentration according to the following SV equation:

$$\left(\frac{\mathrm{IF}_0}{\mathrm{IF}}\right) = 1 + K_{\mathrm{SV}}[\mathrm{Q}] \tag{2}$$

Herein, IF<sub>0</sub> is equal to the emission intensities in the absence of quenchers and IF is equal to the emission intensities in the quencher presentation. The slope of the SV equation,  $K_{SV}$ , is the SV constant, and [Q] is the quencher concentration. The modified SV equation is as follows:

$$\left(\frac{\text{IF}_0}{\text{IF}}\right) = (1 + K_S[Q])(1 + K_D[Q]) \tag{3}$$

 $K_{\rm S}$  and  $K_{\rm D}$  are represented as static and dynamic constants, respectively. Fig. S6† indicates the relative change in the emission intensities of  ${\rm ZrO_2}$ -8-HQS +  ${\rm Zn^{2^+}}$  as a function of quencher concentration. The concept of the SV quenching plot reveals that upward deviation from linearity indicates a combination of static and dynamic quenching, whereas no such deviation

indicates the occurrence of only one type of quenching mechanism. <sup>48</sup> According to the result, both dynamic and static quenching mechanisms are present in this system (Fig. 7). This conclusion is supported by the strong second-degree polynomial correlation observed between IF<sub>0</sub>/IF (fitting data with modified SV equation) and the quencher concentration. The coefficient of determination ( $R^2$ ) exceeded 0.99, indicating an excellent fit between these variables. The ( $K_S \times K_D$ ) and ( $K_S + K_D$ ) values are 0.0012 and 0.0076, respectively.

To further evaluate the quenching mechanism of the optical probe, absorption spectroscopy was performed. The results indicated an isosbestic point at a wavelength of 333 nm following titration with Hg²+ (Fig. 7). Therefore, the quenching process allows the ZrO₂-8-HQS + Zn²+ complex optical probe to detect Hg²+ selectively in aqueous solutions (LoD = 0.8  $\mu M$ ). The interaction of Hg²+ with ZrO₂-8-HQS + Zn²+ occurred rapidly within the first 10 seconds and showed no significant change over 300 seconds, as depicted in Fig. S7.† Table 3 demonstrates the comparison of various sensors that detect Hg²+ reported in previous studies with that demonstrated in this work.

#### 3.3. pH effect

To investigate the pH effects on the as-prepared solid-state optical chemo-probe, a wide range of pH values from 2 to 10 were studied. Fig. S8† illustrates the result of optical chemo-probe performance in the sensing of  $\mathrm{Zn}^{2+}$  ion in a wide pH range. According to the result, the as-prepared probe had good performance in various pH values from 4 to 10. Under harsh acidic conditions, the intensity of the chemo-probe was completely quenched (close to zero). At pH from 2 to 3, the intensity of the probe is approximately the same as fresh  $\mathrm{ZrO}_2$ -8-HQS. Therefore, this optical probe is unable to work under harsh acidic conditions. At pH = 4, the intensity enhanced to about 688, but above this pH, the intensity of the chemo-probe had not changed significantly.

#### 4. Conclusion

In summary, upcycling valuable waste materials can pave the way for preventing the loss of important resources by converting them into high-value-added materials for use in specific applications. In this study, a facile and highly selective optical probe for Zn<sup>2+</sup> in an aqueous environment was developed by upcycling

WBDPs with 8-HQS. The results clearly confirm that the prepared optical probe could selectively detect  $Zn^{2^+}$  with a significant enhancement at  $\lambda_{em}=517$  nm. Furthermore, the as-prepared optical probe could operate within a wide range of pH with high sensitivity. Through the competitive test with various ions, it was observed that  $Hg^{2^+}$  caused quenching effects. It allows the  $Zn^{2^+}$  optical complex to detect  $Hg^{2^+}$  in aqueous media. Therefore, upcycling waste materials to create high-value-added substrates, such as solid-state optical chemoprobes, can contribute to sustainable development.

# Data availability

The data supporting this article have been included as part of the ESI. $\dagger$ 

## Conflicts of interest

There are no conflicts to declare.

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