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Research Paper

# Micro/nanostructured porous ZnO as a new DGT binding phase for selective measurement of Cu(II) in water

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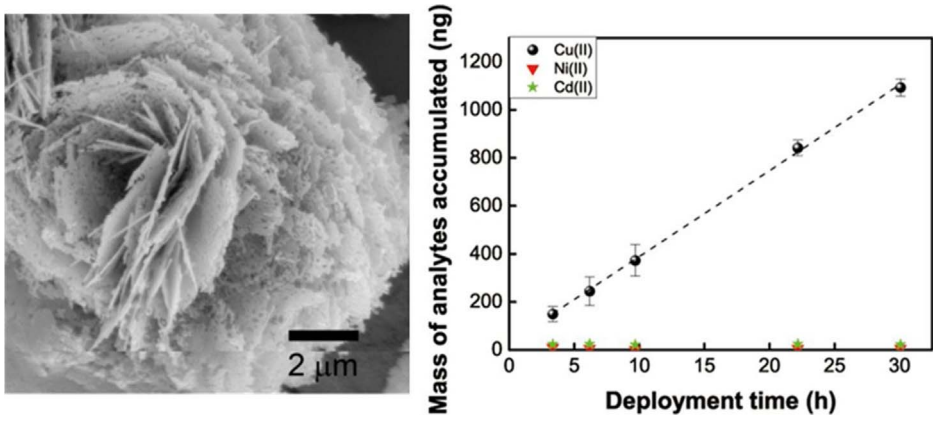
## GRAPHICAL ABSTRACT




## ARTICLE INFO

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## ABSTRACT

Micro/nanostructured porous ZnO was first utilized as a new binding phase in DGT (diffusive gradients in thin film) devices for selective measurement of Cu(II) in water, on the basis of its selective adsorption performance. In this case, the accumulated heavy metal ions onto the binding phase could be easily determined by a simple complete acid-dissolution elution process without the complicated elution experiments including measurement of elution efficiency. The selective adsorption performance of the micro/nanostructured porous ZnO towards Cu (II) was evaluated in single- and ternary-component metal solutions [Cu(II), Ni(II) and Cd(II) ions]. It was found that the adsorption amount and adsorption rate of Cu(II) ions onto the porous ZnO were the highest by comparing with that of Ni(II) and Cd(II) ions, exhibiting strong adsorption and good selectivity toward Cu(II) ions. The adsorption of heavy metal ions on the ZnO can be well described by Pseudo-second-order model, implying chemical bonding related interaction between the porous ZnO and heavy metal ions. Importantly, the ZnO was utilized as binding phase of DGT device for heavy metal ions measurement, the diffusion coefficient of Cu(II) in

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the diffusive gel was calculated to be $6.13 \times 10^{-6}$ $cm^2$ $s^{-1}$, implying such ZnO could be a new potential binding phase towards trace Cu(II) ions detection.

## 1. Introduction

It is well known that heavy metal ions such as copper, is harmful to the health of humans and aquatic life, even at very low concentrations [1–3]. It is therefore important to measure or monitor trace concentrations of heavy metal ions in waters. However, trace heavy metal ions can be difficult to measure accurately by traditional methods owing to their limits of detection (LODs) [4]. Therefore, an effective method to measure trace concentrations of heavy metal ions accurately in water is highly desired.

The diffusive gradients in thin film (DGT) technology is an effective method for detecting or monitoring trace heavy metal ions in water [4]. As shown in Scheme (S1, S2) a DGT device is composed of a binding gel layer, diffusive gel layer and filter membrane. Concentration measurement of the target analytes in water depends on the constant diffusion of target analytes from the bulk solution, through the diffusive gel layer to the binding phase where it is captured. To accurately measure the target analytes in the bulk solution, the accumulated amount of the analyte in the binding phase (M) is proportional to the device deployment time based on Fick's first law of diffusion [5]. There are extensive reports on the detection of trace heavy metal ions using DGT technology [6–12]. Generally, the capture of target analytes by the binding phase depends on its adsorption performance, which is an important physical-chemistry process [13]. For example, complex between the netal ion and the imminodiacetate groups was formed when using Chelex-100 as a binding phase of DGT device [14,15]. Therefore, it is critical for the binding phase to have a stable structure and a selectively strong adsorption to the target analytes [16]. Nanosized adsorbents could be the candidates for such binding phases due to their high surface area. However, nanosized adsorbents can easily aggregate, leading to the reduction in the active surface area. Hierarchical micro/nanostructured materials, which are composed of the microsized objects with nanostructures, could overcome such disadvantages [3,17–20]. These materials with micro/nano-architectures possess large surface to volume ratios, high structural stability, and hence could be used for high efficient binding phase in DGT technology.

Selective adsorption is very important for capturing target analytes in the presence of high concentrations of competing ions [3,19,21,22]. Hence, a binding phase with high selectivity is also needed for accurate measurement of the target analytes [16]. Therefore, micro/nanostructured binding phases with strong, selective adsorption are ideal for DGT technology.

More importantly, in general, the accumulated amount of analytes (M) was often determined by elution experiments including the evaluation of elution efficiency. Such as Chelex-100 [14] and Metsorb [9] based DGT, and so on. The complicated elution process tends to bring deviation in the M value owing to the additional calculation of elution efficiency [9,14]. Thus, it is conceived that the elution efficiency should be 100% if we can complete dissolve the adsorbent of binding gel after deployment. Inorganic oxides could be utilized as excellent adsorbent [23,24] which could be obtained by various methods [25,26]. Among them, ZnO is an environmental friendly amphoteric oxide, which can dissolve easily in strong acid conditions [27]. Inspired by this, the M value could be evaluated by complete dissolving the ZnO binding gel in strong acid solution without measurement of elution efficiency supposing ZnO was utilized as a binding phase of DGT, leading to facile and accurate determination of M values.

However, adsorption performance of ZnO has not attracted much attention. In our previous work, we found that the micro/nanostructured ZnO possessed selective adsorption performance towards Cu (II) based on its adsorption capacity [3,19]. Following that, other researchers demonstrated the excellent adsorption capacity of ZnO toward heavy metal ions [2,28,29]. Therefore, the micro/nanostructured porous ZnO might be an ideal binding phase in DGT for accurate measurement of Cu(II) which has not been reported before. Especially, the kinetic adsorption selectivity towards Cu(II) ions has not been evaluated, which plays important role in DGT technology.

In this work, the selectively kinetic adsorption performance of micro/nanostructured porous ZnO towards Cu(II) was evaluated in single-component and ternary-component solutions. The results showed that the porous ZnO could selectively adsorb Cu(II) in both single-component and ternary-component solutions. Further, such micro/nanostructured porous ZnO was utilized as a new binding phase in DGT devices. After DGT deployment, the accumulated amounts of heavy metal ions (M) were determined through an acid-dissolution elution process without measurement of elution efficiency. It has also exhibited that the M value of Cu(II) was in proportional to the deployment time, indicating that such structured ZnO could be a potential ideal binding phase in DGT devices for selective measurement of Cu(II) in water. To our knowledge, this is the first time that ZnO micro/nanostructured binding phase has been used in DGT devices for the selective measurement of Cu(II) in water.

## 2. Experimental section

### 2.1. Synthesis and characterization of ZnO

All analytical-grade chemicals were purchased from Sigma-Aldrich corporation (USA) and used as received without further purification. The ZnO adsorbent with micro/nanostructure was prepared following previously reported [3]. As a typical procedure, 0.66 g Zn $(CH_3COO)_2{\cdot}2H_2O$ and 0.54 g urea were first dissolved into a 50 mL ethylene glycol solution which has a volume ratio of $V_{EG}/V_{DIW}$ = 1:1(EG denotes ethylene glycol, DIW denotes deionized water). Then, the mixed solution was put into a 70 mL Teflon-lined autoclave. The autoclave was heated to 160 °C and kept in isothermal conditions for 12 h before cooling to room temperature naturally. The white products were collected and washed with deionized water and ethanol. Finally, the micro/nanostructured porous ZnO were obtained by annealing the white products at 400 °C for 2 h in air.

X-ray diffraction (XRD) measurement was carried out on a Philips X'pert diffractometer using Cu Kα radiation of 0.15419 nm in a 2θ range from 10° to 70°. The morphology of the products was observed using a Sirion 200 FEG field emission scanning electron microscope (FESEM). The high resolution transmission electron microscopic (HRTEM) examinations were carried out on a JEOL-2010 microscope attached to an energy dispersive X-ray spectrometer (EDS, Oxford, Link ISIS). ATR-FTIR spectra were obtained on a Nicolet 6700 instrument.

### 2.2. Adsorption experiments

The adsorption performance was evaluated on the basis of adsorption in the single-component heavy metal ions solution and competitive adsorption in the ternary-component solution.

#### 2.2.1. Preparation of ZnO gel disc

The DGT discs were prepared as follows: 7.5 g cross-linker, 23.75 mL $H_2O$ and 18.75 mL acrylamide (40%, m/v) were mixed together to form a gel solution. Then, 10 mL gel solution was added to 0.5 g of the micro/nanostructured porous ZnO, 60 μL 10% (m/v) APS