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A High-performance Polyurethane Sponge for the Detection, Absorption and Separation of Cu^{2+} Ions

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Abstract: Detection and simultaneous separation of copper ions are important. In this study, a fluorescent chemosensor (a copper sensitive molecule), was prepared using 6-Bromo-benzo[de]isochromene-1,3-dione as precursor. The as-prepared fluorescent molecules contains hydroxyl group and aminoquinoline moiety. The hydroxyl group enables the fluorescent molecules to anchor to porous polyurethane (PU) sponge. The chemosensor still remained their recognition ability after they were introduced to PU. Upon the addition of Cu^{2+} ions to the PU sponge, both the color and the fluorescence intensity changed, it suggested that the chemosensor functionalized PU sponges could be used as Cu^{2+} ions sensor. Also, the copper ions could accumulate and be enriched on the sponges. The absorption capacity of the PU sponge (containing 2wt% of the chemosensor) reached 97.26 mg/g, which was higher than that of the solid PU membranes (52.62 mg/g). These polymeric highly sensitive chemosensors may be applied potentially in detection of water pollution, such as electroplate and drain outlet.

Keywords: fluorescent PU sponge, detect and separate Cu^{2+} ions, adsorption ability

1. Introduction

The pollution caused by heavy metal ions, especially heavy metals in water pollution, is one of the most dangerous and serious environmental problems owing to the bioaccumulation of these toxic metal ions[1-2]. Copper plays a vital important role in various biological processes[3] due to its essence of micronutrients to human health[4]. However, copper causes oxidation stress and might be harmful to liver and kidney[5] when the concentrations rose. Hence, the limit of copper had been established below 1.3 ppm in the drinking water by the U.S. Environmental Protection Agency, and the concentration of copper in blood was limited to 100-150 μg/dL (15.7-23.6 μM)[6]. Therefore, a rapid and convenient method for detecting copper was of importance in water quality detection[7, 8] and biological concerns[9,10].

In many works, traditional methods of detecting copper were to synthesize small molecular chemosensor. For example, Yang et al[11] reported three new rhodamine Schiff base sensors. They were sensitive and selective to Cu^{2+} through the rhodamine ring-open approach, and demonstrated the fluorescent imaging of Cu^{2+} in living cells. Lee et al[12] reported some new rhodamine hydrazone derivatives containing an additional phenol group which showed a highly selective ability for Cu^{2+} and showed reversible colorimetric change with Cu^{2+}. Yu et al[13] reported fluorescent chemodosimeter based on the 1,8-naphthyridyl moiety, the chemodosimeter displayed a highly selective behavior for Cu^{2+}. Jung et al[14] developed a fluorescent chemosensor which was a novel coumarin-based fluorescent molecules and showed a high selectivity for Cu^{2+} and a suitable affinity in biologic functions of Cu^{2+}. They also employed the chemosensor for the changes of the fluorescent detection of intracellular Cu^{2+} in cells. However, many of those chemosensors only have a high sensitivity and selectivity for detecting Cu^{2+} [15-17]; they cannot separate Cu^{2+} from the solution, because the chemosensors are aqueous soluble or dispersible. Even after combining with Cu^{2+}, they still remained in the water.

To overcome this drawback, a novel method was brought out that the chemosensor was immobilized on macromolecules, which not only remained the sensitivity, but also improved the operability and convenience for the separation of heavy metals.

In this work, a new chemosensor was synthesized, and it was introduced to porous PU sponge. The chemosensor functionalized PU sponge (FPU) could selectively detect and separate Cu^{2+} ions. The small molecule was firstly synthesized using 6-Bromo-benzo[de]isochromene-1,3-dione reacting with ethanolamine and 8-aminoquinoline, thus the quinoline groups and hydroxyl groups were introduced. The FPU sponge was then formed via reaction of the hydroxyl groups on the chemosensor and the isocyanate groups of 2, 4-tolylene diisocyanate (TDI). The PU was foamed by adding suitable amount of water, and then heated and aged to obtain the porous FPU sponge. This FPU sponge showed excellent detecting and separating ability for Cu^{2+} as low as 10^{-7} mol/L. It is better than the functional solid membranes due to the higher specific surface. The functional sponge may find their potential applications in detection and separation of Cu^{2+} ions pollution.

2. Experimental Section

2.1 Materials

A precursor for the fluorescent co-monomer, 6-Bromo-benzo[de]isochromene-1,3-dione, was purchased from J&K China Chemical Ltd, and recrystallized twice from chlorobenzene. Ethanolamine, 8-aminoquinoline and Tri(dibenzylideneacetone) dipalladium(0) ($Pd_2(dba)_3$) were bought from J&K China Chemical Ltd. (+/-)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) and Sodium tertiary butoxide were products of Aladdin Chemical Co. Ltd.

All the metal salts (Cr^{3+}, Co^{2+}, Pd^{2+}, Zn^{2+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+} ,Cu^{2+}, Fe^{2+} and Fe^{3+}) were purchased from Aladdin Chemical Co. Ltd and used as received.

2,4-tolylene diisocyanate (TDI) and poly(oxyethylene) (PEG 600) with a molecular weight of 600 were from Aladdin Chemical Co.Ltd, and dibutyltin dilaurate, triethanolamine, absolute ethanol, toluene and tetrahydrofuran (THF) purchased from J&K China Chemical Ltd. Ultrapure water ($>17 M\Omega\ cm^{-1}$) from a Milli-Q water system was used throughout the experiment.

2.2 Preparation of 6-Bromo-2-(2-hydroxy-ethyl)-benzo[de]isoquinoline-1,3-dione (BHD)

BHD was prepared by a modified method according to the literature[21]. The process for the preparation of BHD was described as follow: 6-Bromo-benzo[de]isochromene-1,3-dione (0.2 g, 0.7 mmol) reacted with ethanolamine (0.06 mL, 0.7 mmol) by refluxing for 4h in 35 mL of absolute ethanol. After cooling to room temperature, the suspension solution was filtered and washed with ethanol. The crude compound was further purified by recrystallization form ethanol and dried to give the BHD (0.21 g) of a pale yellow product in 90 % yield.

2.3 Synthesis of 2-(2-Hydroxy-ethyl)-6-(quinolin-8-ylamino)-benzo[de]isoquinoline-1,3-dione (HQD)

An dried round-bottomed flask was charged with BHD (0.1 g, 0.3 mmol), 8-aminoquinoline (0.086 g, 0.6 mmol), BINAP (7 mg), $Pd_2(dba)_3$ (5 mg), sodium tertiary butoxide(120 mg). Toluene (50 ml) was added and degassed under a nitrogen atmosphere, stirring for 1 h with ice bath, and then healed to 90℃ for 48 h. The reaction mixture was cooled and filtered through a pad of Celite, and washed with dichloromethane. The residue concentrated in vacuo was purified by flash column chromatography (ethyl acetate: hexane=4:1) to give the HQD (57 mg, 48%).

2.4 Synthesis of chemosensor functionalized PU sponge (FPU sponge)

The porous FPU sponges were prepared by the condensation reaction of the isocyanate groups of TDI and the hydroxyl groups of PEG at the ratio of 1.5:1, and different amount of HQD was added at the room temperature. The catalyst of dibutyltin dilaurate (1 wt%) and triethanolamine (1 wt%) were added after stirring for 10 minutes. Finally water (0.1 mL) was instilled as foaming agent. After heated at 60℃ and aged，the FPU sponge was obtained consequently. the chemosensor, HQD, was added at the weight percentage of 0.5 wt%, 1 wt%, 1.5 wt%, 2 wt% respectively. And then the obtained samples were extracted with ethanol to wash and remove the residual small molecules and the catalysts.

2.5 Synthesis of solid FPU membranes

The preparing process of solid PU membranes was as follows: the ratio of the TDI and PEG was 1.5:1, adding different amount of HQD at 0.5 wt%, 1 wt%, 1.5 wt%, 2 wt% respectively, and THF (30 ml). After stirring for 2 h at 60℃, the solution was poured on a glass slide, dried at room temperature. The solid PU membranes were obtained accordingly.

2.6 Characterization

FTIR and ^{1}H NMR measurements. Fourier transform infrared spectra (FTIR, 4000-500cm^{-1}) were performed on a Nicolet NEXUS 470 spectrometer. The samples were pressed into KBr pellets for measurements. Nuclear magnetic resonance (^{1}H NMR) was measured in DMSO on an AVANCE III-400 (Bruker) spectrometer.

Fluorescence measurements and Fluorescence imaging. Fluorescence spectrum was performed on a Perkin Elmer lambda 35 spectrometer, and it was excitated at 446 nm. Fluorescence images were photographed on a Bx61 fluorescence microscope.

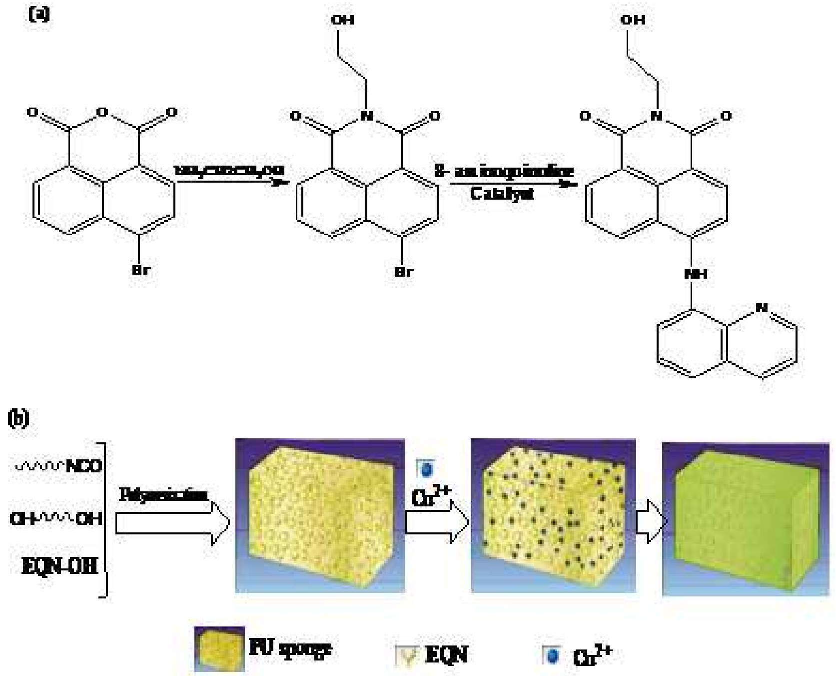
UV-Vis experiments. Solid and liquid samples were measured on a Perkin Elmer lambda 35 UV-Vis spectrometer.

Atomic absorption spectrometry (AAS). The solution of the metal ions was prepared in water, and the solution of the HQD was prepared in DMF solution. A concentration of copper (below 10 mg/L) was determined by an AA-6300 Atomic Absorption Spectroscopy.

XPS measurements. X-ray photoelectron spectroscopy analysis was carried on a spectrometer (Thermo VG Multilab 2000) using an Al Ka X-ray source (300 W PE 25 eV).

3. Results and Discussion

3.1 Synthesis and Characterization of a chemosensor HQD



Scheme 1 (a) the synthetic route of a chemosensor HQD and (b) preparation of the FPU sponge

The HQD was prepared using the procedure showed on **Scheme 1(a)**. Based on the property of 6-Bromo-benzo[de]isochromene-1,3-dione, the amidation reaction of the anhydride was moderate to be conducted. The desired small molecular was synthesized by a Pd-catalyzed (BINAP, $Pd_2(dba)_3$, and sodium tertiary butoxide) aryl amination between 6-Bromo-2-(2-hydroxy-ethyl)-benzo[de]isoquinoline-1,3-dione and 8-aminoquinoline that provided the chemosensor, HQD, in 48% yield after purification by flash column chromatography. **Fig. 1** showed the FT-IR spectra of the small molecule (HQD) and the starting material. The strong C-O-C peak of 1778 cm^{-1} and 1733 cm^{-1} disappeared and the new peaks of 1698 cm^{-1} and 1663 cm^{-1} were determined compared with peaks of 6-Bromo-benzo[de]isochromene-1,3-dione. The

C-Br peak of 556 cm^{-1} disappeared and the new peak C-N of 1366 cm^{-1} emerged. This means that the reaction by a Pd-catalyzed aryl amination between 6-Bromo-2-(2-hydroxy-ethyl)-benzo[de]isoquinoline-1,3-dione and 8-aminoquinoline was successful.

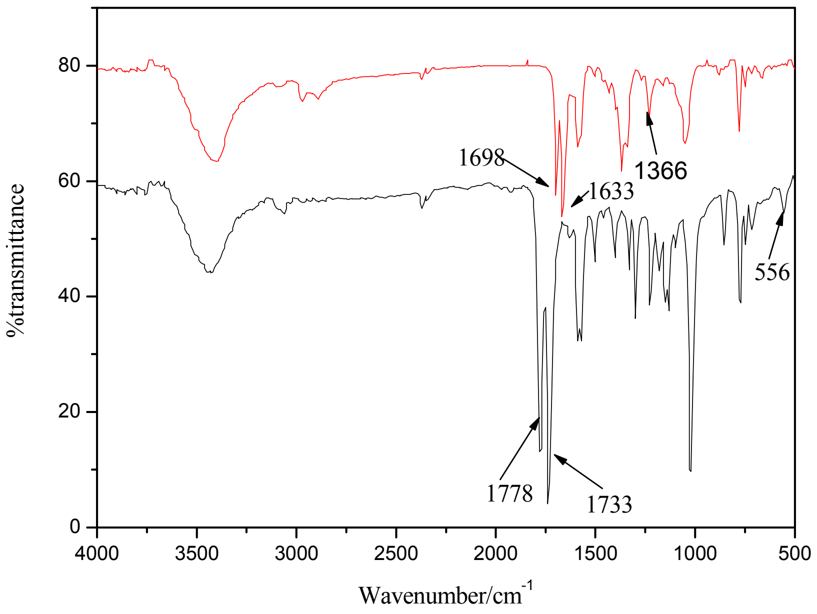


Fig. 1 The FT-IR spectrum of the starting material (the black line) and the chemosensor (HQD) (the upper one).

To further verify the structure of HQD, ^{1}H NMR spectrum was shown in **Fig. 2**. It can be seen that the peaks ranging from 8.2 and 8.7 ppm represent for the H peaks of naphthalene ring, and the peaks of about 4.3 ppm and 3.8 ppm represented for the two -CH$_2$- (the red line in Fig. 2). Compared to the spectra of BHD, the figure of HQD (the lower line in Fig. 2) portrayed that the new peaks of quinoline appeared at between 6.7 ppm and 7.3 ppm and the peak of 5.8ppm. Moreover, the H peaks of naphthalene ring reduced about 0.3 ppm owed to the introduction of quinoline ring.

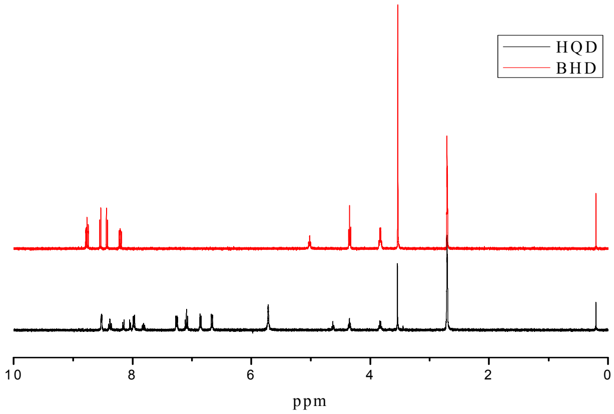


Fig. 2 The ^{1}H NMR spectrum of BHD (the red line) and the chemosensor HQD (the lower line).

3.2 Synthesis and Characterization of Polyurethane sponges

TDI and PEG were usually used to prepare polyurethane films and foams[18-20]. The process for the preparation of the FPU sponge was shown in **Scheme 1(b)**. It was the simple and quick method that The FPU sponge was synthesized using water as foaming agent under the condition of catalyst without solvent. **Fig. 3** showed the XPS scans of PU membrane and the PU sponge upon adsorption Cu^{2+}. In order to confirm the polymerization of the isocyanate groups of TDI and the hydroxyl groups of small sensitive molecule, Br atom was measured after the polymerization reaction of TDI, PEG and BHD. As shown in **Fig. 3a** and **b**, it proved that the small molecule polymerized onto the polyurethane successfully. When the FPU sponge was measured by XPS, the N peaks could not be distinguished easily, because both HDQ and PU contain N atoms. The BHD containing PU was measured to confirm that sensitive molecules could be introduced to PU using this method. The FPU sponge combining with Cu^{2+} (color change from yellow to green) was extracted, rinsed and evaporated, and then measured by XPS, it can be seen that Cu atom could be seen (**Fig. 3c** and **3d**), which further confirmed the formation of the Cu-PU sponge.

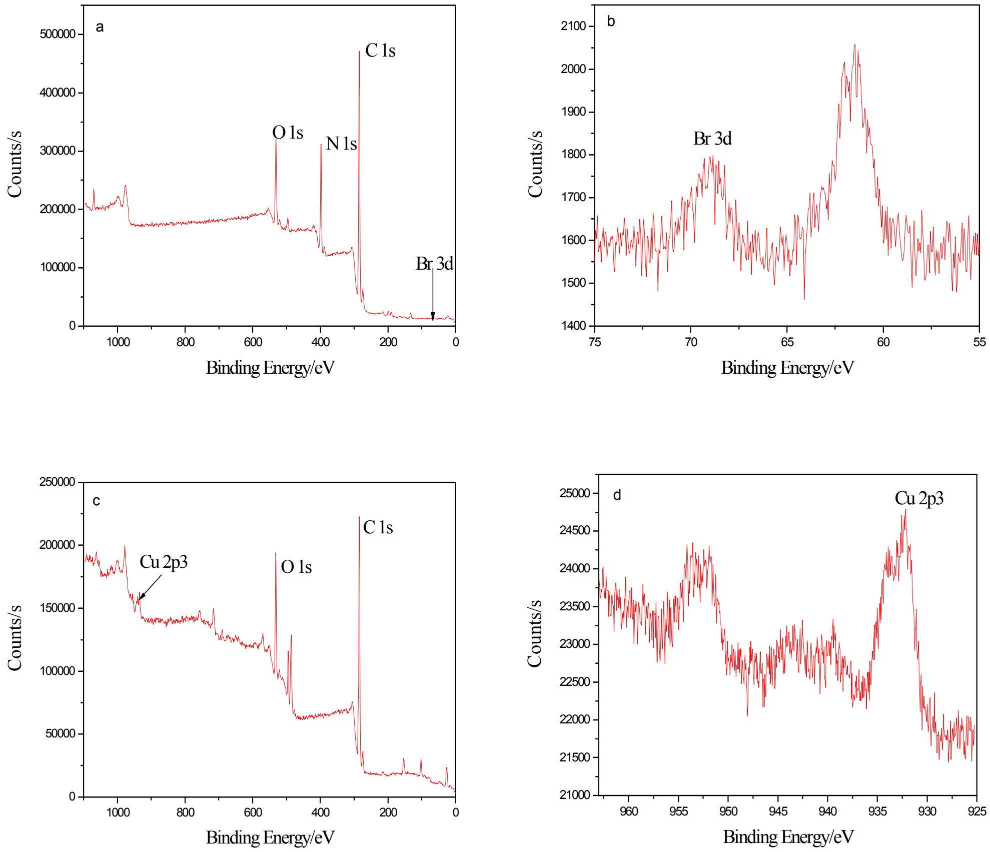


Fig. 3 The XPS spectrum of (a) PU membrane containing small molecule BHD, (b) Br on the PU membrane, (c) adsorption Cu^{2+} of the FPU sponge, and (d) Cu^{2+} on the FPU sponge.

The fluorescence imaging (in **Fig. 4**) further confirmed that the chemosensor was introduced into the PU sponge and displayed the fluorescence without Cu^{2+} ions. And the fluorescence enhanced upon the addition of copper ions.

Fig. 4 Fluorescence imaging of (a) the FPU sponge, (b) the FPU sponge with Cu^{2+} ions, and (c) the solid FPU membranes with Cu^{2+} ions.

3.3 Detection of Cu^{2+} by PU sponges

As shown in **Fig.5a**, the PU sponges bearing 1.0 wt% HQD were cut into species (1 cm × 1 cm × 1 cm), and then soaked in different concentrations of Cu^{2+} solutions (10^{-2} mol/L, 10^{-3} mol/L, 10^{-4} mol/L, 5×10^{-5} mol/L, 10^{-5} mol/L, 10^{-6} mol/L, 0 mol/L). The color of the PU sponges changed obviously from yellow to green (**Fig. 5b, c**). In order to avoid the overlap of the color between the yellow sponge and the blue Cu^{2+} ions, some control experiments were also performed. Under the same conditions, PU sponges were placed into the blue ink and the solution of Cd^{2+}, respectively. It can be seen that the color (yellow) of the PU sponges did not undergo any changes. At the same time, pure PU sponges (no chemosensor containing) were also treated by this way, the results showed that the pure polyurethane sponge have no absorption for Cu^{2+} ions. The above results indicated that the color change only caused by the interaction between of HQD and Cu^{2+} ions. The color change could be seen by naked eye even the concentration of Cu^{2+} ions is as low as 5×10^{-5} mol/L.

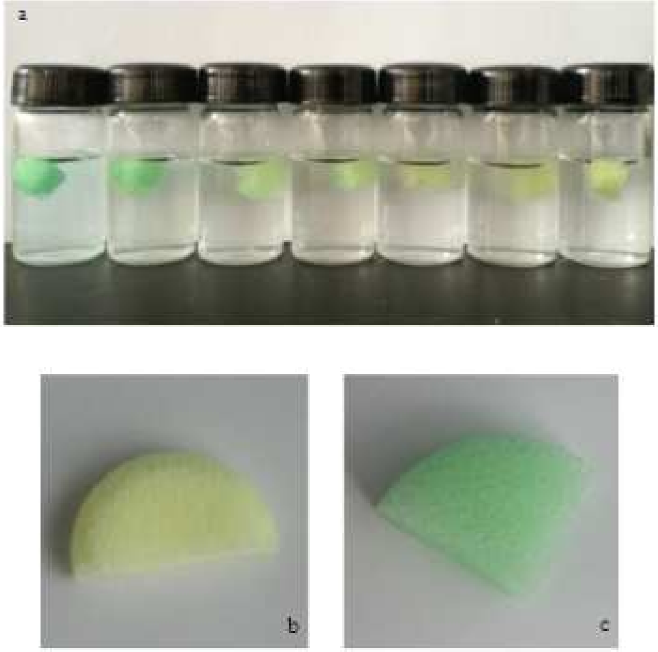


Fig. 5 (a) Photographs of the color change of the FPU sponges under the different concentrations (10^{-2} mol/L, 10^{-3} mol/L, 10^{-4} mol/L, 5×10^{-5} mol/L, 10^{-5} mol/L, 10^{-6} mol/L, 0 mol/L , from the left to the right). (b) Photographs of the color change of the dry FPU sponge without Cu^{2+} , and (c) the dry FPU sponge with Cu^{2+}.

The optical properties of the PU sponge, determined by UV-Vis, were displayed in **Fig. 6.** Obviously, the introduction of the chemosensor can enhance the absorbance of the FPU sponge between 500 nm and 800 nm, and the new absorbance at about 680 nm appeared and increased with the concentration of the Cu^{2+}.

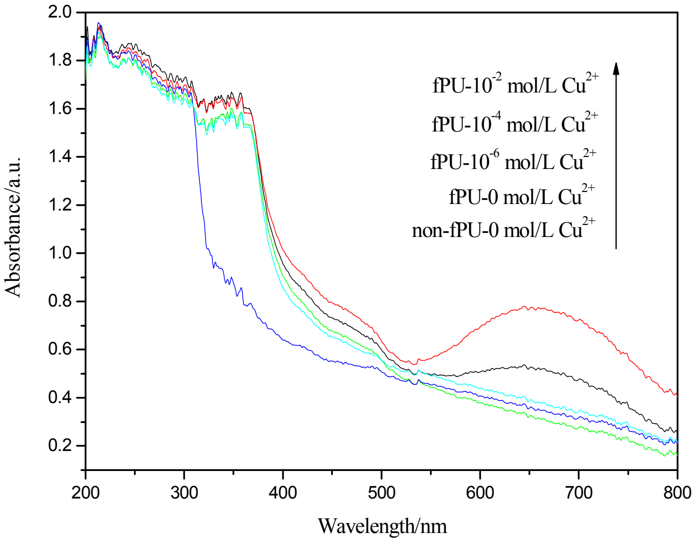
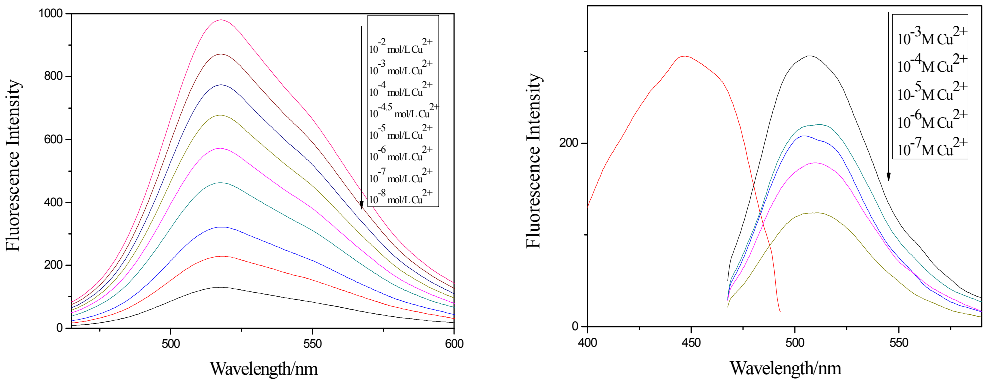


Fig. 6 UV-Vis spectra of the dry FPU sponge and non-FPU sponge (the non-functionalized PU sponge, blue line)

Fluorescent intensity of the PU sponge was measured. The fluorescence of the PU sponge with Cu^{2+} ions was measured as well. **Fig. 7a** showed the fluorescence of HQD, it increased significantly with the increase of Cu^{2+} concentrations at about 516 nm (excited at 446 nm), the stokes shift is about 70 nm. **Fig. 7b** showed that fluorescence of the PU sponges bearing HQD has the same trend as HQD. This means that the performance of the chemosensor still remains when co-polymerised into the PU sponges. Furthermore, the concentration of Cu^{2+} ions could be detected by the fluorescent intensity is as low as 10^{-7} mol/L.

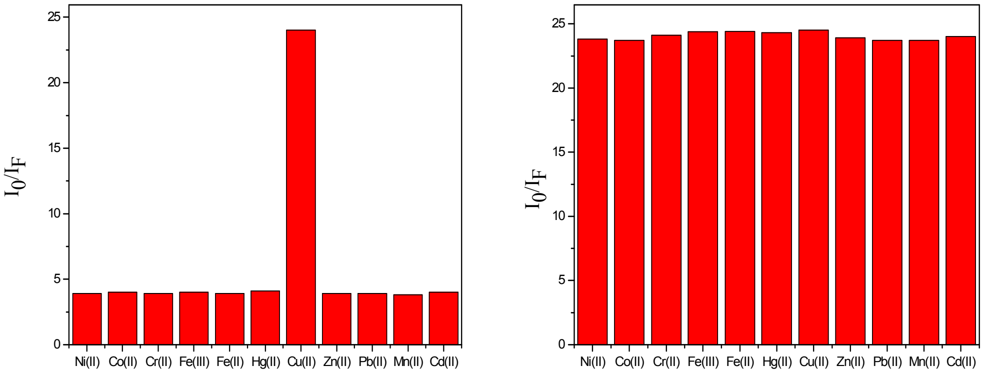


a b

Fig. 7 Fluorescence spectra of the chemosensor (a), and the dry FPU sponge (b).

Besides Cu^{2+} ions, whether other heavy metal ions have interfering effect on the fluorescence intensity of FPU sponges were investigated (**Fig. 8**). It could be seen that the fluorescence intensity of FPU sponge for enhanced clearly by Cu^{2+} ions and there was no obvious response to other heavy metal ions (Ni^{2+}, Co^{2+}, Cr^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Pb^{2+}) (in Fig. 8a). The control experiments (in Fig. 8b) were performed in the presence of 10^{-4} mol/L Cu^{2+} mixed with 10^{-4} mol/L other heavy metal ions respectively, such as Ni^{2+}/Cu^{2+}, Co^{2+}/Cu^{2+}, Fe^{2+}/Cu^{2+}, Fe^{3+}/Cu^{2+}, Cr^{2+}/Cu^{2+}, Hg^{2+}/Cu^{2+}, Zn^{2+}/Cu^{2+}, Mn^{2+}/Cu^{2+}, Cd^{2+}/Cu^{2+}, and Pb^{2+}/Cu^{2+}. As shown in **Fig. 8**, the figures showed that Cu^{2+} was the only specie being detected and no other metal ions interfered the fluorescence intensity. By measuring I_F/I_0 at 516 nm, (I_0 represents for the emission intensity of PU sponge without Cu^{2+} and I_F corresponds to the fluorescence intensity). It could be seen (fig 8b) that in the copper-other metal ion binary mixture, the I_F/I_0 has not been influenced by other common ions in waste water.

The values of I_F/I_0 almost kept the same. The results further indicated that the FPU sponge had a high selectivity for Cu^{2+}.



(a) (b)

Fig. 8 The florescence response of 1 wt% HQD containing FPU sponge to the metal ions (Ni^{2+}, Co^{2+}, Cr^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Pb^{2+}) (a) the single metal ions (10^{-4} mol/L); (b) the mixture of Cu^{2+}(10^{-4} mol/L) and other metal ions (10^{-4} mol/L).

3.4 The effect of pH on absorbing Cu^{2+} of the FPU sponge

The effect of pH on the FPU sponge was measured. A various pH (2-12) values on adsorption of Cu^{2+} ions (3mL, 7mg/L) by the FPU sponge were tested. As shown in **Fig. 9**, the adsorption capacity of the FPU sponge almost didn't change at pH values between 4-10. When pH values were below 4.0 and up to 10, the adsorption capacity decreased obviously. Below 4, the protonation of N atoms occurred, the complexing ability to copper ions decreased. In the strong alkaline condition (pH □ 12), the adsorption capacity of the FPU sponge also decreased. This might be attributed to the following two reasons. The one is under high pH, $Cu(OH)_2$ formed, the copper ions coordinated to the chemosensors decreased. The other is that under high pH, the porous PU sponges were destroyed and collapsed. The high specific surface area decreased, and the absorption ability decreased naturally. It is suggested that this PU sponge could be used with high adsorption to copper ions in the pH range of 4-10.

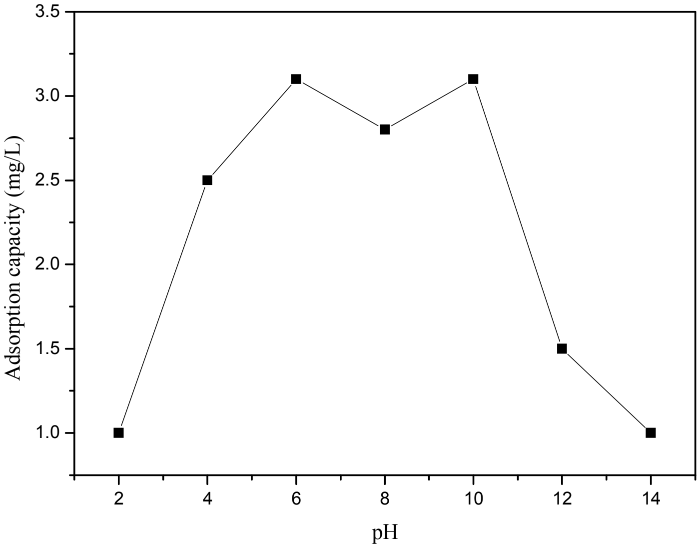


Fig. 9 The adsorption capacity of the FPU sponge to Cu^{2+} ions (3 mL, 7mg/L) at various pH (2-12).

3.5 Dynamic **adsorption capacity of the FPU sponge**

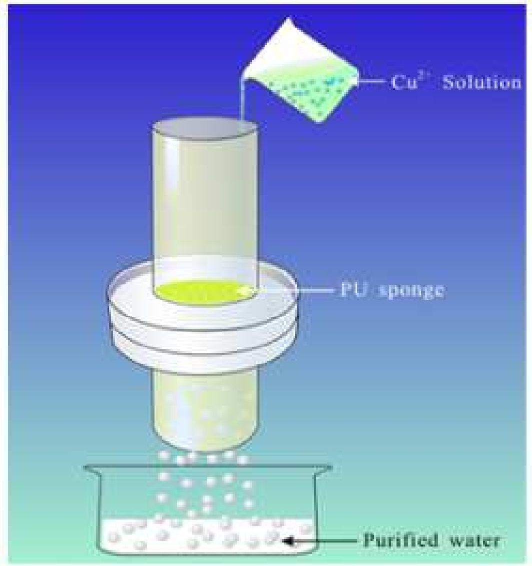


Fig.10. Schematic diagram of dynamic adsorption procedure of Cu^{2+} ions from solution using the fabricated FPU sponge as a filter.

Dynamic adsorption capacity with Cu^{2+} ions has been measured. The as-prepared PU sponge was fixed in the middle of two PMMA columns (**Fig. 10**). A series of same volumes solutions (100 ml) of different concentrations of Cu^{2+} (10^{-6} mol/L, 10^{-5} mol/L, 10^{-4} mol/L) were poured into the PMMA column and passed through the PU sponge, the time-consuming and volume was recorded. The equilibrium concentrations of the solution passing through the PU sponge were measured by the AAS. The adsorption capacity of Cu^{2+} on the PU sponge was calculated as following equations.

$$q = \frac{(c_0 - c_e) \times V}{W} \tag{1}$$

Where q represents the absorptivity capacity (%), C_0 and C_e represent the concentration of Cu^{2+} ions before the adsorption experiment and the equilibrium concentration of Cu^{2+} in mg/ L, respectively. V is the volume of the Cu^{2+} ions solution. W is the weight of the PU sponge.

The results of equilibrium concentrations of the solution passing through the FPU sponge were listed in **table 1**. Under the same continuous flow and time condition, the adsorption capacity significantly enhanced with the increasing concentration of Cu^{2+} ions.

Table 1. Dynamic adsorption capacity per unit content and unit time of the FPU sponge

concentration of Cu^{2+} ions C_0 (mg/L)	0.1596	1.596	7.88	15.96
concentration of Cu^{2+} ions C_e (mg/L)	0.025	0.6280	6.215	14.275

the volume of the Cu^{2+} ions V (mL)	100	100	100	100
Adsorption capacity per unit time (mg/g)	8.87	53.77	92.48	93.57

In addition, static adsorption capacity was measured using FPU sponge and solid FPU membrane. They were put into same volumes and concentrations Cu^{2+} ions solutions, and then removed at the same time. The concentrations before and after Cu^{2+} removal were measured and listed in **table 2**. It could be seen that the content of HQD dramatically affected adsorption capacity of PU sponges. The more the content of HQD contained, the higher the adsorption capacity per unit time. However, solid FPU membrane was inferior to absorb Cu^{2+} ions compared to FPU sponge. It may be attributed to the high specific surface area of FPU sponge which provided more opportunities and spaces to combine and then remove Cu^{2+} ions. These results suggested that the FPU sponge could be used for filtration or purification of Cu^{2+}.

Table 2. Static adsorption capacity per unit content and unit time of the FPU sponge and the solid FPU membrane

the content of HQD(1wt%)	0.5	1.0	1.5	2.0	Solid membrane 2.0
concentration of Cu^{2+} ions C_0 (mg/L)	5	5	5	5	5
concentration of Cu^{2+} ions C_e (mg/L)	4.1693	3.7572	3.3967	3.2494	4.0528
the volume of the Cu^{2+} ions solution V (mL)	100	100	100	100	100
Adsorption capacity per unit time (mg/g)	46.15	69.04	89.07	97.26	52.62

4. Conclusion

In conclusion, a fluorescent monomer, 2-(2-Hydroxy-ethyl)-6-(quinolin-8-ylamino)-benzo[de]isoquinoline-1,3-dione (HQD) was synthesized. And then it was introduced to solid FPU membrane and porous FPU sponge respectively to form macromolecular chemosensor for Cu^{2+} ions. After the chemosensor was co-polymerised into the surfaces of PU sponge, it still remains the performance of fluorescence. Comparing to the PU solid membrane, the FPU sponge had great advantages of specific surface area and adsorption capacity. Furthermore, the as-prepared FPU sponge can not only detect but also remove and recycle Cu^{2+} ions without any complicated post-processing.

Acknowledgments

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A High-performance Polyurethane Sponge for the Detection, Absorption and Separation of Cu^{2+} Ions

FPU Adding Cu^{2+}

A small chemosensor, 2-(2-Hydroxy-ethyl)-6-(quinolin-8-ylamino)-benzo[de]isoquinoline-1,3-dione was firstly synthesized and then was introduced to PU sponge. The as-prepared sponged showed excellent ability to detect and remove Cu^{2+} ions. When the sponge interacted with Cu^{2+} ions, its color changed from yellow to green, and its fluorescent intensity increased greatly. The PU sponge will find its application in dectection and recycling of Cu^{2+} ions.