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Preparation of a boronate affinity material with ultrahigh binding capacity for cis-diols by grafting polymer brush from polydopamine-coated magnetized graphene oxide

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Abstract

Poly(3-acrylamidophenylboronic acid) (PAAPBA) was grafted onto polydopamine-coated magnetic graphene oxide via surface-initiated atom transfer radical polymerization to obtain a new kind of boronate affinity material (BAM). The BAM possesses good water dispersity and adsorption capacities as high as 154, 357, 588 and 1111 $\mu mol \cdot g^{-1}$ for adenosine, salbutamol, dopamine and catechol, respectively. For the molecules without nitrogen atoms, the BAM can selectively capture the cis-diols under the interference of non-cis-diols. For molecules containing nitrogen, the non-cis-diols are also retained, but much less than the cis-diols. The selectivity can be improved by adding salts to facilitate complexation and to suppress the electrostatic interaction between cis-diols and the boronic acid ligand. The BAM was successfully employed to the enrichment of catecholamines from real urine samples. Results indicate that it is a promising material for the pretreatment of real samples.

Keywords Boronic acid · Atom transfer radical polymerization · Magnetic solid phase extraction · Selectivity · Salt effect · Adenosine · Salbutamol · Catecholamines · Urine sample

Introduction

Cis-diols such as nucleosides, saccharides and catecholamines (CAs) can control and regulate the principal functions and behavior of humans. They are the important targets in current research frontiers such as metabolomics, glycomics and proteomics [1, 2]. Boronic acid group can form five- or six-

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member cyclic esters with cis-diol group under alkaline conditions while dissociated in acid solutions. Based on this principle, BAMs can specifically recognize cis-diol-containing molecules. The BAMs are widely used in separation and enrichment of cis-diols [1], biosensors [3–5] and biomedical applications, including cell capture and culture, enzymatic inhibition and in site specific radiation therapy [6]. Various supports, such as monoliths [7], silica [8, 9], organic polymer [10] and magnetic nanomaterials [1] have been utilized to prepare BAMs.

In the area of adsorption and separation, the BAMs with high adsorption capacity are always pursued. Grafting polymer brush on the supports to introduce high density boronic acid groups is an efficient way to enhance adsorption capacity of BAMs. "Grafting to" [7] and "grafting from" [11] are the two typical methods for polymer grafting. Polyethylenimine (PEI) [7, 12] and dendrimer polymers [13] have been separately used as scaffolds to amplify the number of boronic acid moieties, which are usually grafted to the supports via the "grafting to" method. The "grafting from" method mainly includes surface-initiated atom transfer radical polymerization (SI-ATRP) and surface-initiated reversible addition-fragmentation chain transfer polymerization (SI-RAFT).

Wang et al. [8] prepared a high capacity BAM by grafting poly (3-acrylamidophenylboronic acid) (PAAPBA) from silica via SI-ATRP followed by end-functionalization of the polymer chain. SI-RAFT has been also employed to prepare BAMs [10, 14]. Zhang et al. [15] also prepared a high capacity BAM by SI-ATRP, in which poly (acryloyloxyethyltrimethyl ammonium chloride) was firstly grafted from attapulgite, gold nanoparticles were then immobilized onto the polymer chains via electrostatic interaction, and finally 4-mercaptophenylboronic acid (4-MPBA) was attached to the gold nanoparticles. In these works, mesoporous materials are usually employed as the supports for fabricating the BAMs. In this case, the grafted polymer chains would block the porous channels and prevent molecular mass transfer, thus prevent enhancement of adsorption capacity. In principle, planar non-porous supports, such as graphene or graphene oxide (GO) sheets, will overcome this kind of shortcomings. It is exciting that graphene has been used as the support material to prepare BAMs [16–18]. Zhang et al. [18] prepared a BAM by grafting poly(4-vinylphenylboronic acid) (PVPBA) from GO via SI-ATRP and used as a novel matrix for matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. However, it may not be easy to recover the material by centrifugation due to low density of GO. Chen et al. [19] prepared a high capacity BAM by grafting PVPBA brushes from magnetic graphene oxide (mGO) via SI-ATRP for selective enrichment of glycoproteins. The pyrene-based initiators were immobilized on the mGO via noncovalent π-π interaction, this makes the material not stable. In addition, the strong hydrophobicity of mGO, pyrene and the PVPBA skeleton can lead the BAM to possess poor dispersity in water, and result in nonspecific adsorption of hydrophobic molecules. Therefore, more robust strategies to fabricate high capacity of BAMs are strongly anticipated. Additionally, small molecules usually have quite different properties to proteins and may have different adsorption behaviors on a given adsorbent. However, to date, it has not been proven whether magnetic graphene oxide-based BAMs are applicable to adsorption of small cis-diol-containing molecules.

Dopamine (DA) has very good hydrophilicity and can self-polymerize under weak alkaline conditions. Polydopamine (PDA) can form uniform coating on the surface of a variety of materials. The plenty of hydroxyl and amine groups in PDA coating can greatly facilitate the subsequent chemical modification, and improve the surface hydrophilicity of the materials. PDA coated magnetic graphene [20, 21] have been used to prepare various adsorbents. The active groups of the PDA make it easier to anchor initiator molecules on the PDA coated surfaces through covalent bonding, and thus facile to graft polymers from the surface via SI-ATRP [22].

In this work, PDA coated magnetic graphene oxide (magGO@PDA) was used as the support material to prepare a BAM via SI-ATRP. 3-Acrylamidophenylboronic acid

(AAPBA) is more hydrophilic than 4-vinylphenylboronic acid (4-VPBA), and it was used as a monomer to construct the boronic acid polymer brush. The planar geometry of the magGO makes the grafted boronic acid polymer brushes freely access to the cis-diols, resulting in an ultrahigh adsorption capacity. In addition, the BAM has very good water dispersity. The performance of the BAM for adsorption of cis-diol-containing molecules were evaluated, and the material was employed to isolate and enrich CAs in urine samples.

Experimental

Materials and instruments

3-Aminophenyboronic acid (APBA), dopamine (DA), catechol and 5-hydroxytryptamine (5-HT) were purchased from J&K technology Co. Ltd. (Beijing, China, http://www.jkchemical.com). 2-Bromisobutyryl bromide (2-BIBB), 2,2′-dipyridine (Bpy), Ado and 2′-deoxyadenosine (DAdo) were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China, http://www.aladdin-e.com). Quinol, protocatechualdehyde and p-hydroxybenzaldehyde were from Sinopharm Chemical Regent Co. Ltd. (Shanghai, China, http://www.sinopharmholding.com). HPLC grade methanol was supplied by Yongda Chemical Reagent Co. Ltd. (Tianjin, China, http://www.tjydhxsj.com). Deionized water was gotten from Milli-Q water purification system (Millipore, Milford, MA, USA, http://www.millipore.com).

HPLC analysis were performed on a Shimadzu LC-20A HPLC system with a SPD-20A ultraviolet (UV) detector and a RF-10A XL fluorescence detector (FLD) (Tokyo, Japan). A SinoChrom ODS-BP column (5 μm, 4.6 mm × 200 mm, Elite, China, http://www.elitehplc.com) was employed for the analyses, the injection volume was 20 μL and the flow rate was 1.0 mL·min^{-1}. The morphology was observed by transmission electron microscope (TEM, FEI, USA) and scanning electron microscope (SEM, SV8010, Hitachi, Japan). The chemical compositions of the materials were analyzed by Fourier-transform infrared spectrometer (FT-IR, TENSOR27, Bruker, Germany) and X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Fisher Scientific, USA). The magnetic property was determined via a superconducting quantum interface devices (SQUID) magnetometer (MPMS-XL-7, Quantum Design, USA) at 300 K. Powder X-ray diffraction (XRD) measurements were made with CuK$_\alpha$ radiation on a D8 ADVANC (Bruker, Germany). The static contact angles of the materials were measured using a DSA 25 contact angle analyzer (Krüss, Germany). Thermal gravimetric analyses (TGA, STA 449C, Netzsch, Germany) were carried out in a nitrogen atmosphere, the samples were heated at a rate of 10 °C·min^{-1}. Nitrogen adsorption-desorption isotherms

were measured by ASAP 2010 M nitrogen adsorption and desorption analyzer (Micromeritics, USA).

Preparation of the boronate affinity material by grafting polymer brush from PDA coated magnetic graphene oxide

AAPBA was synthesized according to the previous work [10]. GO, magGO and PDA coated magGO were prepared following the refs. [20, 23] with minor modification. The detailed procedures are described in the Electronic Supplementary Material (ESM).

Immobilization of the surface-initiated atom transfer radical polymerization (SI-ATRP) initiator on the PDA coated magGO

The SI-ATRP initiator was immobilized on the surface of PDA coated magGO according to the previous method [22]. 1.0 g PDA coated magGO was dispersed into 20 mL dried tetrahydrofuran and mechanically stirred for 30 min in ice bath. 2.0 mL triethylamine and 2.0 mL 2-BIBB were added dropwise to the above mixture, followed by gently stirred for 3 h. Afterwards, the reaction was continuously stirred for 12 h at 35 °C. The product was washed with methanol and water alternately for several times, and then dried at 40 °C under vacuumed.

Grafting PAAPBA from the surface of PDA coated magGO by surface-initiated atom transfer radical polymerization (SI-ATRP)

The polymers were grafted from the initiator modified surfaces by SI-ATRP. 1.0 g of the initiator immobilized material, 2.0 g AAPBA and 0.23 g Bpy were dispersed into 10 mL N,N-dimethylformamide (DMF) in a three-necked round bottomed flask. The mixture was deoxygenated via two freeze-pump-thaw cycles, 0.12 g CuBr was quickly added to the flask under a nitrogen atmosphere, followed by two freeze-pump-thaw cycles. The polymerization was allowed to react at 95 °C for 16 h with stirring. After washed with methanol and water, the product was immersed in a mixture of methanol and 0.25 M Na_2EDTA (1:1, V/V) for 4 h at 40 °C with stirring. The final product was washed with methanol and water, and dried at 40 °C.

Enrichment of catecholamines (CAs) in urine sample by the boronate affinity material (BAM)

Urine sample was used to optimize the extraction parameters, and to evaluate the capacity of the BAM in selectively enriching CAs from biological matrices. The detailed procedures for preparation of the blank urine samples are described in the ESM.

The enrichment of the CAs in human urine sample were operated as follows. 0.95 mL of the real urine sample was spiked with 0.05 mL standard solution of epinephrine (E), isoprenaline (IP) and DA. The pH of the solution was adjusted to 9.0 with ammonium hydroxide (25%). 3.0 mg of the BAM was added into the mixture and incubated at 25 °C for 1 min with shaking. Then the BAM was collected and rinsed with NH_3-NH_4Cl (50 mM, pH 9.0) and water separately. Finally, the CAs was eluted with 300 μL of 5% HAc, and the eluates were analyzed by HPLC-FLD. The FLD excitation and emission wavelength were set at 280 nm and 330 nm, respectively.

Results and discussion

Synthesis of the boronate affinity material (BAM)

The synthetic procedure of the BAM is illustrated in Fig. 1. Briefly, GO was synthesized by Hummers' method with minor modification. Fe_3O_4 was deposited on the surface of GO by a solvothermal method. The magGO was subsequently encapsulated by PDA via the self-polymerization of DA in alkaline buffer. After immobilized the initiator 2-BIBB, the PAAPBA brush was grafted from the PDA coated magGO via SI-ATRP to yield the BAM.

Characterization of the BAM

The morphology of the materials was characterized by SEM and TEM. Both the SEM (Fig. 2) and TEM (Fig. 3) images show that the GO displays a flexible sheet with wrinkles and folds (Figs. 2a and 3a). Fe_3O_4 particles were successfully deposited and well distributed on the GO sheets. The diameter of the Fe_3O_4 was approximately 200–250 nm (Figs. 2b and 3b). As shown in the SEM image (Fig. 2c), the morphology of the composites changed significantly after coated PDA. The GO sheets were exfoliated to small piece, and the magnetic beads became larger in diameter. From the insert graph in the TEM image of the PDA coated magGO (Fig. 3c), it can be found that the PDA layer has a thickness around 15 nm. After grafted with AAPBA polymer brush, the morphology of the composites became pretty rough (Figs. 2d and 3d).

The chemical compositions of the materials were characterized by XRD (Fig. S1), FT-IR (Fig. S2), XPS (Fig. S3), TGA (Fig. S4a), and their magnetic properties (Fig. S4b) were also tested. The detailed data and figures are shown in the ESM. All the results confirmed the successful preparation of the BAM.

The dispersity of the materials in water were investigated. All the nanoparticles can disperse well in water, forming black homogenous suspensions. The magGO started settling down after 1 min, while the PDA coated magGO and the BAM only showed slight subsidence after 20 min (Fig. S5). In addition, the contact angles of water drop on the magGO and the PDA coated magGO were measured and the figures are shown in Fig. S6. Their contact angles are 63.5° and 57.5°, respectively.
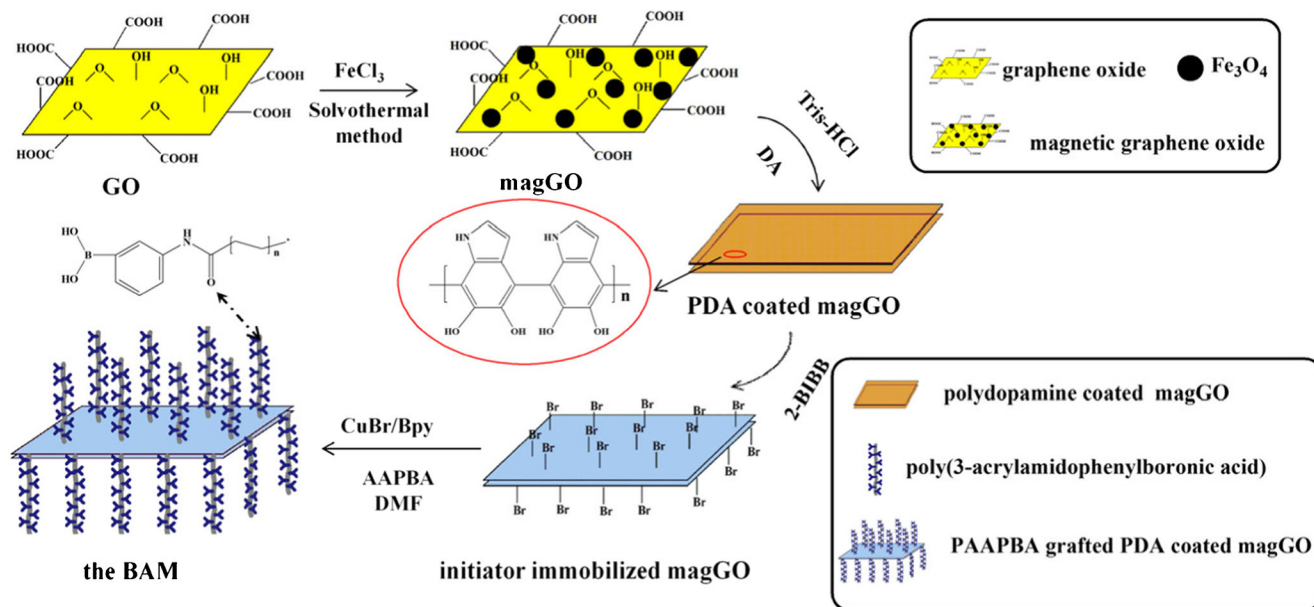
Fig. 1 Schematic of the preparation of the boronate affinity material

These results showed that the PDA coating really increases the hydrophilicity of the magGO.

Optimization of selectivity of the BAM

Four groups of 1, 2-*cis*-diols and their corresponding structure similarity but non-*cis*-diols were used as probes to evaluate the selectivity of the BAM. The *cis*-diols are catechol, protocatechualdehyde, Ado, DA, and the non-*cis*-diols are quinol, p-hydroxybenzaldehyde, DAdo, 5-HT. The adsorption data are shown in the ESM. The results showed that catechol (Fig. 4a) and protocatechualdehyde (Fig. 4b) were selectively captured by the BAM. However, as to Ado/DAdo (Fig. 4c) and DA/5-HT (Fig. 4d) groups, all compounds were retained by the BAM to different extent, but Ado and DA had much more retention than their counterparts. The nonspecific retention of DAdo and 5-HT is probably due to the other interactions except for boronate affinity interaction. These interactions include the boron-nitrogen coordination between the BAM and the nitrogen-containing compounds [24], the electrostatic interaction between the negatively charged boron and positively charged amine [25], the hydrophobic interaction between boronic acid ligands and 5-HT [26]. In fact, BAMs were also used for extraction of 5-HT previously [27].

Fig. 2 SEM images of (**a**) GO, (**b**) magGO, (**c**) PDA coated magGO and (**d**) the BAM
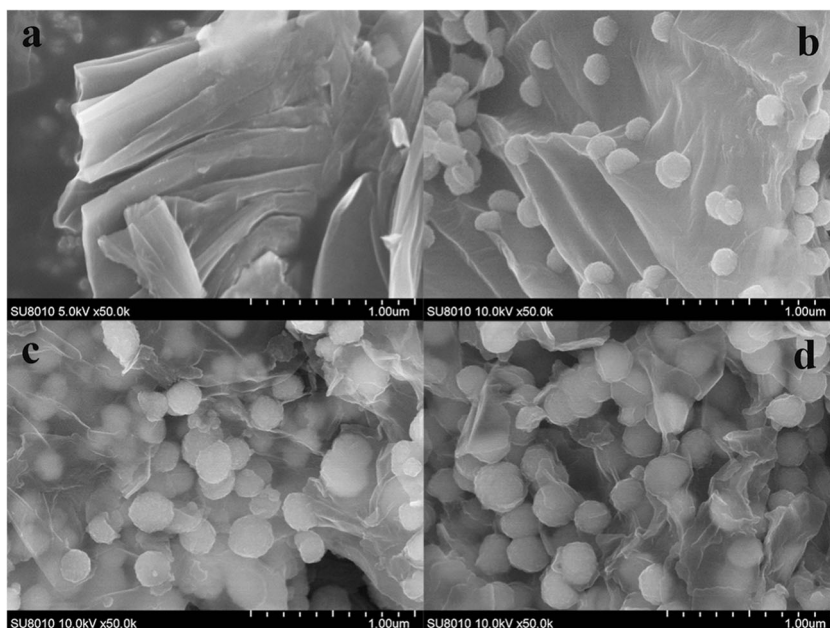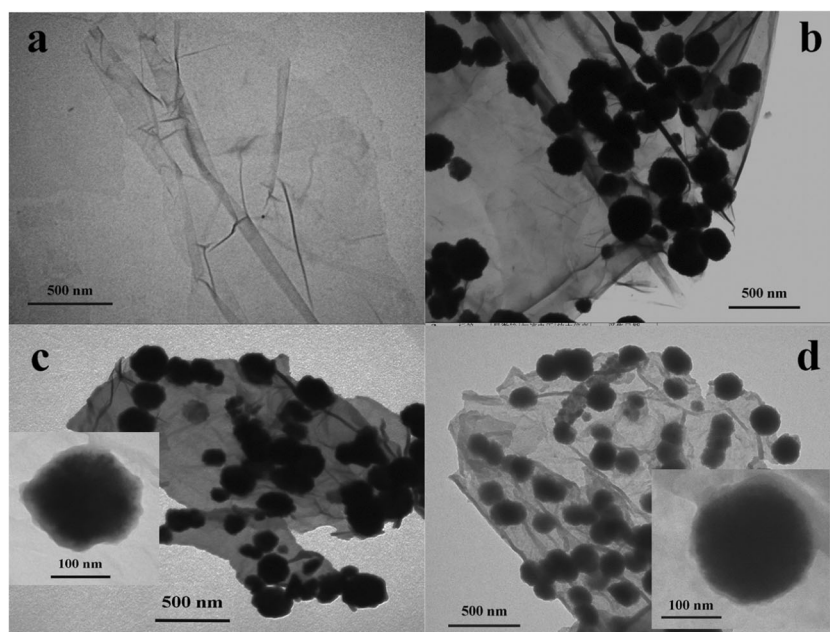
Fig. 3 TEM images of (**a**) GO, (**b**) magGO, (**c**) PDA coated magGO and (**d**) the BAM

In order to enhance the selectivity, the following parameters were optimized: (a) type of added salts; (b) salt concentration and (c) supplement of ethanol and urea. Respective data and figures (Fig. S7-S9) were given in the ESM. The following experimental conditions were found to give the best results: (a) type of added salts: sodium chloride; (b) salt concentration: 1.0 M for Ado/Dado and 0.5 M NaCl for DA/5-HT; (c) Supplement of ethanol can slightly raise the selectivity

factor, while urea has little effect on the selectivity. The detailed results and discussion are in the ESM.

Adsorption capacity of the BAM

The adsorption capacity of the BAM was evaluated using Ado, SAL, DA and catechol as the analytes. The data of adsorption isotherms (Fig. S10a) were fitted by the Langmuir

Fig. 4 Chromatograms of the mixture containing *cis*-diols and non-*cis*-diols (I) before and (II) after enrichment by the BAM; 1, quinol; 2, catechol; 3, protocatechualdehyde; 4, p-hydroxybenzaldehyde; 5, Ado; 6, DAdo; 7, DA; 8, 5-HT. 10 mg adsorbent was dispersed in 5 mL of 10 $\mu g \cdot mL^{-1}$ mixture solution in 50 mM ammonium chloride buffer (pH 9.0) to extract the analytes, the detailed procedures are described in the ESM. HPLC conditions: mobile phase, (**a**) MeOH-50 mM HAc (25:75, *V/V*); (**b**) MeOH-50 mM HAc (2:8, *V/V*); (**c**) MeOH-25 mM KH$_2$PO$_4$ (15:85, *V/V*; pH = 4.5); (**d**) ACN-10 mM, NaH$_2$PO$_4$ (4:96, *V/V*; pH = 3.0). Injection volume, 20 μL; UV wavelength: detection of Ado and DAdo were at 260 nm, all other detection were at 280 nm
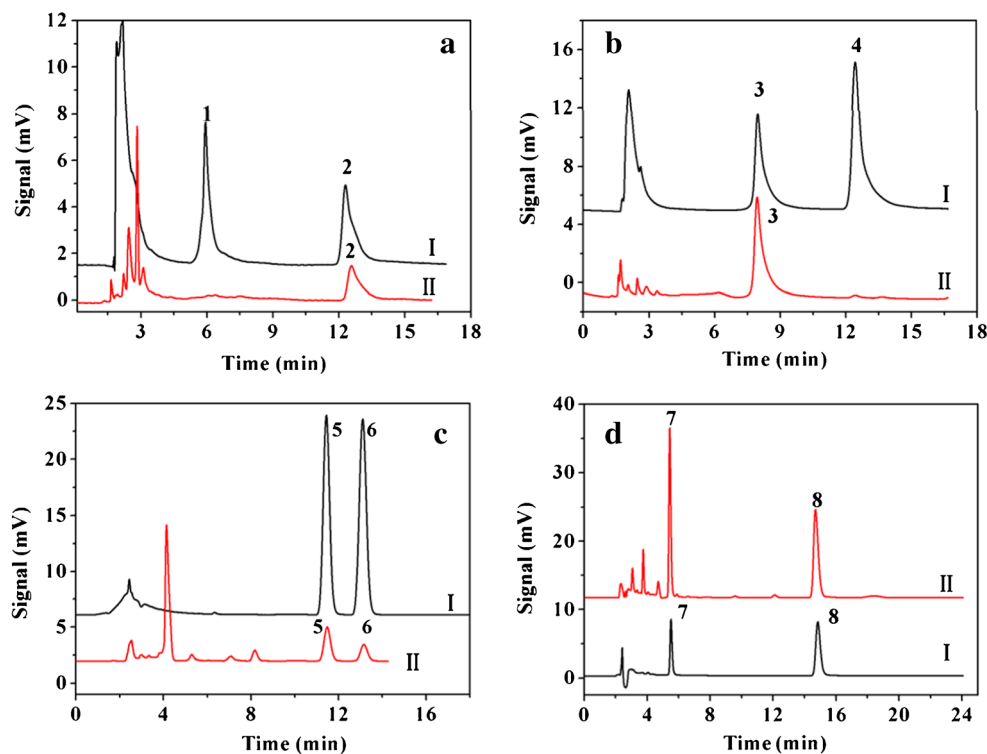
Table 1   Comparison of the adsorption capacity of various BAMs

Solid supports	Preparation methods	Analytes	Adsorption capacity ($\mu mol \cdot g^{-1}$)	Refs.
magGO@PDA	grafting PAAPBA by surface-initiated atom transfer radical polymerization	Ado	154	This Work
		SAL	357	
		DA	588	
		catechol	1111	
Fe$_3$O$_4$	doping zirconium	Ado	142.1	[28]
Fe$_3$O$_4$	coupling of FPBA [a]	catechol	66.0	[29]
		DA	80.6	
Fe$_3$O$_4$@SiO$_2$	coupling of FPBA	catechol	96.0	[30]
		SAL	50.0	
Fe$_3$O$_4$@SiO$_2$	coupling PEI first, and then FPBA	Ado	5.0	[12]
monolithic column	coupling PEI first, and then DFFPBA[b]	Ado	102.0	[7]
attapulgite	coupling of DBA[c]	Ado	73.0	[31]
attapulgite	coupling ploy(AEMA[d]), deposition Au nanoparticles, and then fabricating MPBA	Ado	115.4	[15]
silica	grafting PAAPBA via SI-ATRP followed by end-functionalization	catechol	513.6	[8]
polymer microspheres	grafting PAAPBA via SI-RAFT	Ado	99.2	[10]
Zn-MOF[e]	calcination first, and then coupling 3-APBA	Ado	97.3	[32]
cotton fiber	coupling PEI first, and then FPBA	catechol	2.7	[33]
		Ado	2.6	
		DA	2.4	
Titania	hydrolyzed by boric acid	Ado	0.75	[34]
magnesia-zirconia	coupling DPA-BA[f]	Ado	0.46	[35]

[a] 4-formylphenylboronic acid

[b] 2,4-difluoro-3-formyl-phenylboronic acid

[c] 3,3′-(6-chloro-1,3,5-triazine-2,4-diyl)bis(azanediyl)bis(3,1-phenylene) diboronic acid

[d] [2-(Acryloyloxy) ethyl]trimethylammonium chloride

[e] zinc-based metal-organic framework

[f] (3-N,N-dimethylene-phosphonic acid) benzeneboronic acid

and Freundlich adsorption isotherm models. Parameters from the fitting were presented in Table S2 in the ESM. The results indicated that Langmuir models matches better than Freundlich models for the adsorption. The maximum adsorption capacity were 154, 357, 588 and 1111 $\mu mol \cdot g^{-1}$ for Ado, SAL, DA and catechol, respectively.

Compared with other BAMs reported previously (Table 1), the BAM have much higher capacity. As well known, graphene has an extremely high specific surface area. In order to find out if the high adsorption capacity of the BAM comes from its high specific surface area. The specific surface area of the magGO, PDA coated magGO and the BAM were measured through nitrogen adsorption-desorption experiments, and the results are shown in Fig. S10(b), the BET specific surface areas of magGO, PDA coated magGO and the BAM were 31.27, 28.19 and 28.62 $m^2 \cdot g^{-1}$, respectively. It can be found that the specific surface area of the BAM is not high at all, this is due to the agglomeration of the GO sheets. Previously, a BAM was prepared based on silica gel via surface-initiated atom transfer radical polymerization (SI-ATRP), its maximum adsorption capacity to catechol is 445.0 $\mu mol \cdot g^{-1}$, and its specific surface areas is 207.7 $m^2 \cdot g^{-1}$ [8]. It can be found that the BAM has a much smaller specific surface area than the silica-based BAM, but a much higher adsorption capacity. Thus, we ascribe the higher capacity to the planar geometry of GO, considering both of the two BAMs were prepared via SI-ATRP under very similar polymerization conditions.

Enrichment of CAs in urine sample by the BAM

By virtue of large adsorption capacity, the BAM was employed to enrich the E, IP and DA from urine sample. The experimental parameters were optimized, such as the pH of sample solution, adsorption and desorption time, the mount of the BAM and eluent volume. The respective data and Figures (Fig. S11) were given in the ESM. Under the optimization conditions, the extraction recoveries for E, IP and DA at each concentration of 100 $ng \cdot mL^{-1}$ were 35.7%, 38.3% and 32.1%, respectively.
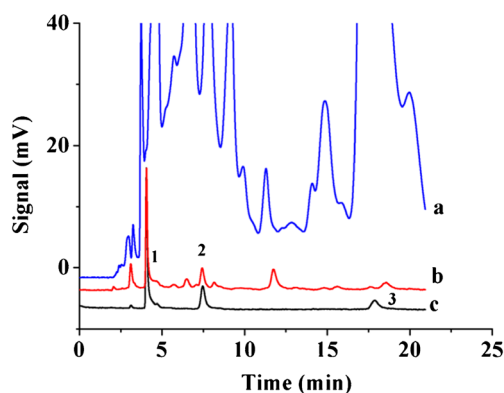
Fig. 5 Chromatograms of blank urine samples spiked with 20 ng·mL^{-1} of CAs (**a**) before and (**b**) after enrichment by the BAM, (**c**) standard solution of 40 ng·mL^{-1} of CAs. 3.0 mg adsorbent was dispersed in 1.0 mL urine sample to extract the CAs, the detailed procedures are described in the section 2.3. HPLC conditions: the mobile phase is MeOH-10 mM NaH$_2$PO$_4$ (pH 3.0) (1/99, *V/V*), the FLD excitation and emission wavelength were set at 280 nm and 330 nm, respectively

Under the optimal conditions, the BAM was used to extract CAs in one real urine sample collected from a healthy volunteer. Figure 5 shows the chromatograms of standard CAs and the spiked urine samples. The strong interferences were almost removed after extraction by the BAM, and the CAs were well retained. The feature of the method was investigated and the results are shown in Table S3, the limits of detection (LODs) and limits of quantification (LOQs) are in the range of 0.32–4.5 ng·mL^{-1} and 1.06–13.7 ng·mL^{-1}, respectively. The analytical method recoveries were measured by analyzing the spiked human urine at three different concentrations (5, 40 and 80 ng·mL^{-1}). The results showed that the analytical method recoveries were in the range of 81.3–105% (Table S4). The results demonstrated that the BAM has excellent clean capacity for complex biological samples, and can be applied in real sample analysis.

Conclusions

In summary, a new BAM was prepared by surface-initiated atom transfer radical polymerization using PDA coated magGO as the support material and AAPBA as the monomer. The BAM possesses good water dispersity. The BAM can afford much higher adsorption capacity than the previous BAMs. For the molecules without nitrogen atoms, the BAM can selectively capture the *cis*-diols under the interference of non-cis-diols. However, for the ones with nitrogen, the non-*cis*-diols can also be retained besides the *cis*-diols, but the retention is much less. The selectivity of the BAM can be improved by adding salts to enhance the boronate affinity interaction or suppressing the other secondary interactions. As a real application, the BAM can remove most interfering substances and selectively capture CAs in urine samples. It

should be pointed out, based on the boronate affinity principle, the saccharides, glycoproteins and RNA also can be extracted by the BAM. Thus, we expect the wide application of the BAM in the field of proteomics, metabolomics and glycomics. In addition, the present work shed light on producing high capacity adsorbents by grafting polymer brush from planar solid supports via surface-initiated atom transfer radical polymerization . However, the procedure for the preparation of the BAM is time-consuming, but it is still a good alternative for preparing high capacity BAMs as the involved procedures are not difficult to execute.

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