Dual-template docking oriented ionic imprinted bilayer mesoporous films with efficient recovery of neodymium and dysprosium

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A B S T R A C T

Rare earth elements (REEs) are critical materials to many cutting-edge technologies but are difficult to separate from one another because of their chemical similarity. We present ionic imprinted mesoporous bilayer films (IIBFs) as an ideal adsorbent for selective separation of neodymium (Nd) and dysprosium (Dy) from sintered neodymium magnets. IIBFs were prepared according to dual-template docking oriented ionic imprinting (DTD-OII). Due to different imprinted compositions of bilayer films, IIBFs exhibited high specific surface area, fast binding equilibrium, and Janus properties for simultaneous selective adsorption of different rare earth ions, which made our imprinted bilayer mesoporous films a specialized adsorbent for adsorption of Nd(III) and Dy(III) at the same time. The adsorption capacities of optimized IIBFs were 17.50 mg g^{-1} for Dy(III) and 12.15 mg g^{-1} for Nd(III) at pH = 4.0. Moreover, we grafted thermo-responsive polymer on the one surface of IIBFs to realize controlled release of Nd(III) and Dy(III) by temperature. IIBFs demonstrate a high degree of reusability by cycling experiments by DTD-OII, which develop their promising applications for the REE recycling and separation industry.

1. Introduction

Rare earth elements (REEs) are frequently cited critical materials for electronic devices, fluorescence and metallurgy [1–3]. The unique properties of REEs have led to their application in more consumer products than nearly any other element group. Among them, Neodymium (Nd) is a key component of sintered neodymium magnets (NdFeB) [4]. Dysprosium (Dy) are also a key element of this permanent magnets which can increase its intrinsic coercivity [5]. Especially, some high-performance NdFeB magnets include up to 9% Dy by total magnet weight [6]. Since the increasing demand for the NdFeB magnets and tightening export of China, Dy and Nd has been categorized as "critical materials" by European Commission and the U.S. Department of Energy because of their supply problems and importance to technology [3,7,8].

With a large number of applications of REE products, the environmental problems caused by the REE production has received substantial media coverage during these years. Numerous newspaper reported appalling conditions such as natural environment devastated by primitive metallurgy. In order to alleviate scarcity of REEs and environmental burden, recycling REEs were announced [9,10]. However, recovery of REEs are notoriously difficult, and only several kind of REEs (Nd or Dy, etc.) in supply crisis are economically valuable [11].

Therefore, it is crucial to develop an efficient strategy for recovery of certain and high-priced REEs from mining waste or end-of-life rare earth products. NdFeB magnets are comprised of an Nd$_2$Fe$_{14}$B matrix phase with minor admixtures of praseodymium, gadolinium, terbium, and especially Dy [4]. Among these elements, only recovery of Nd and Dy are practically applicable considering composition of NdFeB magnets and the economic viability. Industrial recovery of REEs mostly is based on hydrometallurgy [12]. However, such technique requires organic solvents and leads to significant amounts of undesired wastes. In comparison, liquid-solid extraction is recognized as a greener alternative and has received increasing attention [13]. Currently, some studies using resins as adsorbents have been reported [14–17]. Our group has successfully synthesized different functional mesoporous silica materials with respect to gadolinium and Dy adsorption [18,19]. However, the major bottleneck of adsorbents lies in their low adsorption selectivity and poor adsorption capacity. Moreover, most of the adsorbents only can adsorb one certain rare earth ion selectively. Selective separation and recovery of two or more REEs simultaneously (such as recovery of Nd and Dy from NdFeB magnets) cannot be achieved now.

Bilayer films that can undergo property changes based on differential component of the layers can be designed as Janus film materials.

These innovative films are attractive for applications in drug delivery and dual-adsorption [20–22]. To simultaneous extract Nd and Dy from NdFeB magnets by Janus films, critical strategy is to reach highly selective adsorption of individual rare earth for each domains of Janus films. However, separation of the rare earths is extraordinarily difficult because of their almost identical physicochemical properties. To make up for this deficiency, we inducted ionic imprinted technology to improve the adsorption capacity and adsorption selectivity of materials [23]. Recently, ionic imprinted polymers (IIPs) have found important applications such as separation due to their artificial specific selection to recognize certain ions and tolerance to acid and base [24–27]. Traditional IIPs prepared by a bulk imprinting approach exhibit low capacity and poor accessibility. Thus, new materials that can fully demonstrate the usefulness of IIPs are highly desirable. Mesoporous materials with highly ordered pore structure can solve above problem. Rong successfully prepared imprinted mesoporous silica by structure-directing agents [28]. Our group also successfully synthesized imprinted SBA-15 for selective recovery dysprosium ions form acidic solution [19]. Mesoporous imprinted materials have showed promising features in research of recovery of REEs. However, the benefits of mesoporous imprinted Janus materials in adsorption of two different REE ions have never been explored. Incorporation of mesoporous imprinted materials and Janus materials could advance prospective practical applications of materials because of dual-compartment Janus mesoporous imprinted structure. This inspired us to design imprinted mesoporous Janus films for dual-adsorption of Nd(III) and Dy(III).

Herein, we reported ionic imprinted mesoporous bilayer films that allowed for a unique combination of high adsorption capacity and simultaneous dual-adsorption. Imprinted mesoporous bilayer films selectively adsorbed two different ions due to different imprinted sites on surface of different layers. Our approach for preparation of imprinted mesoporous bilayer films was based on a simple layer-by-layer fabrication method. We proposed dual-template docking oriented ionic imprinting (DTD-OII) for each layer based on the development of dual-template docking oriented molecular imprinting [29,30]. This method is simpler than traditional imprinted mesoporous materials just based on evaporation-induced self-assembly (EISA). As illustrated in scheme, imprinted template was docked onto the surface of cellulose nanocrystallines (CNCs, structure-directing templates) to form the template-template docking configuration through electrostatic attraction. Then, Si precursor and functional monomers were introduced to form ionic imprinted mesoporous single films by EISA. Because of DTD-OII and EISA, all the imprinted sites were on the surface of the mesoporous films, which improved imprinted efficiency and adsorption selectivity apparently. The bottom layer remains intact and stable during deposition of the upper layer. Two layers differ only in selective functional monomers and REE ions. Subsequently, both the structure-directing template and imprinted template were removed to obtain dual-template docking oriented ionic imprinted mesoporous bilayer films (IIBFs). The resulting IIBFs exhibit high selectivity, dual-adsorption, fast binding equilibrium, and excellent reusability in an acidic system. Further, we grafted thermo-responsive polymer on the surface of IIBFs to realize controlled release of Nd(III) and Dy(III) by temperature.

2. Experimental

2.1. Materials and methods

All chemicals unless otherwise stated, were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. Dual-template docking oriented ionic imprinted mesoporous bilayer films (IIBFs) were synthesized according to a modified reported method. Schematic diagram of IIBFs was showed in Scheme 1.

2.2. Preparation of IIBFs

2.2.1. Preparation of CNCs

CNCs were prepared in a typical procedure based on our previously reported [31]. Briefly, the milled cotton was hydrolyzed in sulphuric acid (50 wt%) with vigorous stirring for 120 min at 45 °C. The suspension was then diluted with cold deionized water for the termination of hydrolysis. The supernatant was decanted and the resulting thick cloudy layer was washed by deionized water 3 times to remove all soluble cellulosic materials. The thick white suspension gained after centrifugation was placed inside dialysis membrane tubes (12,000–14,000 molecular weight cut-off) and dialyzed until the value of pH equals 2.4. The suspension was dispersed by subjecting it to ultrasound treatment for 10 min and then diluted to the desired concentration (3 wt%).

2.2.2. Preparation of dual-template docking oriented ionic imprinted mesoporous bilayer films (IIBFs)

For the preparation of IIBFs, iminodiacetic acid derivative of the silane and acetylacetone modified silane were prepared firstly. The iminodiacetic acid derivative of silane was obtained following the procedure reported by published work [32]. The synthesis is briefed as follows: 4.25 g of iminodiacetic acid (IDA) was dissolved in 50 mL of DDW, whose pH was then adjusted to 11.0 with 10 M NaOH. The solution was placed in an ice-bath and 1.4 mL of (3-glycidyloxypropyl) trimethoxysilane (GLYMO) was slowly added to the mixture with stirring. The mixed solution reacts for 6 h with stirring at 65 °C, followed by cooling the resultant solution in an ice-bath for 10 min. When the temperature of the solution was 0 °C, 1.6 mL of GLYMO was further added slowly with vigorous stirring. The temperature of above solution was raised to 65 C for further reaction for 6 h under stirring. Similarly, as above, 1.7 mL of GLYMO was again added into the above solution and incubated overnight with stirring at 65 °C. Finally, the pH of prepared GLYMO-IDA-silane solution was adjusted to 2.4 by using concentrated HNO$_3$. For synthesis of acetylacetone modified silane was based on our previous studies [19]. Briefly, (3-Chloropropyl)-triethoxysilane (CPTES, 50 mmol, 12.0 g) and sodium iodide (60 mmol, 9.0 g) were allowed to react in 125 mL of acetone for 48 h in nitrogen, opaque background, and reflux conditions. Then the acetone was removed under vacuum and n-hexane was added. The resulting suspension was stirred for another 30 min and then filtered at nitrogen atmosphere to remove the precipitate. The n-hexane was removed under vacuum and the product distilled under reduced pressure. (Et$_3$O)$_3$Si(CH$_2$)$_3$I was obtained as a yellow oil. Subsequently, 5.6 g of potassium was added in 97 mL of dried ^{t}BuOH. After the potassium had dissolved, 4.5 g of acetylacetone (ACAC) was added. After stirring for 30 min at 50 °C, 14.6 g of yellow liquid (Et$_3$O)$_3$Si(CH$_2$)$_3$I was added and the mixture was reacted at reflux for 20 h. The solvent was removed under vacuum and n-hexane was added, the suspension was stirred for another 10 min. Then the suspension was filtered at nitrogen atmosphere. The filtrate was concentrated and the product distilled under reduced pressure. The resulting CPTES-ACAC-silane was an orange oil. For the preparation of bottom layer of IMFs, 7 ml of 3% CNCs suspension (pH = 2.4) was sonicated for 10 min. D(+)-Glucose (50 mg) and a series of different concentration of Nd(NO$_3$)$_3$ were added into the CNCs suspension and the mixture suspension was stirred at 25 °C for 1.0 h, then tetramethoxysilane (TEOS, 280 μL) and 110 μL of GLYMO-IDA-silane were added into solution. After stirred at 60 °C for 2.0 h, a homogeneous mixture was obtained. This mixture was left to dry for 6–8 h at room temperature on a polystyrene Petri dish. During the time, synthesizing the upper layer was the same as the bottom expect that Dy(III) template was in place of Nd(III), and the derivative of the silane was not GLYMO-IDA-silane solution, but the CPTES-ACAC-silane. The homogeneous mixture rapidly paved in the bottom film. Almost two days slow evaporation at room temperature, the bilayer films were obtain. For simultaneously removal of the CNCs, Nd(III) and Dy(III) templates,