Controlled Architecture of Glass Fiber/Poly(Glycidyl Methacrylate) Composites via Surface-initiated ICAR ATRP Mediated by Mussel-Inspired Polydopamine Chemistry for Lithium Isotopes Separation

Wenqing WANG[1*], Paziliya JULAITI[1], Gang YE[1], Xiaomei HUO[1] and Jing CHEN[1]

[1] *Collaborative Innovation Center of Advanced Nuclear Energy Technology, Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing, 100084, China*

A new material system, consist of glass fiber/poly(glycidyl methacrylate) composites, was synthesized by integrating surface-initiated atom transfer radical polymerization (SI-ATRP) technique with the mussel-inspired polydopamine (PDA) chemistry. The homogenous PDA layer deposited onto the glass fiber mats (GFMs) facilitated the anchoring of ATRP initiators and controlled growth of poly(glycidyl methacrylate) (PGMA) brushes from the GFMs were then performed by the initiators for continuous activator regeneration (ICAR) ATRP method. Post functionality for GF/PGMA composite (GFPGMAC) was realized by nucleophilic substitution of the abundant epoxy groups and 4'-aminobenzo-15-crown-5 (B15C5). Lithium isotopes separation by GFPGMAC-B15C5 exhibited a maximum adsorption capacity of 6.46 mg g^{-1} and separation factor was 1.307±0.002 in optimal experimental conditions.

1. Introduction

The separation of lithium isotopes has been attracted much attention due to the need for isolated and enriched ^{6}Li and ^{7}Li isotopes in nuclear fusion industry, which supply sufficient energy as well as cleaner production [1]. Normally, ^{6}Li is employed as the nuclear breeding materials in deuterium-tritium fusion power reactors while ^{7}Li is the most ideal heat transfer agent for fusion power reactor and neutral medium of thorium based fused salt reactor [2]. Owing to the same extra-nuclear structure, it is challenging for lithium isotope separation just relying on tiny mass differences. Among current methods, including electrophoresis, membrane, laser, ion exchange, solvent extraction, and chromatography, macrocyclic ligands and ionic liquid (IL) are two main promising candidate for efficient lithium isotope separation by using liquid-liquid extraction or column chromatography method [3-5]. To ameliorate the drawbacks for potential industrial scale utility inherent in the previous methods, such as water solubility, low mass transfer rate, the immobilization of lithium efficient extractants, i.e, crown ether and IL, onto solid supports was developed using a liquid–solid extraction method. Traditionally, porous materials, including mesoporous silica, resins, were chosen as solid support by physical impregnation or chemical grafting [6-8]. In the present study, macrocyclic ligands functionalized glass fiber/poly(glycidyl methacrylate) composites via surface-initiated ATRP [9,10] mediated by mussel-inspired polydopamine chemistry was prepared and the behavior for lithium isotopes separation was evaluated.

2. Experimental

2.1 Reagents

Nonwoven glass fiber mat with 7.0 *wt.*% polyvinyl alcohol (PVA) binder (Craneglass 230) was provided by Crane & Co. Inc (Dalton, MA). 4'-aminobenzo-15-crown-5 (NH_2-B15C5) was synthesized according to previous reports [11]. glycidyl methacrylate (GMA), ethyl 2-bromo-2-methylpropionate (EBiB), 2,2'-azobis(isobutyronitrile) (AIBN), trimethylamine (TEA) etc, were all purchased from J&K Scientific Ltd. (Beijing, China), as analytical-grade reagents. All the solvents, including N,N-Dimethylformamide (DMF), anisole, butylene oxide (THF), anisole, were of highest purity grade and provided by J&K Scientific Ltd. (Beijing, China).

2.2 Preparation of GFPGMAC-B15C5

Glass fiber mats (GFMs) were cut into ca. 2.0 × 1.0 cm pieces, and then added into 90.0 mL water/ethanol (*V:V*=4:3) mixture under magnetic stirring with determined amount of dopamine hydrochloride (pH=8.5, 10 mM) to prepare PDA coated GFMs. BiBB anchored GFMs@PDA were completed in an excess BiBB contained TEA/DMF mixture at room temperature. GFMs@PDA-Br was added in a 50 mL Schlenk flask, followed by adding 3.0 mL anisole, 3.0 mL GMA, 33.0 μL EBiB, 0.74 mL of 1.0 g L^{-1}AIBN/DMF sequentially. The reaction system was sealed and vacuum-argon inflation cycle was operated for several times. In argon protection, 1.0 mL of 1.0 g L^{-1} $CuBr_2$/TPMA (*wt*:*wt*=1:3) dissolved DMF mixture was added to flask through a syringe. The molecular ratio of the reagents was: [GMA]:[EBiB]:[macroinitiator]:[AIBN]:[$CuBr_2$]:[TPMA]=100:1:0.01:0.02:0.02:0.05. The prepared GF/PGMA composite (GFPGMAC) were post functionalized in NH_2-B15C5/DMF solution at concentration of 40 g L^{-1} at 70 ℃ for 6 h. The final product GFPGMAC-B15C5 was rinsed and dried.

2.3 Adsorptive separation of lithium isotopes

Adsorption of lithium was performed under batch mode. Typically, 10.0 mL of Li(I) aqueous solution with particular initial concentrations and pH values was added in a set of 20 mL glass conical flasks, followed by adding 3.0 mg GFPGMAC-B15C5. In a thermostatic oscillator, the mixture of Li(I) and GFPGMAC-B15C5 was agitated for a predetermined time interval. Adsorption capacity (q) was defined as follows,

$$q = \frac{(C_0 - C_e)\cdot V}{m} \times 1000 \qquad (1)$$

where q is the adsorption capacity for lithium, mg g^{-1}; C_0 and C_e are the initial and equilibrium Li(I) concentrations in aqueous phases respectively, mg L^{-1}; V is the volume of the solution, mL; m is the mass of the absorbent, mg.

Lithium isotopes separation was evaluated by the measurement of the lithium isotopes using High Resolution Inductively coupled plasma mass spectrometry (HRICP-MS). The single-stage separation factor (α) for $^6Li/^7Li$ was defined by Eq. (2). The subscripts 's' and 'l' represent the concentrations of lithium isotopes in solid phase and liquid phase, respectively.

$$\alpha = \frac{([^6Li]/[^7Li])_s}{([^6Li]/[^7Li])_l} \qquad (2)$$

3. Results and Discussion

3.1 Preparation of GFPGMAC-B15C5

The digital photos and SEM images for GFPGMAC and the counterparts in the synthesis were shown in Figure 1. Evidently, the morphology of GFMs made an obvious change and preserved the original mat form as well. After surface modification, a core-shell structure was observed, while the pristine fiberglass owned smooth cylindrical shape as the "core" and a polymer "shell" with thickness of 2.1 μm.

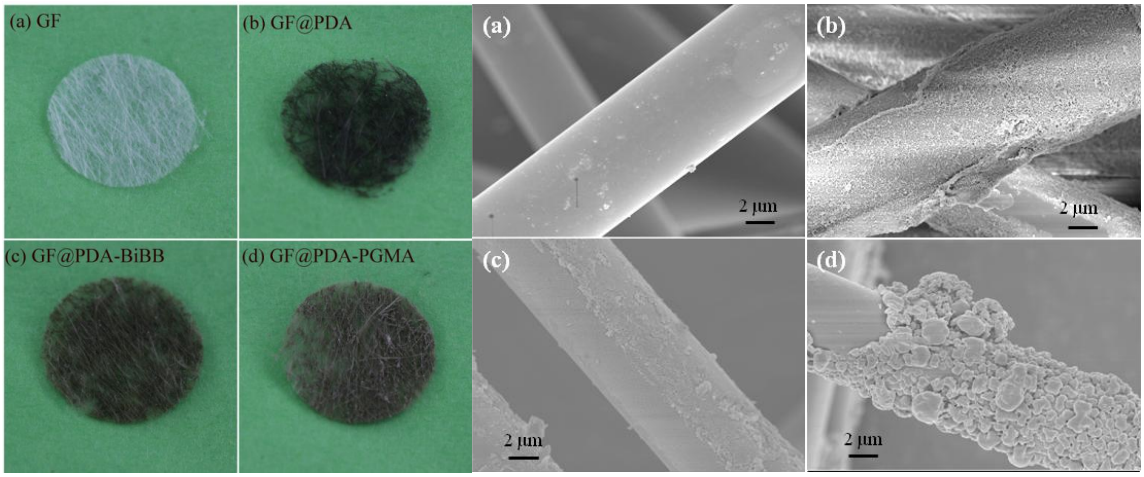

Figure 1. Morphology for GFPGMAC and the counterparts in SI-ATRP synthesis

Table 1 illustrated the compositional analysis results. From XPS analysis, it can be seen that, the carbon content increased with the introduction of organic components on the GFMs. Especially after the ATRP growth of PGMA brushes, *C* Atomic% increases from 52.12 % to 68.55%. For pristine GFMs, there was 13.08% Si content because of the main composition of glass fiber, SiO_2. When PDA coating was deposited onto GFMs, N content obviously increased for the contribution of the amino groups in PDA. After BiBB anchoring, an obvious peak at 76.85 eV could be recognized as the Br 3d adsorption peak, indicating the successful introduction of initiator BiBB with a Br content of 1.85%. Due to the abundant surface epoxy and ester group of GMA monomers, N atomic% relatively reduced but a slight increase (from 0.82% to 0.98%) after NH_2-B15C5 macrocyclic ligands grafted onto the composites' surface.

Table 1 Compositional analysis of the GFPGMAC-B15C5 and the counterparts

Samples	XPS Surface Atomic%				
	Si	Br	C	N	O
GFMs	13.08	Null	52.12	0.10	34.70
GFMs@PDA	2.88	0.06	68.96	7.21	20.89
GFMs@PDA-Br	5.22	1.85	61.21	6.17	25.55
GFPGMAC	Null	0.14	69.6	0.82	29.44
GFPGMAC-B15C5	Null	0.05	68.55	0.98	30.42

3.2 Adsorptive separation of lithium isotopes

Li(I) adsorption selectivity was investigated by static adsorption in Li(I) containing aqueous co-existence with other alkali metal ions, including Na(I), K(I) and Cs(I), at the same concentration of 100 mg g^{-1} in neutral pH and the results were shown in Figure 2a. As shown in Figure 2a, GFPGMAC-B15C5 exhibited selective binding ability towards Li(I) against the other alkali metal ions due to the matched ion size to the macrocyclic ligand diameter. The effect of counter ions for Li(I) uptake was also studied by dissolving different Li(I) salt, i.e, LiI, $LiNO_3$ and CF_3COOLi, into deionized water at Li(I) concentration of 100 mg g^{-1}. Apparently, the adsorption capacity showed an upward trend in the following order: CF_3COO^->NO_3^->I^-. It could be explained by the fact that softer ions have more affinity to organic solvent based on hard and soft acids and bases (HSAB) theory. Solvent influence was also studied by preparing Li(I) aqueous using three kinds of solvents, i.e., water, acetone and acetonitrile and Li(I) adsorption capacity was illustrated in Figure 2c. Li(I) adsorption capacity showed a decrease trend in the following order: acetone>water>acetonitrile. This result violated the previous study. Normally, in the solvents with lower dielectric constants were beneficial for cation, i.e., Li(I), desolvation, and then was helpful for ion mass transfer and adsorption onto solid phase. This results maybe contributed to the adsorbent properties, which against lithium isotope separation in pure liquid-liquid extraction system.

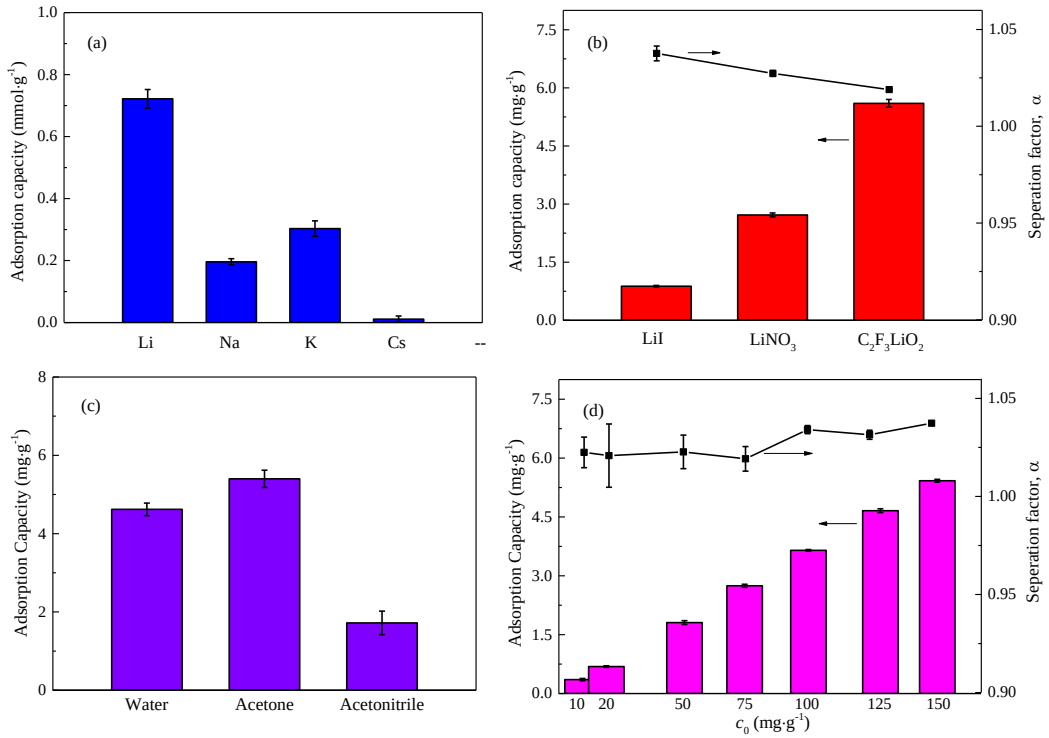

Figure 2. Adsorption and Seperation for ^{6}Li and ^{7}Li by GFPGMAC-B15C5 under different conditions: cations (a); anions (b); solvents (c) and concentrations (d)

Lithium isotope separation was also evaluated and the results were given in Figure 2b and 2d. Evidently, with the increasing of Li(I) concentration, Li(I) uptake and ^{6}Li and ^{7}Li separation factor increased with a maximum separation factor α of 1.037±0.002 in experimental conditions. Another

interesting finding was that the separation factor was counterintuitive to the Li(I) adsorption in different counter ions. The hypothesis was that counter ions would be exchanged to the macrocyclic ligands with the accompany of Li(I) but larger counter ions showed disadvantages for ^{6}Li and ^{7} Li exchange in a confined structured absorbent, leading to a reduced separation efficiency.

4. Conclusion

In this study, a new kind of material system, NH_2-B15C5 functionalized glass fiber/poly(glycidyl methacrylate) (GFPGMAC-B15C5), for lithium isotope separation was prepared using surface initiated ATRP strategy combined with protein inspired polydopamine chemistry. GFMs were considered as ideal support for crown ether stabilization due to their excellent erosion resistance, good strength and easy accessibility. Macrocyclic ligands immobilization was realized through surface initiated ATRP mediated by mussel-inspired PDA chemistry. The good control of PGMA brushes grown from the support, including defined molecular weight and polydispersity, could be beneficial for the post ligands grafting. The behavior of Li(I) uptake onto GFPGMAC-B15C5 and isotope separation was evaluated, in which softer counter ions were beneficial for Li(I) adsorption but separation efficiency inversely. Lithium isotope separation factor of 1.037±0.002 was achieved in optimal conditions. More importantly, this “grafting-from” methodology assisted by polydopamine chemistry opened a new avenue for some other macroscopic support surface modification/functionality for broaden application.

Acknowledgement

This study was financially supported by the Changjiang Scholars and Innovation Research Team in University (IRT13026), the National Science Fund for Distinguished Young Scholars (51425403), National Natural Science Foundation of China under Projects U1430234, 51673109, and 51473087.

References

1) J. R. Black, G. Umeda, B. Dunn, W. F. McDonough, A. Kavner, *J. Am. Chem. Soc.*, **131**, 9904-9905 (2009).
2) Y. A, K. Makhijani, MIT Press: Cambridge, MA, (2000).
3) T. Hoshino, T. Terai, *J. Nucl. Mater.*, **417**, 696-699 (2011).
4) M. Saleem, S. Hussain, M. A. Zia, M. A. Baig, *Applied Physics B*, **87**, 723-726 (2007).
5) A. Ishikawa, M. Sasaki, S. Narita, A. Takeuchi, H. Ohki, K. Yoshino, *Micropor. Mesopor. Mat.*, **248**, 115-121 (2017).
6) Y. Ban, M. Nomura, Y. Fujii, *J. Nucl. Sci. Technol.*, **39**, 279-281 (2002).
7) F. Yan, H. Liu, H. Pei, J. Li, Z. Cui, B. He, *J. Radioanal. Nucl. Ch.*, **311**, 2061-2068 (2017).
8) S. Fujine, K. Saito, K. Shiba, , **20**, 439 −440 (1983).
9) J. Wang, K. Matyjaszewski, *Macromolecules*, **28**, 7901-7910 (1995).
10) M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules*, **28**, 1721-1723 (1995).
11) R. Ungaro, B.E. Haj, J. Smid, *J. Am. Chem. Soc.*, **98**, 5198-5202 (1976).