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Separation and Recycling for Rare Earth Elements by Homogeneous Liquid-Liquid Extraction (HoLLE) Using a pH-Responsive Fluorine-Based Surfactant

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Abstract: A selective separation and recycling system for metal ions was developed by homogeneous liquid-liquid extraction (HoLLE) using a fluorosurfactant. Sixty-two different elemental ions (e.g., Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, La, Lu, Mg, Mn, Mo, Nb, Nd, Ni, Os, P, Pb, Pd, Pr, Pt, Re, Rh, Ru, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Te, Ti, Tl, Tm, V, W, Y, Yb, Zn, and Zr) were examined. By changing pH from a neutral or alkaline solution ($\text{pH} \geq 6.5$) to that of an acidic solution ($\text{pH} < 4.0$), gallium, zirconium, palladium, silver, platinum, and rare earth elements were extracted at >90% efficiency into a sedimented Zonyl FSA[®] ($\text{CF}_3(\text{CF}_2)_n(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{COOH}$, $n = 6-8$) liquid phase. Moreover, all rare earth elements were obtained with superior extraction and stripping percentages. In the recycling of rare earth elements, the sedimented phase was maintained using a filter along with a mixed solution of THF and 1 M sodium hydroxide aqueous solution. The Zonyl FSA[®] was filtrated and the rare earth elements were recovered on the filter as a hydroxide. Furthermore, the filtrated Zonyl FSA was reusable by conditioning the subject pH.

Keywords: homogeneous liquid-liquid extraction; HoLLE; phase separation phenomenon; fluorosurfactant; ion association; rare earth elements; separation and recycling; hydrometallurgy

1. Introduction

Many kinds of rare earth elements such as neodymium, europium, and gadolinium have been recently used in the development of new materials. However, the production of scandium, yttrium, and lanthanoids, collectively referred to as rare earth elements, is not yet widespread across the world. Hence, the potential production of these materials via waste recycling processes has become increasingly important; however, the costs and efficiencies of these recycling processes pose inherent problems. The mutual metal separation method is generally classified into wet and dry methods. Here, the wet method has been employed for reasons such as separation accuracy and energy savings. This typical method utilizes a solvent extraction process which uses solvents that are immiscible with each other. In addition to this process, various separating agents and methods for metal separation have also been recently developed. These include solvent extraction using ionic liquids [1,2], phase separation extraction using stimuli-responsive polymers [3–6], and solid-phase extraction using the adsorption effect of biological materials [7–9]. Among these, it is especially noteworthy that in 1988, Igarashi and Yotsuyanagi discovered the pH-dependent phase separation phenomenon, resulting from the addition of acid to a perfluorooctanoic acid (PFOA) aqueous solution containing trace amounts of acetone [10]. An oily, small secondary phase is resultantly produced, with the target substance ultimately being extracted from therein. Furthermore, the formation of a stable liquid phase which consists of PFOA^- and quaternary salt (Q^+ such as tetrabutylammonium ion (TBA^+)) was subsequently reported in the following year (1989) [11,12]. The produced liquid phase is stable in water and air; hence, it is known to be the same type as the early ionic liquid reported in 1992 [13] because the liquid is produced at room temperature by ionic associations of the subject cationic and anionic organic compounds (e.g., melting point; $-2.3\text{ }^\circ\text{C}$ in $\text{PFOA}^-/\text{TBA}^+$ [14]). This formation reaction of an ionic liquid is applied at the same time as the homogeneous liquid-liquid extraction method (HoLLE, type I in Figure 1). Many research papers have been published from the viewpoint of microextraction methods for trace components [15–20]. Hence, HoLLE, a separation method that uses these characteristics effectively, was conceived. In HoLLE, because an aqueous phase and an organic phase are in a homogeneous state at the starting point of extraction, a mechanically vigorous agitation for increasing the contact interface between the aqueous and organic phases in the solvent extraction process is not necessary. This separation method is the extraction to the water-immiscible sedimented phase for the target substance by providing stimuli such as changes in pH, temperature, and light. Some separation and concentration methods for metal chelates using surfactants such as PFOA and slight amounts of water-miscible organic solvents (such as acetone, tetrahydrofuran, *etc.*) have been reported [15–17,19]. In addition, a concentration method for rare earth elements using phosphoric acid and di(2-ethylhexyl)ester (D2EHPA) as an extracting agent in $\text{PFOA}^-/\text{TBA}^+$ has also been reported [21].

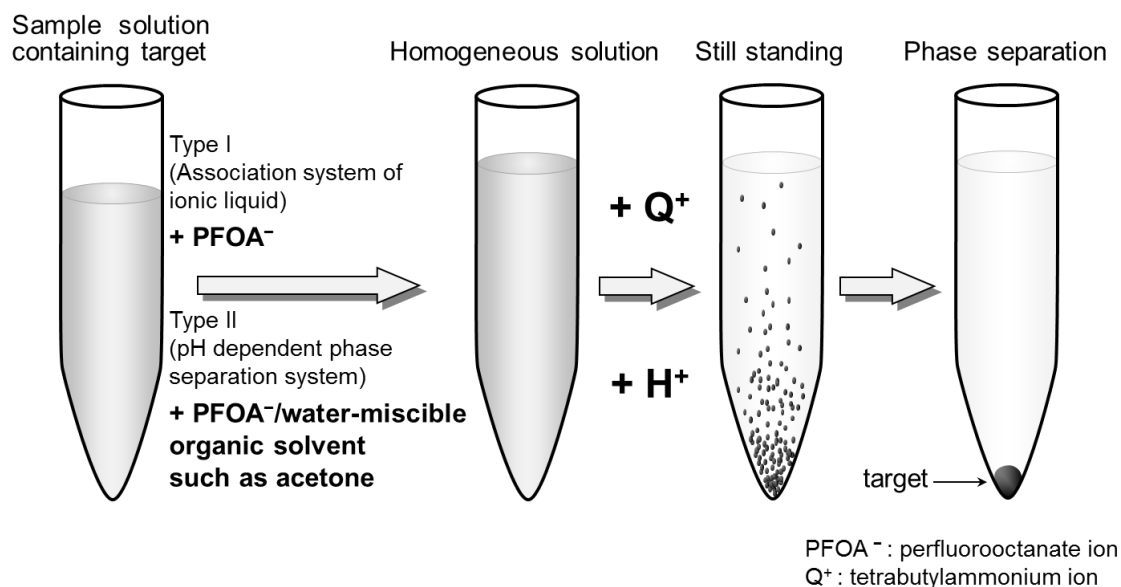


Figure 1. Scheme of homogeneous liquid-liquid extraction method (HoLLE).

In this study, Zonyl FSA[®], which is an alternative substance of PFOA⁻, was used as a phase separation agent in HoLLE. Zonyl FSA[®] is a 3-[2-(perfluoroalkyl)ethylthio]propanoic acid (CF₃(CF₂)_{*n*}(CH₂)₂S(CH₂)₂COOH, *n* = 6–8), with an acid dissociation constant (p*K*_a) of approximately 6 [22]. Therefore, this compound displays weak acidity because a spacer of some methylene groups is introduced between the fluorocarbon chain and the hydrophilic group, as compared to the strongly acidic PFOA. Applications of the separation and concentration of chlorophyll-a [22], silver complex [23], copper complex [24], indium complexes [25], and aluminum/titanium with 1,10-phenanthroline complexes [26] have been reported by HoLLE using this phase-separating agent.

In this paper, the extraction for 62 kinds of elements were examined and a high-efficiency separation and recycling system of rare earth elements using Zonyl FSA[®] as a phase-separating agent based on HoLLE, without the use of a chelating reagent, is described.

2. Experimental Section

2.1. Reagents

Zonyl FSA[®] was purchased from DuPont (Wilmington, DE, USA). Sixty-two types of elemental ions (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, La, Lu, Mg, Mn, Mo, Nb, Nd, Ni, Os, P, Pb, Pd, Pr, Pt, Re, Rh, Ru, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Te, Ti, Tl, Tm, V, W, Y, Yb, Zn, and Zr) were selected and their predetermined concentrations were prepared by diluting 1000-ppm standard solutions (received from Kanto Chemicals, Tokyo, Japan) with distilled water. Concretely, Ag(I), Al(III), Ba(II), Be(II), Bi(III), Ca(II), Cd(II), Ce(III), Co(II), Cr(VI), Cu(II), Dy(III), Er(III), Eu(III), Fe(II), Ga(III), Gd(III), Hg(II), Ho(III), In(III), La(III), Lu(III), Mg(II), Mn(II), Nd(III), Ni(II), Pb(II), Pd(II), Pr(III), Sc(III), Se(IV), Sm(III), Sr(II), Tb(III), Tl(I), Tm(III), V(V), Y(III), Yb(III), Zn(II), and Zr(IV) were 0.01–1 M of nitric acid aqueous solution. As(III), Au(III), Ir(IV), Mo(VI), Os(IV), Pt(II), Rh(III), Ru(III), Sb(III), Sn(II), and Te(IV) were 0.4–6 M of hydrochloric acid aqueous solution. Hf(IV), Nb(V), and Ta(V) were 1–3 M of hydrofluoric acid aqueous solution.

Ge(IV) and Si(IV) were 0.2–0.4 M potassium hydroxide solution. Ti(IV) was 2 M sulfuric acid aqueous solution. Each of B(III), P(V), Re(VII), and W(VI) were aqueous solution of oxo acid salts containing some ammonium ion. All element solutions were diluted with distilled water to 100 fold. Tetrahydrofuran (THF), acetic acid, sodium acetate, sodium hydroxide, acetone, and all other reagents used were of commercially available analytical grade unless otherwise specified. The utilized filter (for all cases) was a Merck Millipore hydrophilic PTFE filter JAWP02500 (Omnipore, pore size: 1.0 μm , Billerica, MA, USA).

2.2. Apparatuses

The following apparatuses were used: pH meter = Model F-51, manufactured by Horiba Ltd. (Kyoto, Japan); centrifugal separator = Model LC-100, manufactured by TOMY SEIKO Co., Ltd. (Tokyo, Japan); vacuum pump = Model MDA-015, manufactured by ULVAC (Kanagawa, Japan); ICP optical emission spectrometer = Model iCAP6300, manufactured by Thermo Fisher Scientific (Waltham, MA, USA).

2.3. Experimental Procedure

2.3.1. Extraction Characteristics of Elements by HoLLE with Zonyl FSA[®]

The following were added into a glass vial: 0.5 mL of elemental mixed solution (each element concentration: 10 ppm), 1.0 mL of THF, and 1.0 mL of Zonyl FSA[®]. Next, 7.5 mL of acetic acid/sodium acetate buffer solution (pH = 4) were added to bring the total mixture volume up to 10 mL. The mixture was then centrifuged for 10 min at 2000 rpm to separate the sedimented (Zonyl FSA[®]) phase and the supernatant (aqueous) phase. Each rendered post-centrifugal phase volume was $V_{\text{aq.}} = 9.95 \text{ mL}$ and $V_{\text{Zonyl FSA}^{\text{®}}} = 50 \text{ }\mu\text{L}$. The concentration of elemental ions in the aqueous phase was determined by ICP-OES.

The extraction percentage ($E \%$) of elemental ions was calculated as

$$E \% = 100 (1 - C_{\text{aq.}}/C_{\text{Total}}) \quad (1)$$

where C_{Total} and $C_{\text{aq.}}$ represent the total concentration of the added element and the concentration of the element in the aqueous phase after separation, respectively. Of note, the error range of each element's extraction percentage is $\pm 5\%$ or less.

2.3.2. The Recovery of Elements from the Zonyl FSA[®] Phase and the Redissolution of the Zonyl FSA[®] Phase

A water-immiscible Zonyl FSA[®] phase has retained the state of a stable liquid phase in the aqueous solution, and the elemental ions were recovered by filtration. In the recovery of targets, rare earth elements (Sc, Y, and lanthanoids) were well extracted by the experiment described in Section 2.3.1, and they were thus selected as targets. A Zonyl FSA[®] phase (approximately 50 μL) was produced after rare earth elemental extraction, which held on the hydrophilic PTFE filter. Water-immiscible Zonyl FSA[®] was filtered by adding 1 mL of sodium hydroxide and THF solution, which were mixed at a volume ratio of 1:1. The elements were trapped on the filter as hydroxides, the recovery percentage of elemental ions

in the filtrate phase was determined by ICP-OES. Furthermore, the rare earth elements were recycled again by the same procedure outlined in Section 2.3.1 using the filtrated Zonyl FSA®.

3. Results and Discussion

3.1. The Extraction of THF within the Phase Separation Phenomenon

As solubilizing agents for Zonyl FSA®, acetone and THF are examined. THF was selected from the viewpoint of its concentration time and operability, because it was already reported that the sedimented volume and its associated viscosity increase in the case of using acetone [22]. The relationship of the volume percentage of THF in the sedimented volume showed linear behavior in the range of 10–35 vol. % for the THF volumes shown in Figure 2 below. In the case of below 10 vol. % THF, the Zonyl FSA® phase precipitated fine solid particles. Moreover, Zonyl FSA® did not form a sedimented phase in the case of THF exceeding 50 vol. %. Therefore, THF volume in this system was ultimately deemed appropriate for 10 vol. %.

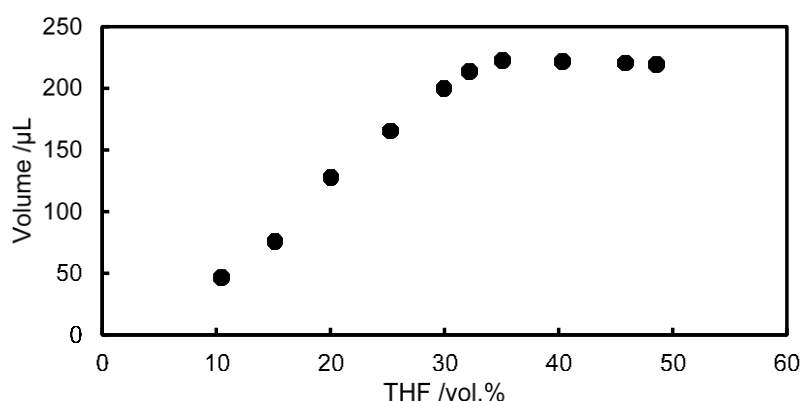


Figure 2. Relationship between the volume percentage of THF and the volume of sedimented phase. (Zonyl FSA®) = 10 vol. %; pH = 4.

3.2. Screening of Elements

The experimental procedure was performed according to Section 2.3.1. The percentage of extracted element ions in the sedimented phase is shown in Figure 3. Here, some element ions in the sample solution are estimated to exist as different type species such as a free metal ion, an anion complex such as gold chloride complex or platinum chloride complex, and an oxo anion species such as boric acid or phosphoric acid. Gallium, zirconium, palladium, silver, platinum, and rare earth elements (except for praseodymium) were obtained with a high extraction percentage; however, gold, indium, and germanium were obtained with a very low extraction percentage. With respect to rare earth elements, most rare earth elements are stable in the trivalent state, and they do not produce a hydroxide unless the pH range is of weak basicity to neutrality, e.g., since the solubility product constant (K_{sp}) of lanthanum is 1.0×10^{-19} [27], it does not precipitate as a hydroxide during the extraction procedure (pH = 4.0). On the other hand, only cerium was obtained with a notably low extraction percentage. This is because cerium is thought to exist in trivalent and tetravalent states in an aqueous solution with a pH of approximately 4. Based on this reason, tetravalent cerium is precipitated as a hydroxide in an acidic condition and, thus, is still

susceptible to hydrolysis [28,29]. Therefore, the extraction into the sedimented Zonyl FSA[®] phase can present inherent challenges because of the fact that tetravalent cerium has usually already hydrolyzed at the time of extraction in a pH equal to 4.

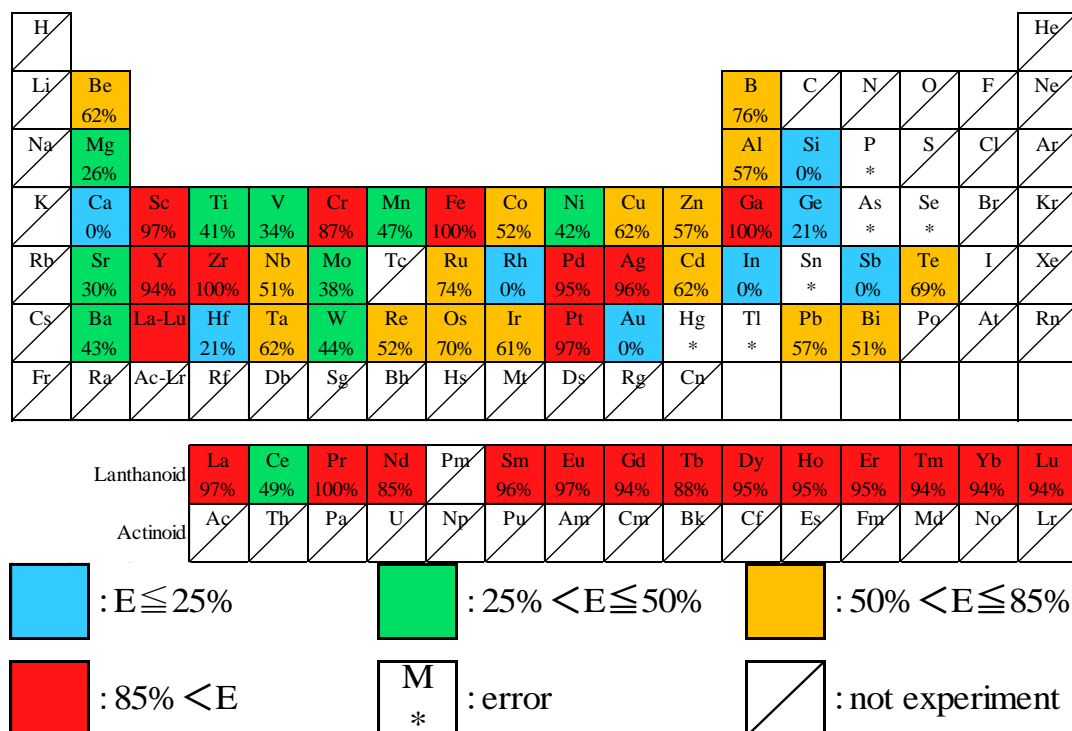


Figure 3. Summary of the extraction percentages for elemental ions with Zonyl FSA[®].

3.3. Stripping of Rare Earth Elements

The extraction behavior of elements into the Zonyl FSA[®] liquid phase was examined by focusing on rare earth elements. Filtration operation by the filter was evaluated for the sedimented phase containing rare earth elements. The sedimented phase was held/maintained by a microsyringe on a Teflon filter (Pore size: 1 μm). The rare earth elements were collected on the filters as hydroxides by a 1:1 mixed solvent of 1 mL THF and 1 M sodium hydroxide aqueous solution, whereas the Zonyl FSA[®] was dissolved in the procedure. That rare earth elements had been stripped was confirmed by measuring Zonyl FSA[®] aqueous solution that was dissolved and filtrated using ICP-OES (Table 1).

Table 1. Stripping percentages of rare earth elements from the Zonyl FSA[®] phase.

Metal	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Recovery %	81	92	88	90	91	88	91	92	92	91	92	92	84	92	92	92

3.4. Reuse of Spent Zonyl FSA[®]

The subject rare earth elements could be separated from the sedimented Zonyl FSA[®] phase by filtration, and the sedimented liquid phase similar to what existed before extraction was formed by adding a buffer solution (pH = 4) in the filtrate containing the Zonyl FSA[®]. Based on this phenomenon, the stripping experiments for rare earth elements were performed again using the spent Zonyl FSA[®].

The related findings are shown below in Table 2. Part of the heavy elements has a higher extraction percentage in the second extraction compared to the first extraction. Because part of the Zonyl FSA was lost during the recycling procedure, the component balance was changed in each fluorinated carbon chain number (6–8) of Zonyl FSA[®]. Thereby, the extraction selectivity for heavy elements was relatively increased. Zonyl FSA[®] was found to be reusable for the extraction and stripping of rare earth elements.

Table 2. Comparison of extraction percentages in first and second extraction times.

Metal	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1st Extraction %	97	94	97	49	100	85	96	97	94	88	95	95	95	94	94	94
2nd Extraction %	80	100	93	53	100	84	100	100	100	94	100	100	94	100	100	100

3.5. Overview of Separation and Recycling System of Rare Earth Elements Using Zonyl FSA[®]

Extracting rare earth elements by Zonyl FSA[®] is a plausible recovery technique using a simple filtration operation, and the spent Zonyl FSA[®] can be reused. Therefore, a separation and recycling system for rare earth elements using Zonyl FSA[®] was constructed, with the subject scheme shown below in Figure 4. In this system, the Zonyl FSA[®] and THF were added to metal solutions containing rare earth elements (depicted in the figure), with the solution resultantly forming a homogeneous state by gentle shaking. In addition, a weak acid buffer solution is introduced into the solution to extract the rare earth elements, and the Zonyl FSA[®] is subsequently aggregated by centrifugation for a period. The sedimented Zonyl FSA[®] phase is ultimately retained on the filter. Then, only Zonyl FSA[®] is filtrated and the rare earth elements are recovered on the filter as hydroxides. In contrast, Zonyl FSA[®] solution is obtained as a filtrate to around a neutral pH ($\text{pH} \geq 6.5$). Accordingly, it is capable as a second recycling product to be used again for separation and recovery, as demonstrated below in the figure.

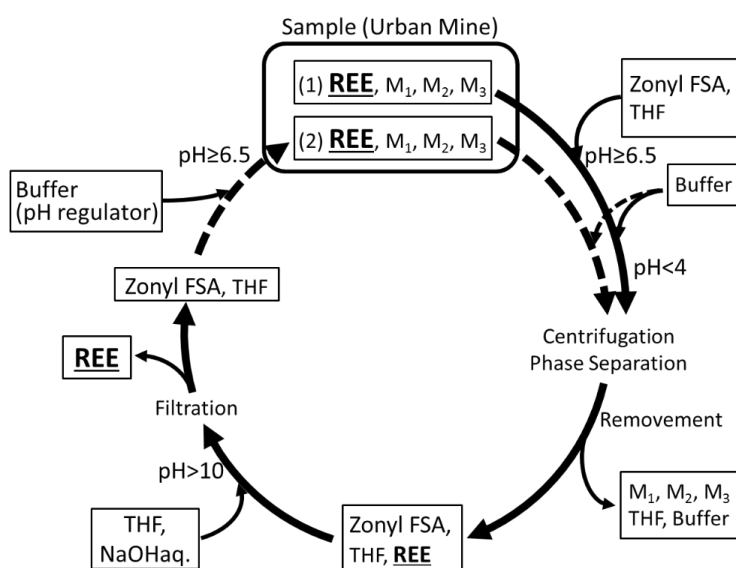


Figure 4. Separation and recycling system for rare earth elements using Zonyl FSA[®]. REE: rare earth elements; M_x: coexistent metals.

4. Conclusions

A homogeneous liquid-liquid extraction method (HoLLE) for metal elements using a Zonyl FSA[®] fluorosurfactant instead of a chelating agent was proposed. As a result, metal elements such as palladium, platinum, and rare earth elements were extracted at a very high percentage. This method is highly capable of extracting and stripping (with high efficiency) rare earth elements by HoLLE via the use of Zonyl FSA[®]. This method is expected to be a preprocessing technique for separating and recycling rare earth elements in electrical appliance components. Moreover, the developed process is capable of both the recycling of rare earth elements and the reuse of Zonyl FSA[®] as an extraction agent.

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Author Contributions

S.S. and S.I. conceived the experiments, and wrote the paper; S.S. designed experiments with contributions from S.I., O.O., T.K. and H.Y.; H.Y. was measured of metals by ICP-OES; S.S. performed experiments and interpretation.

Conflicts of Interest

The authors declare no conflict of interest.

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