Fabrication of Graphene Fiber Fabrics as Electrodes for Electrochemical Sorption of Uranium in Seawater

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1. Introduction

7 million of technically recoverable uranium resources has been identified in the geology. Assuming the same uranium consumption rates, the uranium resources will be exhausted within a century [1]. On the other hand, seawater contains about 4 billion tons of inexhaustible uranium resources. However, the extremely low concentration (3.3 μg/L) and the complex chemical species forms (Ca^{2+}-UO_2^{2+}-CO_3^{2-}) of uranium in seawater have limited the economical utilization.

Solid adsorbents are the most preferred methods for uranium extraction from seawater because it is economical, easy of handling, and eco-friendly. Amidoxime (AO, -R-C(NH_2)=NOH) has been known as an organic functional group which can form a strong covalent bonding with uranyl ions, selectively. Therefore, lots of solid adsorbents have been developed by functionalizing AO on the surface. As an adsorbent templet, various types of large surface materials have been suggested such as graphene hydrogel[2], graphene-magnetite composite[3], mesoporous silica[4], or metal-organic frames[5]. Those solid adsorbents have also serious limitations for real applications which are repulsive forces between adsorbed cations and free cations, slow diffusion kinetics due to the low concentration, and completion with co-existed ions such as Ca^{2+}. In order to overcome the problems, electrochemical sorption method has been suggested, recently [6]. The method overcomes the problems by applying alternative electrical potentials to guide the ions on the surface of AO functionalized carbon felt.

Carbon fibers have been considered as promising functional materials due to its high mechanical strength, electrical conductivity. Also, high permeability and chemical stability have excellent advantages for the electrochemical application. However, conventional carbon fiber fabrics are fabricated with binders, the fiber filaments do not link well. Therefore, the adhesion points are mechanically weak and electronically poor. Graphene fiber fabrics, a new type of carbon-based fabric, has been recently developed with wet-fusing of graphene oxide gel fibers. By using fusing methods, the junction points of the fabrics are graphically strong bonds, so it can maintain the mechanical and electrical properties. Furthermore, the rich functionalities of graphene oxide and its mild graphitization process can achieve hybridization with other materials. In this study, we have investigated the graphene fiber fabrics as electrochemical sorption electrodes for extracting uranium from seawater.

2. Methods and Results

2.1 Preparation of graphene oxide

Expanded graphite was made by microwave-assist expansion of natural graphite flake (-10 mesh). Then using Kovtyukhova's and modified Hummers' methods, graphene oxide were prepared. Impurities in the prepared graphene oxide solution were washed by centrifugation with 10 vol.% of HCl and DI water.

2.2 Graphene fibers fabrics

Graphene fiber fabrics were fabricated as followed the reference [7]. 5ml of graphene oxide solution was doped on a syringe and injected into a fast-rotating coagulation bath contains 5 wt.% of calcium chloride solutions through 0.31 mm of a spinneret. The volume flow rate of the syringe pump and the ration speed of the bath were 50 μL/min and 50 rpm, respectively. Then, short fibers were collected in the bath. The short fibers were washed for removing remained calcium ion and collected on a membrane filter. The collected short fibers were vacuum dried at 60 °C for 12 h and re-dispersed in alcohol and water mixture in the ratio of 50:50 (v/v). After that, the re-dispersed fibers were collected again through vacuum filtering and dried at 80 °C for 12 h. During the drying process, each graphene oxide fibers were connected by shrinkage and formed non-woven fabrics. At the last, the graphene fiber fabrics were made by chemically reducing the graphene oxide fiber fabrics with HI at 80 °C for 12 h.

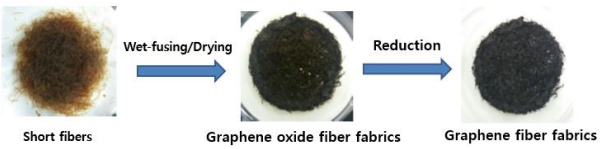

Fig1. Fabrication process of graphene fiber fabrics

2.3 Functionalization of AO

Before the reduction steps, polyacrylonitrile (PAN) was functionalized on the graphene oxide fiber fabrics by an in-situ polymerization method. And then acrylonitrile functional groups were converted to AO groups by reaction with hydroxyl amine.

3. Results

The graphene fiber fabrics show randomly oriented fiber structure as shown in Fig. 2. Because graphene oxide fibers are well dispersed in alcohol and water mixture media, the short fibers were randomly assembled after filtering process. Also, short fibers were strongly bonded without binder by shaping the raw materials of graphene fiber fabrics. Due to junction points and randomly oriented structure, the carbon-based fabrics can have desired mechanical properties and uniform electrical properties.

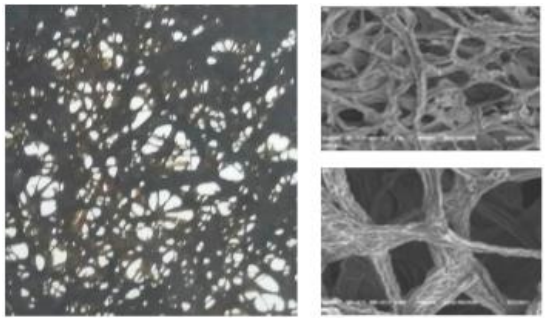

Fig2. The morphologies (left) and SEM image (right) of graphene fiber fabrics

4. Conclusion

Uranium recovery from seawater is the way of making nuclear power as unlimited energy but the low concentration of uranium and co-existed cation hinder the economic extraction process. Electrochemical sorption method with carbon felt was proposed for effective adsorption of uranium. However, interfaces between carbon fibers in commercial carbon felt are attached with binders that could be unwanted properties for the electrochemical sorption. Therefore, we proposed that the graphene fiber fabrics, binder-free carbon-based fabrics, can be used as electrochemical sorption electrodes in this study. In future work, the effective functionalization of AO groups on graphene fiber fabrics and the electrochemical properties of the fabrics will be researched

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