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Graphene fiber for radioactive iodine adsorption and the effect of silver functionalization

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1. Introduction

Used Nuclear Fuel (UNF) reprocessing plays an important role in reducing the generation of high level waste (HLW) and also a growing priority for the research and development of the radioactive waste management. In this reprocessing of UNF the majority portion of radionuclide emission takes place as it is chopped and dissolved in boiling nitric acid [1]. Off-gas stream of the reprocessing plant mainly contains ^{129}I, ^{14}C, ^{3}H and noble gases (^{85}Kr and multiple Xe isotopes). Iodine-129 is a primary concern in reprocessing plant due to its very long half-life of 1.6×10^7 y as well as high mobility and volatile contaminant which bio accumulates concentrating in the thyroid gland affecting bio metabolism [2]. For this reason, the Environmental Protection Agency (EPA) has implemented strict regulations on the release of ^{129}I from the reprocessing facilities, which require an effective capture efficiency in excess of 99% (decontamination factor > 167) [3]. This has created the necessity of suitable iodine sorbents and waste forms for reprocessing systems and geological disposal [4].

Iodine capture technologies can be classified into two groups such as wet scrubbing and solid sorbent where solid sorbents based adsorption technique is an effective and advantageous than wet processes [5]. Silver exchanged zeolite (AgZ) is the common methods of iodine adsorption where silver content is highly selective for elemental iodine [6,7]. Currently Ag-functionalized silica aerogels, and chalcogen-based aerogels are investigated and found successful for iodine adsorption but may be costly to produce, either due to fabrication techniques or precursor materials [8,9]

Graphene as a two dimensional basal plane of graphite has become a focus of interest for a wide range of application. Due to the large theoretical specific surface area (2630 m^2 g^{-1}) for a single layer graphene, in combination with its highly controllable defects and functional group concentration, interest has grown on the use of graphene as a sorbents material for gasses, though primarily for potential gas detectors [10,11]. Besides this graphene-based nanomaterials such as graphene powders and aerogels that have high adsorption capacities for iodine (~50 mass%) [12]

This work presents the graphene fiber as potential sorbents for ^{129}I in spent nuclear fuel reprocessing off-gas and will investigate the sorption capacity of graphene fiber for $I_2(g)$ in a saturated iodine environment. The fabrication process of graphene fiber is provided in addition to analysis of the sorption capacity and thermal stability of the iodine loaded samples. Also the effect of silver functionalization on the iodine adsorption application.

2. Experiments

In this section, the graphene fiber fabrication process, the silver functionalization of graphene fiber and iodine uptake experiments are described.

2.1 Wet spinning of graphene oxide fibers

Graphene oxide solution (GO), purchased from Grapheneall Co. Ltd., injected into a rotating coagulation bath with a fixed rate of 300uL/min. The solution at the coagulation bath was prepared by mixing 5wt% CaCl2 into the solution of ethanol/water (1/3 v/v). the coagulation bath was rotated at a speed of 6 rpm while the spinning nozzle is dipped in the coagulation bath. The GO fibers were immersed in a coagulation bath for 10min and washed with the solution of ethanol/water (1/3 v/v) and dried at room temperature for 4 hours. Finally, the retained GO fibers were dried in a vacuum oven at 60 °C for 12 hours. Fig. 1 shows the schematic diagram of the wet spinning process.

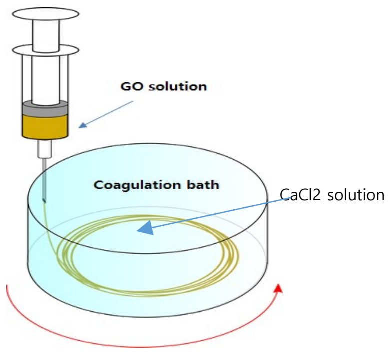

Fig. 1. schematic diagram of the wet spinning process.

2.2 Chemical reduction of GO fiber (rGO fiber)

The dried GO fibers were then reduced with HI. The HI was added on the fibers and heated at 70°C for 12 hours. The reduced GO (rGO) fibers were washed with distilled water once and ethanol solution. Finally, the rGO fibers were dried in a vacuum oven at room temperature.

2.3 Silver (Ag) functionalization of the fiber

For the silver functionalization of the graphene fiber an ex-situ process was applied. After the fabrication of the fiber from the coagulation bath, the viscous fiber was then immersed into a 1 mM silver nitrate ($AgNO_3$) solution. So a silver particle coating was created on the surface of the graphene fiber. Fig. 2 shows the images of the fabricated graphene oxide fiber and Ag functionalized graphene oxide fiber. These functionalized fibers are then reduced by HI. After washing and drying the final silver functionalized graphene fiber is found.

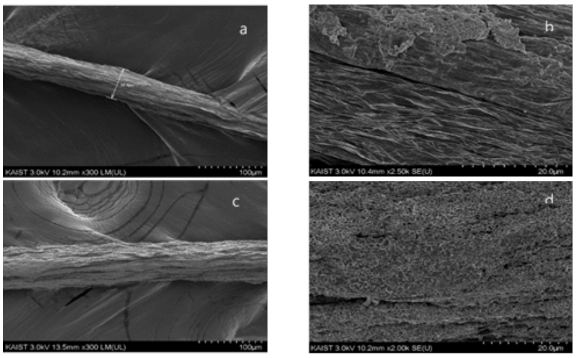

Fig. 2. SEM images of Graphene oxide (GO) fiber(a,b,) and silver functionalized GO fiber (c,d)

2.3 Iodine uptake

The graphene fibers will be exposed to a saturated iodine environment through the use of a desiccator, in which solid iodine crystals will be placed. Iodine uptake will be determined through the change in mass of the tested samples before and after exposure to the saturated iodine environment. Due to the sublimation of iodine, quick saturation state of the chamber will help to drive the adsorption of I_2(g) to reach the maximum sorption capacity within reasonable times. Exposure to a saturated iodine environment allows for simple comparison of graphene fibers to other sorbent materials currently being considered for iodine capture.

3. Characterization techniques

The microstructure of the samples will be observed with a scanning electron microscope (SEM). Thermogravimetric analysis (TGA) will be carried out as a primary method for confirming the iodine uptake of the samples. TGA will also demonstrate the thermal stability of the sorbents and indicate the temperature threshold for iodine desorption. X-ray photoelectron spectroscopy (XPS) will be conducted to measure the elemental composition and chemical state. Brunauer–Emmett–Teller (BET) surface area measurements will be conducted to analyze the adsorption of I_2(g) on the solid surface of the graphene fiber.

4. Conclusions

In this work graphene fiber is reported as a sorbent of radioactive iodine ^{129}I which may have exceptional iodine uptake capacity and kinetics. Silver(Ag) functionalized graphene fiber may also show good adsorption characteristics by the chemisorption of iodine whereas physisorption occurred in the graphene fiber. This functionalization may also enable the graphene fiber for the high temperature adsorption application.

Acknowledgment

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