Video Article

An Efficient Method for Selective Desalination of Radioactive Iodine Anions by Using Gold Nanoparticles-Embedded Membrane Filter

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Abstract

Here, we demonstrate a detail protocol for the preparation of nanomaterials-embedded composite membranes and its application to the efficient and ion-selective removal of radioactive iodines. By using citrate-stabilized gold nanoparticles (mean diameter: 13 nm) and cellulose acetate membranes, gold nanoparticle-embedded cellulose acetate membranes (Au-CAM) have easily been fabricated. The nano-adsorbents on Au-CAM were highly stable in the presence of high concentration of inorganic salts and organic molecules. The iodide ions in aqueous solutions could rapidly be captured by this engineered membrane. Through a filtration process using an Au-CAM containing filter unit, excellent removal efficiency (>99%) as well as ion-selective desalination result was achieved in a short time. Moreover, Au-CAM provided good reusability without significant decrease of its performances. These results suggested that the present technology using the engineered hybrid membrane will be a promising process for the large-scale decontamination of radioactive iodine from liquid wastes.

Video Link

The video component of this article can be found at https://www.jove.com/video/58105/

Introduction

For several decades, huge amount of radioactive liquid wastes has been generated by medical institutes, research facilities, and nuclear reactors. These pollutants have often been a palpable threat to environment and human health[1,2,3]. Especially, radioactive iodine is recognized as one of the most hazardous elements from nuclear plant accidents. For example, an environmental report on the Fukushima and Chernobyl nuclear reactor demonstrated that the amount of released radioactive iodines including ^{131}I ($t_{1/2}$ = 8.02 days) and ^{129}I ($t_{1/2}$ = 15.7 million years) to the environment was larger than those of other radionuclides[4,5]. In particular, the exposure of these radioisotopes resulted in high uptake and enrichment in human thyroid[6]. Moreover, released radioactive iodines can cause severe contamination of soil, seawater and ground water owing to their high solubility in water. Therefore, a lot of remediation processes using various inorganic and organic adsorbents have been investigated to capture radioactive iodines in aqueous wastes[7,8,9,10,11,12,13,14,15,16,17,18,19,20]. Although extensive efforts have been devoted for the development of advanced adsorbent systems, the establishment of a decontamination method showing satisfactory performances under continuous in-flow condition was very limited. Recently, we reported a novel desalination process showing good removal efficiency, ion-selectivity, sustainability, and reusability by using hybrid nano-composite materials made of gold nanoparticle (AuNPs)[21,22,23]. Among them, gold nanoparticle-embedded cellulose acetate membranes (Au-CAM) facilitated highly efficient desalination of iodide ions under a continuous-flow system compared with those of existing adsorbent materials. Moreover, the whole procedure could be finished in a short time, which was another advantage for the treatment of nuclear wastes generated from post-use in medical and industrial applications. The overall goal of this manuscript is to provide a step-by-step protocol for the preparation of Au-CAM[24]. We also demonstrate a rapid and convenient filtration process for ion-selective capture of radioactive iodine using the engineered composite membranes. The detailed protocol in this report will offer a useful application of nanomaterials in the research field of environmental science.

Protocol

1. Synthesis of Citrate-Stabilized Gold Nanoparticles

1. Wash a two-neck round-bottom flask (250 mL) and a magnetic stir bar with aqua regia, a mixture of concentrated hydrochloric acid and concentrated nitric acid in a 3:1 volume ratio.

CAUTION: Aqua regia solution is extremely corrosive and may result in explosion or skin burns if not handled with extreme caution.
2. Rinse the glassware thoroughly with deionized water to remove residual aqueous acid.
3. Add 120 mL of chloroauric acid solution ($HAuCl_4$, 1 mM) to the two-neck round-bottom flask (250 mL) and heat it to reflux under constant stirring.
4. Add 12 mL of sodium citrate tribasic (35 mM) solution quickly to the two-neck round-bottom flask and reflux the resulting mixture for another 20 min for the complete reduction of the gold salt.
5. Allow the colloidal suspension of nanoparticles (deep red) to cool down to room temperature.
6. Measure the concentration of the gold nanoparticles (AuNPs) with UV-vis spectroscopy at a wavelength of 520 nm (extinction coefficient of 2.8×10^8) using a quartz cuvette (1 cm path length).
7. Add a single drop of AuNPs suspension onto a carbon-coated copper grid (400 mesh) and dry it at room temperature. Measure the size of AuNPs with transmission electron microscopy (TEM).
8. Keep the colloidal gold nanoparticle suspension at 4 °C.

2. Preparation of Hybrid Membrane (Au-CAM)

1. Preparation of gold nanoparticles-embedded membrane filter using a syringe unit
    1. Wash a cellulose acetate membrane (pore size: 0.45 µm, diameter: 25 mm) supported by a filter unit with deionized water (10 mL) for three times.
    2. Withdraw 10 mL of citrate-stabilized AuNPs (10 nM) with a sterile syringe (20 mL) and add it slowly into a pre-washed cellulose acetate membrane filter (**Figure 1**).
    3. Wash the filter unit with 10 mL of deionized water three times to remove non-immobilized AuNPs.
    NOTE: AuNPs immobilized on the cellulose acetate membrane are highly stable, and thus Au-CAM can be stored under ambient condition for several weeks without the loss of their chemical properties or stability.

2. Preparation of gold nanoparticle membrane filter by the vacuum pump
    1. Place the cellulose acetate membrane (pore size: 0.45 µm, diameter: 47 mm) between a filter holder fritted glass support (diameter: 40 mm) and a graduated funnel (300 mL).
    2. Connect a combined unit of the fritted glass support and graduated funnel to a recover flask (500 mL) and a vacuum pump.
    3. Add 10 mL of citrate-stabilized AuNPs (10 nM) into the graduated funnel and then apply vacuum until all AuNPs are passed through the cellulose acetate membrane (approximately 20 s).
    4. Repeat the same procedure (step 2.2.3) on the other side of the membrane to immobilize AuNPs on both sides of the membrane.
    5. Analyze the surface of Au-CAM using scanning electron microscope (SEM) under the high-performance conditions with the accelerating voltages up to 15 kV (**Figure 2d**).
    NOTE: To check the stability of nanoparticles on Au-CAM in a high salt condition, the composite membrane was immersed in 1.0 M NaCl solution for 2 h and then visual inspection was performed to confirm the stability of the Au-CAM.

3. Adsorption of Radioactive Iodine Using Au-CAM in a Batch System

1. Dilute the radioactive iodine ([^{125}I]NaI, 2.2 MBq) in 3 mL of pure water, 1.0 M NaCl, or 10 nM NaI and add each solution into a Petri dish (50 mm diameter × 15 mm height).
CAUTION: The oxidized radioactive iodine can be volatile and must be handled with adequate lead shields and lead vials. All radiochemical steps should be performed in a well-ventilated charcoal-filtered hood, and the experimental procedures need to be monitored by radioactivity detectors.
2. Place the Au-CAM which is prepared by using a vacuum filter into radioactive iodine solutions and shake them gently at room temperature.
3. Withdraw 10 µL of the radioactive iodine solution from the Petri dish at given time points (0, 5, 10, 30, 60, 120 min) and measure the radioactivity of the aliquot using automatic γ-counter.
4. Rinse the Au-CAM with purified water after 120 min and then measure the amount of radioactivity captured on the membrane using automatic γ-counter (**Figure 3**).

4. Desalination of Radioactive Iodine under Continuous In-Flow Condition

1. Removal of radioactive iodine anions ($^{125}I^-$) using an Au-CAM filter
    1. Dissolve the radioactive iodine (3.7 MBq) in 50 mL of pure water, PBS 1x, 1.0 M NaCl, 0.1 M NaOH, 0.1 M HCl, 10 mM CsCl, 10 mM $SrCl_2$, synthetic urine, or sea water.
    2. Withdraw 50 mL of each solution with a sterile syringe (50 mL) and pass through the Au-CAM filter unit at an in-flow rate of about 1.5 mL/s using a syringe pump (**Figure 1**).
    3. Transfer 5 mL of the filtrate into a plastic vial for quantifying the radioactivity in the solution.
    4. Measure the amount of residual radioactivity in the filtrate solution using automatic γ-counter (**Figure 4**).

2. Reusability test of Au-CAM filter
    1. Dissolve the radioactive iodine in a synthetic urine or seawater (3.7 MBq/50 mL).
    2. Withdraw 50 mL of solution with a sterile syringe (50 mL) and add it into the Au-CAM filter unit at an in-flow rate of about 1.5 mL/s using a syringe pump.
    3. Repeat the same filtration procedure (step 4.2.2) for seven times using a single Au-CAM filter unit.
    4. Transfer 5 mL of the filtrate into a plastic vial for quantifying the radioactivity in the solution.
    5. Measure the amount of radioactivity in seven filtrate solutions by using automatic γ-counter.

Representative Results

We have demonstrated simple methods for the fabrication of Au-CAM using citrate-stabilized AuNPs and cellulose acetate membrane (**Figure 1a**). The surface of Au-CAM was observed by SEM which showed that the nanomaterials were incorporated stably on the cellulose nanofibers (**Figure 2**). The nanoparticles incarcerated on the membrane were sustained stably and were not released from the membrane by continual washing with aqueous solutions such as 1.0 M NaCl. The adsorption capacity of an Au-CAM was approximately 12.2 μmol of iodide anion per 1 g of AuNPs[24]. To evaluate the desalination performance, the Au-CAM prepared by the vacuum-assisted method were immersed into aqueous solutions containing 2.2 MBq of [^{125}I]NaI (**Figure 1b**). After 30 min incubation, most of the radioactive iodine (>99%) in pure water and 1.0 M NaCl was captured by Au-CAM (**Figure 3**). On the other hand, the adsorption of radioactivity was inhibited completely in the presence of non-radioactive NaI, because the surface of AuNPs was occupied by access amount of iodide anions ($^{127}I^-$).

For more useful application of the current method, Au-CAM filter was applied to a continuous desalination process. The radioactive iodine solutions (3.7 MBq/50 mL) were passed through a filter unit containing Au-CAM at an in-flow rate of 1.5 mL/s (**Figure 1c**). The amount of the residual radioactivity in the filtrate was measured using a γ-counter. The removal efficiency (%) was defined by the following equation (1).

$$\text{Removal efficiency (\%)} = (C_0 - C_e)/C_0 \times 100 \quad (1)$$

Where C_0 is the concentration of radioactive iodine before filtration step and C_e is the concentration of radioactive iodine after filtration step.

As shown in **Figure 4**, the concentration of radioactive iodine was decreased significantly, and the excellent efficiency was obtained through a filtration step. In particular, the desalination performance of Au-CAM was not suppressed by high concentration of inorganic salts such as sodium, cesium, and strontium and several organic substances. In all cases, the removal efficiency of Au-CAM was higher than 99.5%. Au-CAM showed high removal efficiency under neutral and basic condition (up to pH 13), however, it dropped to ca. 90% under acidic condition (pH 1). Furthermore, Au-CAM could be reusable for repetitive desalination of radioactive iodine in synthetic urine and seawater. During the consecutive filtration process, more than 99% of radioactivity in aqueous media was captured efficiently using a single Au-CAM filter unit[24].

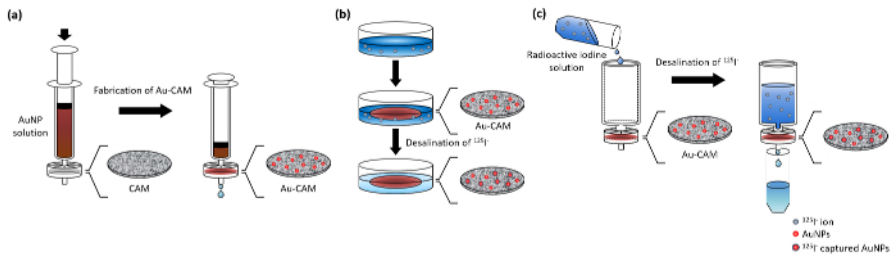

Figure 1. Schematic illustration of the desalination procedure in this protocol using Au-CAM. (a) Fabrication of Au-CAM by using a syringe filter unit. (b) Adsorption of radioactive iodine in a batch system. (c) Filtration of radioactive iodine under continuous in-flow condition. Please click here to view a larger version of this figure.

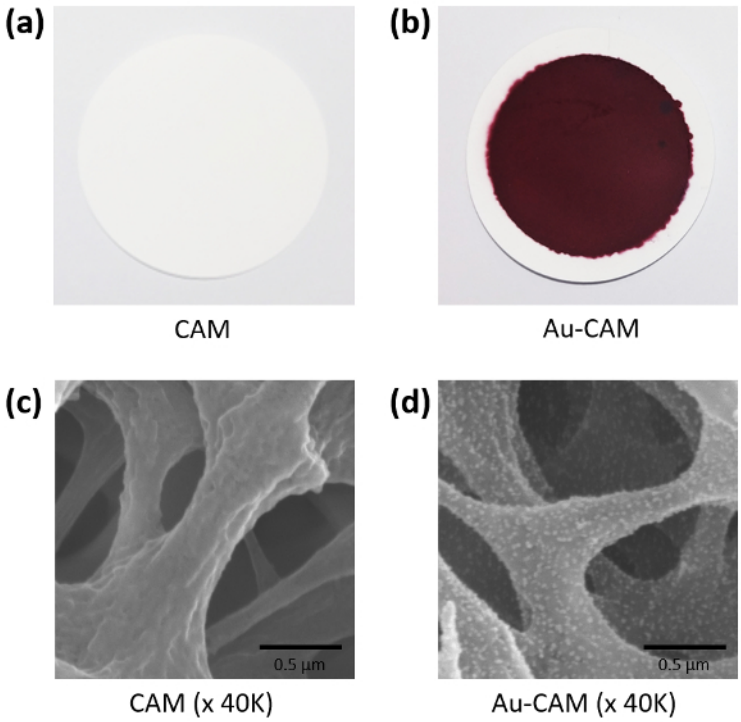

Figure 2.**Characterization of Au-CAM**. (a) A photographic image of cellulose acetate membrane (diameter 47 mm). (b) A photographic image of Au-CAM (diameter 47 mm). (c) SEM image of cellulose acetate membrane (40,000X). (d) SEM image of Au-CAM (40,000X). Please click here to view a larger version of this figure.

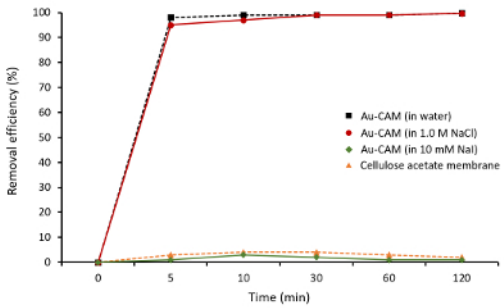

Figure 3.**Time-dependent removal efficiency of radioactive iodine using Au-CAM in pure water, 1.0 M NaCl, and 10 mM NaI.** Please click here to view a larger version of this figure.

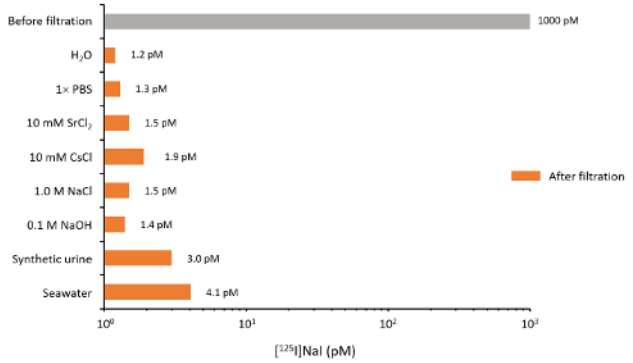

Figure 4. Filtration of radioactive iodine anions in several aqueous solutions using Au-CAM. Please click here to view a larger version of this figure.

Discussion

In recent year, various engineered nanomaterials and membranes have been developed to remove hazardous radioactive metals and heavy metals in water based on their specific functionality in adsorption techniques[25,26,27,28,29,30,31,32,33,34,35,36,37]. In this study, we demonstrated highly useful method for rapid and efficient separation of radioactive halogen species. By using citrate-stabilized AuNPs and a commercially available cellulose acetate membrane, Au-CAM can easily be prepared and the fabrication step is highly reproducible. As iodide anions is spontaneously chemisorbed on the surface of AuNPs, Au-CAM can be applied to the remediation of radioactive iodines in various aqueous media. Among various radioisotopes of iodine, we selected $^{125}I^-$ as a target element in this study because it emits a low radiation energy compared to other radioactive iodines and the decay half-life (59.5 days) is long enough to develop an optimized process. But the reactivity of $^{125}I^-$ is identical with other iodine isotopes, and thus this method will be utilized to remove more hazardous radioelements such as $^{131}I^-$ and $^{129}I^-$.

In the presence of high concentration of competing anions such as phosphate, chloride, and hydroxide, the nano-hybrid membrane (Au-CAM) showed excellent desalination efficiency and good reusability. Another significant advantage is that immobilized nanoparticles on a cellulose acetate membrane is stable under high salt conditions and varied pH. It appears like that AuNPs on the membrane of carbohydrate were stabilized by oxygen atom containing functional groups including hydroxyl and carbonyl groups[38,39]. Thus, the hybrid membrane can be stored for several weeks without the loss of its performance and chemical stability. As shown in **Figure 4**, Au-CAM showed excellent removal efficiency in various aqueous media. The limitation of the present method is that Au-CAM would not be useful in organic solvent system including alcohols and dimethyl sulfoxide, because cellulose acetate is partially dissolved in these media and thus AuNPs can be released from the membrane.

There have been several reports describing the desalination of radioisotopes in contaminated water using various adsorbents including engineered membranes[40,41,42]. The continuous process in the present study is superior to conventionally used methods in terms of removal efficiency, ion-selectivity and reusability. Using a single Au-CAM (diameter: 25 mm), ca. 90 mL of aqueous waste can be purified in 1 min. It is anticipated that a lot of Au-CAM filters will be easily produced in a short time, because large-scale synthesis and characterization of the citrate-stabilized AuNPs were well-established. Taken together, Au-CAM will be a promising adsorbent system worth to investigate for the practical remediation of industrial and medical radioactive iodine wastes.

Disclosures

The authors have nothing to disclose.

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