

Nanohybrid of Silver-MXene: A Promising Sorbent for Iodine Gas Capture from Nuclear Waste

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The increasing reliance on nuclear energy as a significant low-carbon power source necessitates effective solutions for managing radioactive emissions. This study introduces a novel application of MXene nanohybrids, specifically silver-MXene (Ag-Ti₃C₂T_x), as an effective sorbent for radioiodine off-gas capture at an operating temperature of 150 °C. Through comprehensive material characterization, including X-ray diffraction, scanning and transmission electron microscopies, energy-dispersive X-ray spectroscopy, Raman spectroscopy, thermogravimetric analysis, inductively coupled plasma optical emission spectroscopy, and gas sorption analyses, the successful loading of Ag nanoparticles onto $Ti_3C_2T_y$ is confirmed and the subsequent formation of AgI upon iodine capture. The results demonstrate that Ag-Ti₃C₂T_y exhibits superior iodine uptake compared to traditional silver-based sorbents such as silver mordenite zeolite (AgZ) and silver-functionalized silica aerogel (AgAero). The Ag-Ti₃C₂T_y achieves an iodine loading of 946 mg g^{-1} , significantly outperforming AgZ (131 mg g^{-1}). These findings highlight the potential of Ag-Ti₃C₂T_y as a highly efficient, thermally stable sorbent for radioiodine capture, and potentially addressing key limitations of existing materials.

1. Introduction

Having become the largest low-carbon source of power and contributing more than 10% to the global power supply.^[1] nuclear

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energy has become increasingly critical to sustainability, providing cleaner energy to meet global demand at a lower price. The U.S. runs light water reactors (LWRs) for power production under a once-through (open) fuel cycle. One of the challenges with nuclear power production is the effective capture and immobilization of fission products released from solid uranium oxide (UOX) fuels if the fuels are reprocessed, which could be done to recycle the burnable actinides from the used nuclear fuel. If the fuel is breached, fission products can be released that include volatile and longlived radionuclides, such as radioiodine $(^{129}$ I, with a $t_{1/2}$ of 1.6×10^7 years). These potential environmental challenges require effective capture processes to prevent re-release during disposal within a nuclear waste repository.^[2] Consequently, there is a growing need for the development of novel

materials capable of effectively sorbing iodine gas $(\rm I_{2(g)})during$ reprocessing according to U.S. regulations (40 CFR 190).

The primary criteria defining the effectiveness of iodine sorbents include their loading capacity, which correlates with the presence of iodine-absorbing getters (chemisorption) and/or iodine-adsorbing surfaces (physisorption), the durability of the sorbent (e.g., chemical, mechanical, thermal), the selectivity of the sorbent, and the properties of the loaded sorbent toward a disposal pathway, ensuring the irreversible capture of iodine and high stability at elevated temperatures.^[3-5] Various materials have been explored as solid sorbents for iodine capture, including activated carbon, zeolites, chalcogen-based aerogels, silica-based aerogels, and metal-organic frameworks (MOFs).^[4,6-9] However, these materials still present limitations, such as low capacity, weak physisorption, slow iodine uptake kinetics, and inadequate thermal stability. For instance, activated carbon exhibits poor thermal stability at high temperatures, leading to preferential water adsorption over iodine capture as well as it being an explosion hazard.^[10] While MOFs offer tunable porosity, many suffer from structural instability at elevated temperatures, limiting their practicality. An example MOF is HKUST-1, which degrades within 50-150 °C range due to solvent loss,^[11] and thermogravimetric analysis (TGA) shows that dehydration can cause irreversible structural change well before decomposition, limiting their applicability for high-temperature iodine capture.^[12]





A variety of metals were investigated to evaluate iodine adsorption capacity, kinetics and thermal stability.^[13-15] Silvercontaining materials have emerged as the most efficient sorbents among those tested over the last 50 years due to their high chemisorption capabilities and the strong bonding formed upon reaction with iodine gas, resulting in the formation of silver iodide (i.e., α -AgI, β -AgI, and/or γ -AgI), alongside the notable thermal and chemical stability of AgI. Consequently, increased research endeavors have been focused on the utilization of silver in iodine sorbents. Among the explored candidates, silver mordenite zeolite (AgZ) is the current U.S. baseline iodine sorbent for reprocessing conditions^[16] and silver-functionalized silica aerogel (AgAero) has shown high promise as a replacement sorbent in recent years.^[17] Across different static I_{2(g)} capture experiments, AgZ (IONEX Ag-900) showed iodine loading up to \approx 93–131 mg g^{-1[18]} while AgAero showed a higher iodine loading up to 408 mg g^{-1} .^[17]

Aside from the previously mentioned sorbent materials, MXenes are a rapidly expanding class of 2D materials, consisting of transition metal carbides, nitrides, and carbonitrides with the general chemical formula $M_{n+1}X_nT_x$.^[19] In this formula, M represents early transition metals (e.g., Ti, V, Nb, Mo), X is carbon and/or nitrogen, and T_x refers to surface terminations such as -OH, -O, -Cl, or -F. These materials exhibit fascinating physical and chemical properties, including customizable surface terminations,^[20,21] tunable interlayer spacings,^[22–24] high specific surface areas (SSAs), and excellent electronic conductivities.^[25,26] Owing to these versatile properties, MXenes have demonstrated outstanding performance in various applications, including energy storage,^[27-29] catalysis,^[30,31] water purification,^[32,33] and coating materials.^[34,35] Recently, MXene and their hybrids/composites have been found to be particularly efficient in treating nuclear wastewater, successfully adsorbing radionuclides like Cs, Sr, U, Re, Th and I.[36-42] For example, hydroxyl-terminated MXene Ti3C2(OH)2 was used to adsorb Cs+ ions from nuclear wastewater,^[43] and the introduction of pores on MXene surfaces was found to increase the availability of hydroxyl groups, thus enhancing U(VI) adsorption.[44] In terms of iodine removal from aqueous solutions, MXene hybrids have demonstrated strong potential.^[45] The MXene-Ag nanowire composite, for instance, efficiently adsorbs iodine by forming stable AgI, achieving an adsorption capacity of 84.7 mg g⁻¹, while maintaining performance across varying pH levels and competing ion conditions.^[46] Similarly, the MXene-polydopamine-Ag₂O₄ composite, enhanced by a polydopamine coatings for uniform silver oxide nanoparticle deposition, reaches an iodine adsorption capacity of 80 mg g⁻¹ through rapid AgI formation.^[47] However, while there have been extensive studies on iodine capture in liquid nuclear wastes, the potential of MXenes for capturing iodine gas remains largely underexplored.

This study introduces a novel MXene nanohybrid, Ag-MXene (Ag-Ti₃C₂T_x), designed for efficient iodine gas capture at an operating temperature of 150 °C. To maximize sorbent performance, we optimized the Ag-Ti₃C₂T_x by exploring various parameters, including the concentration and treatment time of AgNO₃ during synthesis. Our findings demonstrate that Ag-Ti₃C₂T_x achieves a notable iodine loading capacity of up to 946 mg g⁻¹, significantly outperforming conventional silver-based sorbents. By leveraging the unique properties of MXenes and the chemisorption capabilities of Ag, this work addresses key limitations of existing iodine sorbents and offers a promising solution for high-capacity, thermally stable iodine capture in nuclear waste applications.

2. Experimental Section

Figure 1 provides a schematic illustration of the procedures used for synthesizing the base Ti_3AlC_2 , followed by the production of multilayered MXene (m- $Ti_3C_2T_x$), delaminated MXene (d- $Ti_3C_2T_x$), $Ti_3C_2T_x$ aerogel, and the Ag-MXene (Ag- $Ti_3C_2T_x$) hybrid materials. It also provides additional steps involved in the overall process, starting from the MXene synthesis to iodine capture testing.

2.1. Synthesis of Ti₃AlC₂ MAX Phase and Ti₃C₂T_x MXene

 $Ti_{3}AlC_{2}$ synthesis was done by mixing the powders of titanium (Ti, -325 mesh, 99%, Thermo scientific), aluminum (Al, -325 mesh, 99.5%, Thermo scientific) and graphite (C, 7–11 µm, 99%, Alfa Aesar) with a molar ratio of Ti:Al:C equal to 3.0:1.2:1.88, respectively. Ten 10 mm-diameter yttria stabilized zirconia (YSZ) balls were placed inside a high density polyethylene (HDPE) bottle along with the powders. Then, a Turbula T2F mixer was used to mix them at 56 rpm for 3 h. The mixed powders were loaded into an alumina crucible and placed at the center of an alumina tube furnace. The crucible was heated to 1600 °C for 2 h while argon (Ar) was continuously flowing through it at a rate of 0.2 L min⁻¹. The heating process was conducted at a rate of 10 °C min⁻¹. After the heating cycle, the mixture was allowed to cool down to reach room temperature in the furnace under the Ar flow. The resulting material was a lightly sintered Ti₃AlC₂ brick that was then ground, and the powder was sieved to maintain a particle size below 45 µm.

Ti₃C₂T_x MXene was synthesized by selective etching of aluminum from Ti₃AlC₂. The used etching s was prepared from 9 M hydrochloric acid (HCl, Fischer chemicals) in water (the volume ratio was 20 mL of solution for each gram of Ti₃AlC₂) and adding 9 moles of potassium fluoride (KF, 99%, Thermo scientific) per mole of Ti₃AlC₂. The powders of Ti₃AlC₂ were added slowly to the etching solution and magnetically stirred at 500 rpm at 45 °C for 48 h. The etched powder was washed by dividing it equally into 50 mL centrifuge tubes, using one tube per 0.5 g of Ti₃AlC₂. De-ionized (DI) water was added, and the tubes were centrifuged at 3500 rpm for 2 min. The supernatant was decanted, fresh DI water was added, and the sediments were redispersed using a vortex mixer. This washing process was repeated several times until the pH of the solution was >6.

2.2. Delamination of Ti₃C₂T_x MXene and Aerogel Fabrication

For delamination of the $Ti_3C_2T_x$ MXene, 1 g of the washed $Ti_3C_2T_x$ was soaked in 40 mL of 1 M lithium chloride (LiCl, 99%, Thermo scientific) for 24 h at room temperature. After soaking, the sample was washed using 50 mL of DI water and centrifuged at 3500 rpm for 5 min. This washing step was repeated





Figure 1. Schematic illustration of the procedure, starting with the etching of the Ti₃AlC₂ MAX phase and concluding with the iodine capture test.

three times. The sample was then sonicated for 1 h, followed by centrifugation at 3500 rpm for 1 h. The resulting colloidal solution was collected and filtered through a Celgard 3501 membrane overnight, producing a free-standing paper of delaminated $Ti_3C_2T_x$ with no residual salts. The paper was then redispersed in DI water by sonication. The dispersion was then frozen by soaking in liquid nitrogen followed by freeze-drying at -50 °C under vacuum for 72 h to obtain the aerogel.

2.3. Silver Loading on Ti₃C₂T_x Aerogel

An aqueous solution of silver nitrate (AgNO₃, 99.85%, Thermo Scientific) was prepared at various molarities (0.1, 0.2, 0.5, 1, and 2 $mathbb{M}$). Ti₃C₂T_x was redispersed in DI water at a concentration of 2.5 mg mL⁻¹. The AgNO₃ solution was then slowly added to the Ti₃C₂T_x colloidal solution at a volume ratio of 1:4, respectively. The mixture was magnetically stirred at 400 rpm for 30 min at room temperature, followed by three cycles of washing with DI water. Then, samples were dried overnight using vacuum-assisted filtration.

2.4. Characterization of Materials

X-ray diffraction (XRD) patterns were recorded using a Rigaku D/Max-2200 powder diffractometer with a 2θ step size of 0.02° and a scan rate of 0.1° min⁻¹, using Cu K α radiation set at 40 kV and 40 mA. Scanning electron microscopy (SEM) images were taken using a Hitachi S-4800 with an acceleration voltage of 3 kV. Energy-dispersive X-ray spectroscopy (EDS) analysis was performed to determine the chemical composition, utilizing an INCA system integrated with a Hitachi S-4800 microscope at an accelerating voltage of 40 kV. The samples for transmission electron microscopy (TEM) were prepared by redispersing the powders in DI water through bath sonication for 10 min, followed by diluting the supernatant. The colloidal dispersion was then drop-cast onto a copper grid. TEM images were taken by using an FEI TECNAI G2-F30 at an accelerating voltage of 300 kV. Raman spectroscopy was employed to analyze the structure and surface chemistry of the $Ti_3C_2T_x$ MXene using a WiTec Confocal Raman microscope with a $100 \times$ magnification objective. A laser with a wavelength of 532 nm was selected, operating at a power of 1 mW to minimize laser-induced damage. The

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acquisition time was set to 0.5 s per scan, with 2000 accumulations, to ensure a high signal-to-noise ratio while preventing sample degradation. The TGA was performed with a TGA Q50 (TA Instruments, USA). The samples were subjected to a temperature range of 30–900 °C ramped at 10 °C min⁻¹ under flowing argon of 90 μ L min⁻¹.

The surface area was measured using nitrogen adsorption/desorption isotherms with a Quadrasorb EVO/SI gas sorption system (Quantachrome Instruments, Anton Paar). Prior to analysis, the samples were degassed under vacuum at 120 °C for 15 h. Nitrogen (N₂) adsorption/desorption was carried out at a constant temperature of 77.3 K, and the amount of N₂ adsorbed or desorbed at varying relative pressures was recorded to generate adsorption isotherms. The SSA was calculated from the adsorption isotherms using five data points in the BET (Brunauer-Emmett-Teller) method after inputting the sample masses used in the experiments.^[48]

Quantitative analysis for Ti and Ag was conducted using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Model: ICAP Duo, Thermo-Fisher Scientific, UK) utilizing multiple emission lines for each element (Ag - 328.0 and 338.2 nm; Ti – 190.8, 334.9, 336.1, and 368.5 nm). A small amount (≈40 mg) of each Ag-MXene sample was weighed accurately into 7 mL volume clean perfluoro alkoxy (PFA) vials (Savillex, USA). Then a 1 mL concentrated Optima grade HNO₃ (Fisher Scientific, Canada) was added to each sample and exact weights were taken. Each sample was allowed to sit for ≈ 1 h in the capped vial with the HNO3 before 0.2 mL of concentrated HF was added and its weight taken. The samples were then observed to dissolve completely in 5-10 min after the HF addition, without heating. Adding HF without the delay appeared to block the dissolution process. Weighed aliquots of the dissolved Ag-MXene solutions were then quantitatively diluted by a factor of 1000 in 2% v/v HNO₃ for analysis to yield expected Ti and Ag concentrations in the range 1–5 μ g g⁻¹. Calibration standards for Ag and Ti, ranging from 0.5 to 5 μ g g⁻¹, were prepared by serial dilution of 1 mg g⁻¹ stock solutions (Inorganic Ventures, USA) in 2% v/v HNO₃. The concentrations of Ti and Ag in the samples were measured, corrected for dilution, and subsequently used to calculate the percentage of each element relative to the total weight of dissolved material in the Ag-MXene samples.

2.5. Static Iodine Capture Performance of Ag-Ti₃C₂T_x

The Ag-loaded samples were placed in a vacuum oven at 110 °C for 4 h to remove any retained moisture before iodine gas capture test. The samples were then placed into 4 mL borosilicate glass vials (Qorpak GLC-00980). The glass vials were weighed before and after filling with samples using a digital balance. An additional empty vial served as a reference for iodine adsorption onto the glass and was included in a 1-L PFA jar (100-1000-01; Savillex; Eden Prairie, MN) covered with the lid. The 4 mL vials were securely fitted inside pieces of silicon rubber to provide support within the jar during handling. Iodine crystals (>99.5%, Thermo Scientific Chemicals) were placed into a 20 mL scintillation vial (DWK Life Sciences Wheaton Glass), positioned inside the center of the 1-L jar alongside the other sample vials. It was ensured that the mass ratio of iodine to total sample mass was >2 to maintain

a saturated $\rm I_{2(g)}$ environment during the experiment. The entire assembly was placed inside a muffle furnace and heated at 150 °C for 24 h. Following cooling, the lid was removed, and the jar was reheated at 150 °C for an additional hour in the absence of the iodine to eliminate any loosely physisorbed iodine. Subsequently, the sample vials were removed from the jar and weighed using an analytical balance. To assess the kinetics of the iodine adsorption, exposure time was varied (1, 15, and 45 min, 1, 3, 12, and 24 h). To confirm the complete removal of physisorbed iodine, the reheating step in air at 150 °C was extended to 24 h and further to 72 h.

3. Results and Discussion

3.1. Materials Characterization

XRD results for Ti₃AlC₂, Ti₃C₂T_x aerogel, Ag-Ti₃C₂T_x, and the iodine-loaded Ag-Ti₃C₂T_x are shown in **Figure 2a**. The complete disappearance of Ti₃AlC₂ peaks following the etching process confirms the full removal of Al, which subsequently affected the crystallinity of the structure. In **Figure 3a**, TEM image reveals an absence of oxide particles within the flakes of Ti₃C₂T_x. The SEM image in Figure 3d shows few-layer sheets of Ti₃C₂T_x, confirming the delamination of Ti₃C₂T_x.

To further assess the thermal stability of $Ti_3C_2T_r$ under the conditions used in the iodine capture experiment, a pristine aerogel sample was heated at 150 °C for 24 h in air. The sample exhibited only a small weight gain of $\approx 0.65\%$, indicating minimal oxidation. This is consistent with EDS results (Table S1, Supporting Information), which show only a slight increase in oxygen content after heating. Furthermore, XRD analysis before and after heating (Figure S1, Supporting Information) confirms that the MXene structure remained intact, reinforcing its stability under these conditions. Previous studies have reported that oxidation of $Ti_3C_2T_x$ in oxygen-containing environments typically begins above 200 °C, supporting that the adsorption temperature of 150 °C is below the threshold for significant oxidation.^[49] As for Ag loaded $Ti_3C_2T_r$, The SEM image in Figure 3e shows Ag nanoparticles embedded between Ti₃C₂T_x sheets. The XRD pattern (Figure 2a) confirms that Ag crystalline nanoparticles were effectively loaded onto the surface of $Ti_3C_2T_x$ by directly reducing AgNO₃ in a $Ti_3C_2T_x$ colloidal solution. The TEM image in Figure 3b shows Ag nanoparticles, represented by dark spots in the bright-field micrographs, homogenously distributed within the $Ti_3C_2T_x$ matrix, with measured particle sizes ranging from 50 to 110 nm. The Raman spectra of the selected samples in Figure 2b confirm the presence of $Ti_3C_2T_x$ throughout the process, including after iodine gas capture. The characteristic Raman peaks of $Ti_3C_2T_x$ are observed at ≈ 200 , 384, 580 to 620, and 720 cm^{-1.[50]} Following Ag loading, the peaks at 384, 620 and 720 cm⁻¹ remain evident. Notably, after the iodine capture experiment, the characteristic peaks at 384, 620 and 720 cm⁻¹ remains distinct, confirming the continued presence of $Ti_3C_2T_x$. The persistence of these peaks indicates that the MXene structure remains intact even after capturing iodine and the formation of AgI.

After the iodine capture test of Ag-Ti₃C₂T_x, the XRD pattern in Figure 2a confirms the complete formation of crystalline AgI [i.e., a mixture of β -AgI (*P*6₃*mc*) called iodargyrite and γ -AgI (*F*-43*m*)

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Figure 2. Characterization of $Ti_3C_2T_x$ aerogel at various stages of synthesis, Ag loading, and iodine capture. a) XRD patterns for Ti_3AlC_2 (PDF# 52–0875), $Ti_3C_2T_x$ aerogel, Ag(0.1 M)- $Ti_3C_2T_x$ (Ag, PDF# 07–0783), and iodine-treated Ag(0.1 M)- $Ti_3C_2T_x$ (Agl, PDF# 09–0374). b) Raman spectra for $Ti_3C_2T_x$ aerogel, Ag(0.1 M)- $Ti_3C_2T_x$ and iodine-treated Ag(0.1 M)- $Ti_3C_2T_x$ (Agl, PDF# 07–0783), and iodine-treated Ag(0.1 M)- $Ti_3C_2T_x$ (Agl, PDF# 07–0783), and iodine-treated Ag(0.1 M)- $Ti_3C_2T_x$ (Agl, PDF# 07–0783), and iodine-treated Ag(0.1 M)- $Ti_3C_2T_x$ (around the treated Ag(0.1 M)- $Ti_3C_2T_x$ around the treated Ag(0.1 M)- $Ti_3C_2T_x$ around the treated Ag(0.1 M)- $Ti_3C_2T_x$ (Agl, PDF# 07–0783), and iodine-treated Ag(0.1 M)- $Ti_3C_2T_x$ around the treated Ag(0.1 M)- $Ti_3C_2T_x$ around the treated Ag(0.1 M)- $Ti_3C_2T_x$. c) N₂ adsorption–desorption isotherms for Ag- $Ti_3C_2T_x$ using different AgNO₃ concentrations (0.1 and 0.5 M).

of the zinc blende structure], which is considered as a desirable compound for creating stable waste forms.^[6] The TEM image in Figure 3c demonstrates the growth of AgI over large areas of the $Ti_3C_2T_x$ matrix. Moreover, the SEM image in Figure 3f reveals the formation of AgI within $Ti_3C_2T_x$ sheet as iodine gas was captured by the embedded Ag nanoparticles between $Ti_3C_2T_x$ sheets. The EDS results in Table S2 (Supporting Information) indicate that more than 90% of the available Ag is utilized to form AgI. These findings confirm that the Ag within $Ti_3C_2T_x$ layers facilitates AgI growth by serving as nucleation points where iodine molecules adsorb and react during the iodine capture test.

To investigate the effect of AgNO₃ concentration on the SSA of Ti₃C₂T_x, BET nitrogen adsorption-desorption measurements were conducted, as shown in Figure 2c. The SSA of the Ag(0.1 m)-Ti₃C₂T_x sample was found to be 37 m² g⁻¹, while the Ag(0.5 m)-Ti₃C₂T_x sample exhibited a reduction in SSA to 24 m² g⁻¹. Interestingly, the crystallite size calculated using Scherrer's formula^[51] for Ag(0.1 m)-Ti₃C₂T_x and Ag(0.5 m)-Ti₃C₂T_x (Figure S2, Supporting Information) revealed that Ag(0.5 m)-Ti₃C₂T_x sample had a significantly smaller crystallite size (31 nm)

compared to the Ag(0.1 M)-Ti₃C₂T_x (57 nm), aligning with the particle size range observed in the TEM image for Ag(0.1 M)-Ti₃C₂T_x in Figure 3b (50–110 nm). The reduction in crystallite size at higher AgNO₃ concentrations, despite a lower SSA, is likely attributed to the agglomeration of Ag nanoparticles on the MXene surface.^[52] These findings suggest that even at higher AgNO₃ concentrations, MXene sheets can effectively host active Ag particles, maintaining structural integrity.

In addition to structural and compositional analysis, TGA was performed to assess the thermal stability of Ag(0.5 M)-Ti₃C₂T_x before and after iodine capture (Figure S3, Supporting Information). In the pre-iodine Ag-Ti₃C₂T_x sample, the weight loss is primarily attributed to the evaporation of physically adsorbed water and gases. At higher temperatures, additional weight loss occurs due to the pyrolysis of surface terminations (-OH, -O, -F) on the MXene nanosheets.^[53] While for the post-iodine Ag(0.5 M)-Ti₃C₂T_x, it exhibits a significant weight loss beginning above 600 °C and continuing up to 900 °C, which corresponds to the decomposition of AgI and the subsequent release of iodine gas.^[54] These results further



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Figure 3. a–c) Bright-field TEM micrographs of (a) $Ti_3C_2T_x$ aerogel, b) Ag(0.1 m)- $Ti_3C_2T_x$, and (c) iodine-loaded Ag(0.1 m)- $Ti_3C_2T_x$. d–f) SEM micrographs of (d) $Ti_3C_2T_x$ aerogel, (e) Ag(0.1 m)- $Ti_3C_2T_x$, and (f) iodine-treated Ag(0.1 m)- $Ti_3C_2T_x$.

support the strong interaction between iodine and $Ag-Ti_3C_2T_x$ and confirm the stability of the captured iodine up to elevated temperatures.

3.2. Static Iodine Uptake on Ag-Ti₃C₂T_x Sorbent

To evaluate static iodine loading after the iodine capture experiment, Equation (1) and Equation (2) were used, where $m_{(s)}$ is the mass of sample before iodine capture, $m_{(s+i)}$ is the mass of the sample after iodine capture, Δm is the change in mass obtained after the iodine capture experiment and q_e is the iodine mass loading in equilibrium conditions, defined the iodine captured mass per the initial mass before iodine (in mg g⁻¹).

$$\Delta m = m_{(s+i)} - m_{(s)} \tag{1}$$

$$q_e = \frac{\Delta m}{m_{(s)}} * 1000 \tag{2}$$

To determine the static iodine adsorption equilibrium, a set of mass measurements were made over time intervals during the iodine capture experiments, as demonstrated in Figure S4a (Supporting Information). The results indicate rapid initial adsorption stage, followed by equilibrium after 1 h, where no significance increase in iodine uptake is observed. These findings provide confirmation of the iodine capture efficiency of Ag(0.5 m)- $Ti_3C_2T_x$ over time.

To confirm the effective removal of physisorbed iodine, an extended desorption experiment was conducted by heating iodine-loaded Ag-Ti₃C₂T_x at 150 °C in air for up to 72 h. As shown in Figure S5 (Supporting Information), no significant iodine desorption was observed beyond the initial heating period, confirming that the applied conditions are sufficient for the removal of weakly bound iodine. This further supports that the remaining iodine is chemically bound to the material, ensuring strong retention and stability under these conditions.

Figure 4 illustrates the effect of AgNO₃ concentration on the iodine loading after the iodine capture experiment. The intrinsic contribution of pristine $Ti_3C_2T_x$ was assessed, with an iodine loading of 81 mg g⁻¹. Iodine loading increases with AgNO₃ concentration until reaching a saturation point. At 0.1 M, the loading was 662 mg g⁻¹. Doubling the concentration to 0.2 M resulted in similar value of 683 mg g⁻¹. A substantial increase occurred at 0.5 M, where the loading reached 946 mg g⁻¹. Further increases to 1 and 2 M led to minimal changes, with loadings of 986 m g⁻¹ and 1003 mg g⁻¹, respectively. This trend suggests that the iodine loading approaches a saturation plateau at \approx 0.5 M,



Figure 4. Effect of AgNO₃ concentration on the iodine loading after the iodine capture experiment.

indicating that the Ti₃C₂T_x surface is nearly fully loaded at this concentration and AgNO₃ concentrations much higher than this are likely not needed due to incomplete utilization (discussed below). Table S2 (Supporting Information) summarizes the iodine loadings for Ag-Ti₃C₂T_x under various conditions, including different AgNO₃ concentrations, treatment times, and drying methods. Reducing the AgNO₃ treatment time from 2 h to 30 min did not impact iodine capture performance, nor did changing the drying method from vacuum-assisted filtration to freeze-drying. While these findings establish Ag-Ti₃C₂T_x as a highly efficient and thermally stable sorbent for radioiodine gas, dynamic flow studies are essential for a more comprehensive evaluation of its capture behavior under realistic operation conditions. Such studies will provide deeper insights into breakthrough performance and long-term stability.

To further understand the adsorption behavior of I_2 over time, kinetic experiments were conducted at varying exposure durations to iodine vapor. The adsorption kinetics were analyzed using the pseudo-second-order model, described by Equation (3):^[55]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(3)

where q_t and q_e represent the adsorption capacity (mg g⁻¹) of captured iodine at time *t* and at equilibrium, respectively, and k_2 is the equilibrium rate constant of the pseudo-second-order kinetic model. The iodine adsorption curve, along with its corresponding linear fit are shown in Figures S4a and S4b (Supporting Information), respectively. Based on the fitted data, the rate constant k_2 was determined to be 2.4×10^{-2} g (mg·h)⁻¹, while the equilibrium adsorption capacity q_e was estimated at 948 mg g⁻¹. The model exhibited an excellent fit with a high coefficient of determination (R² = 0.99995), indicating a chemisorption-related mechanism.^[56]

To estimate the sliver utilization, we compared the measured iodine loading and the theoretical iodine loading, calculated based on ICP-OES measurements of Ag wt.% in both Ag(0.1 M)- $Ti_3C_2T_r$ and Ag(0.5 M)- $Ti_3C_2T_r$ samples (Table S3, Supporting Information). For the Ag(0.1 M)-Ti₃C₂T_x, which contains 51.5 wt.% Ag, a discrepancy of +5.6% was observed between the theoretical and measured iodine loadings. This discrepancy can be attributed to the iodine capture capability of the $Ti_3C_2T_x$ MXene surface, underscoring the potential contribution of the MXene surface chemistry to iodine adsorption. In contrast, the Ag(0.5 M)-Ti₃C₂T_x sample, containing 87.3 wt.% Ag, exhibited a discrepancy of -8.1%, indicating a minimal amount of unutilized Ag. Consistent with the EDS results, both discrepancies are within 10% of their corresponding theoretical values. This suggests that at higher Ag loading, iodine capture is predominantly governed by Ag rather than MXene, as less of the MXene surface is exposed to the $I_{2(g)}$, limiting its interaction with iodine during the capture process.

Table S4 (Supporting Information) presents a comparison of the iodine loading capacities of Ag-Ti₃C₂T_x with various Agbased sorbents reported in the literature under nuclear reprocessing conditions (T \approx 150 °C). While AgZ and AgAero reached a maximum of 131 mg g^{-1[18]} and 408 mg g^{-1,[17]} respectively, Ag-Ti₃C₂T_x significantly surpassed these values. Aluminosilicate ADVANCED MATERIALS INTERFACES

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aerogels (NAS-11a-Ag°) and heat-treated Ag-Al-Si-O xerogel (Ag-HTX) demonstrated higher iodine loadings of 555 mg g^{-1[18]} and 429 mg g^{-1} ,^[57] respectively. However, Ag(0.5 M)-Ti₃C₂T_x exhibited an exceptional iodine loading of 946 mg g⁻¹, emphasizing its superior performance in iodine capture under reprocessing conditions. Although 3D macroporous silver-silica aerogel (3DOM-SA) was reported to achieve a similarly high iodine loading of 925 mg g^{-1} , ^[58] this value likely reflects contributions from both physisorption and chemisorption processes. This comparison with other Ag-based sorbents underscores the efficiency of the silver-MXene hybrid in iodine capture, positioning it as a highly promising material for applications in nuclear waste management and beyond. While these comparisons highlight the efficiency of Ag-Ti₃C₂T_x, the iodine capture experiments were conducted under air exposure, demonstrating strong iodine selectivity. However, in dissolver off-gases from used nuclear fuel reprocessing, iodine is accompained by NO_x, water vapor and other volatile species.^[4] Further studies are needed to evaluate its performance under such conditions.

4. Conclusion

In this study, we demonstrated the effectiveness of silver-MXene $(Ag-Ti_3C_2T_x)$ hybrids as a sorbent for capturing radioiodine gas at elevated temperatures. Our material characterization, supported by XRD, TEM, SEM, EDS, TGA, Raman spectroscopy, ICP-OES, and BET analyses, confirmed the successful integration of silver nanoparticles onto $Ti_3C_2T_r$ and the formation of crystalline AgI upon iodine capture. The Ag-Ti₃C₂T_x sorbent, treated with 0.5 м AgNO₃, achieved a remarkable iodine loading of 946 mg g⁻¹, significantly exceeding the performance of established silver-based sorbents such as silver mordenite zeolite (AgZ) and silver-functionalized silica aerogel (AgAero). Notably, the saturation of Ag-loaded nanoparticles on the surface of $Ti_3C_2T_x$ at a 0.5 м concentration of AgNO₃ resulted in an optimal iodine capture efficiency. The sorbent also demonstrated consistent performance across varying AgNO₃ treatment times and drying methods, highlighting its robustness and reliability. These findings highlight the potential of $Ag-Ti_2C_2T_2$ as a highly efficient and thermally stable sorbent for radioiodine gas, offering a promising solution to the environmental challenges associated with nuclear energy production.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

2D materials, iodine gas capture, MXenes, nuclear waste, sorbent materials

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