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Supporting Information

Atomically thin TiO_2 nanosheets synthesized using liquid metal chemistry

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1. MATERIALS AND METHODS

1.1 Materials

Gallium (Ga, 99.99%) was purchased from Roto Metals, titanium (Ti, 99.99%) and hydrochloric acid (HCl, ACS reagent, 37%) were purchased from Sigma-Aldrich. All chemicals were used directly without any additional processing or purification.

1.2 Preparation of gallium-titanium (Ga-Ti) alloy

30 g of gallium were melted in a hot water bath (~80 °C) and then transferred into an Ar glove box with <10 ppm oxygen in order to reduce the oxidation of gallium. Then, 1 wt% of titanium metal was added in the form of a micrometer sized powder. In order to facilitate the alloying process, mortar and pestle were used and the mixture was manually ground to break down the titanium micro powder. This process was conducted on a hot plate (~80 °C) to keep the liquid gallium in a liquid state. After 45 min of vigorous grinding, the surface of the Ga-Ti alloy developed a shiny metallic luster and any grey metallic Ti powder had been dissolved, indicating that the alloying process was successful. The prepared alloy was checked using energy-dispersive X-ray spectroscopy EDXS before starting further steps of the synthesis. EDXS maps confirm that the micron-sized titanium powder has been successfully dissolved, leading to a final alloy concentration of ~ 99 wt% Ga and ~1 wt% of Ti (Fig. SI2). SEM-based elemental analysis was also conducted after the completion of the gas injection synthesis process. The used Ga-Ti alloy featured similar morphology and no change in the concentration and Ti distribution within the alloy was observed (Fig.SI3). This finding confirms that the alloy is stable within the experimental timeframe and that the alloy might be used for further experiments. The fact that the concentration of Ti remained unchanged was to be expected since only small quantities of TiO_2 were produced. This finding confirms that the Ti is not consumed in any side reactions.

1.3 Fabrication of 2D TiO_2

TiO_2 nanosheets were synthesized using a gas injection approach. 5 mL of deionized water (DI water) containing 0.2 mol/L of HCl were used as the aqueous phase. 15 g of the prepared Ga-Ti alloy were placed inside a narrow glass vial (20 ml) with the aqueous phase being placed above the alloy. A glass

Pasteur pipette was used as an air nozzle for the gas injection. The pipette was connected to a silicon tube (3/8" ID x 1/2" OD) and placed inside the liquid metal. A glass nozzle was used to avoid any unwanted reaction that may occur between the warm liquid metal and the tubing material. The glass Pasteur pipette was placed in the middle of the liquid metal to facilitate efficient bubbling. To ensure controlled synthesis conditions, a mass flow controller (MKS) was employed in order to control the compressed air flow rate which was set to 50 sccm. A hot plate (~80 °C) was used to keep the alloy in a liquid state throughout the experiment. After preparing Ga-Ti alloy atomically thin 2D TiO_2 nanosheets could be synthesized by exploiting Cabrerra-Mott oxidation (self-limiting oxidation of metal surfaces). This was achieved by applying the gas injection method. During the synthesis, gas bubbles (air) are injected into the alloy. This creates an atomically thin interfacial oxide layer composed of TiO_2 and possibly Ga_2O_3 on the surface of the bubble that resides within the metal. Since the density of the air bubble differs considerably from the alloy, the bubble, together with the thin oxide layer, rises toward the surface. 5 mL of DI water and 0.2 mol/L of HCl was placed as an aqueous phase on top of the liquid metal since it can assist in removing any residual liquid metal[1] while dissolving any produced 2D Ga_2O_3 nanosheets by converting gallium oxide into highly soluble gallium chloride $GaCl_3$ following the below reaction:

$$Ga_2O_3 + 6HCl \rightarrow 2GaCl_3 + 3H_2O$$

During the process, the atomically thin TiO_2 nanosheets will accumulate in the solvent. These dispersed nanosheets were collected as colloidal suspension and centrifuged for 15 minutes at 500 RCF to remove any residual alloy droplets that may be present in the aqueous phase. Subsequently, syringe-based filtration followed, which allowed washing the produced nanosheets with deionized water. This process allowed us to purify the 2D TiO_2 nanosheets and to remove the HCl and $GaCl_3$. Afterward, the syringe filter was opened and the isolated TiO_2 nanosheets were re-dispersed in a solvent for further analysis using brief bath sonication (~5 s).

2. Characterization methods

Samples were deposited on clean SiO_2/Si substrates and on holy carbon TEM grid for further analysis. An atomic force microscope-Bruker Dimension Icon (AFM) in the ScanAsyst air mode with a ScanAsyst tip was used to measure the thicknesses and lateral dimensions of 2D TiO_2 nanosheets. Transmission

electron microscopy (TEM) on a JEOL 1010 at the voltage of 100 kV to study morphology and lateral dimensions of the obtained nanosheets. High-resolution transmission electron microscopy (HRTEM) using a JEOL-2100F at the voltage of 200 kV alongside with a Gatan Tridium Imaging Filter (EELS Spectrometer) and Gatan Orius SC1000 CCD Camera have been conducted to analyze electron energy loss spectroscopy (EELS). The EELS spectrum was obtained with an energy resolution of 1 eV. Raman spectra were collected using a Horiba Scientific LabRAM HR evolution system, with an excitation wavelength of 532 nm and an 1800 mm^{-1} grating and an exposure time of 10 s to study the structural fingerprint of the nanosheets. A FEI Quanta 200 environmental scanning electron microscope ESEM (2002) equipped with an Oxford X-MaxN 20 energy dispersive X-ray spectroscopy (EDXS) Detector was utilised for the EDXS analysis of the alloyed metals. Elemental maps of the Ga-Ti alloy were conducted using Oxford instrument Aztec software. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Thermo Scientific K-Alpha instrument spectrometer with a monochromatic Cu Kα radiation source (λ = 1.5406 Å). Peak fitting was conducted using the Thermo Scientific Avantage software.

3. Supplementary data

Fig. SI1. Optical images of preparing the Ga-Ti alloy. a) 0.3 g of Ti (~ 1 wt%) was added in the form of a grey powder to 30 g of Ga. b- f) photographs of the mixture taken at different times during the grinding process. The surface continuously becomes flatter and more homogeneous. After 45 mins the alloy's surface showed a shiny metallic luster and smooth interface (The pink-brown section in f is a mirror reflection image of the background).

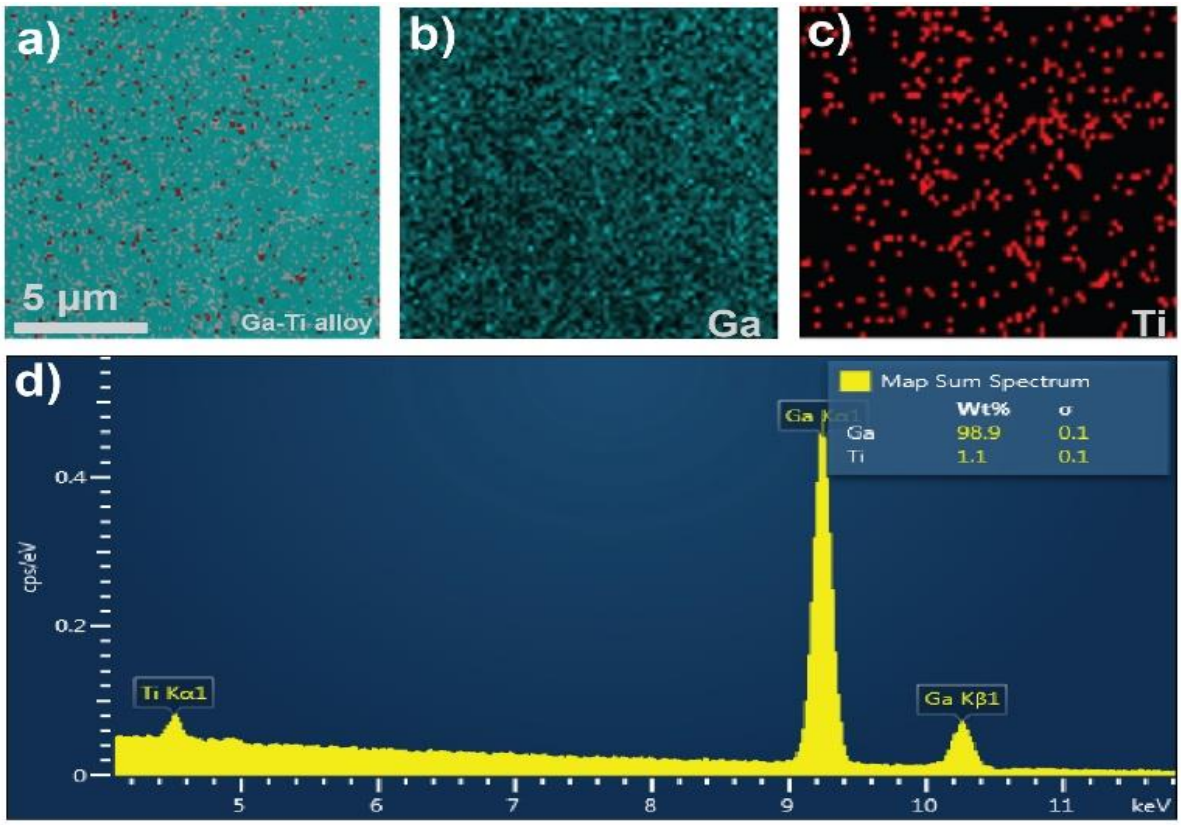

Fig. SI2. Characterization of the dispersion of fresh Ga-Ti alloy using energy-dispersive X-ray spectroscopy EDXS. a) EDXS layered image of Ga-Ti alloy. b) and c) Element maps of Ga and Ti, respectively. d) EDXS spectrum demonstrates the amalgamation of Ga and Ti has been successfully achieved with a final concentration of the Ti metal of ~ 1wt% within the gallium melt ~ 99wt%.

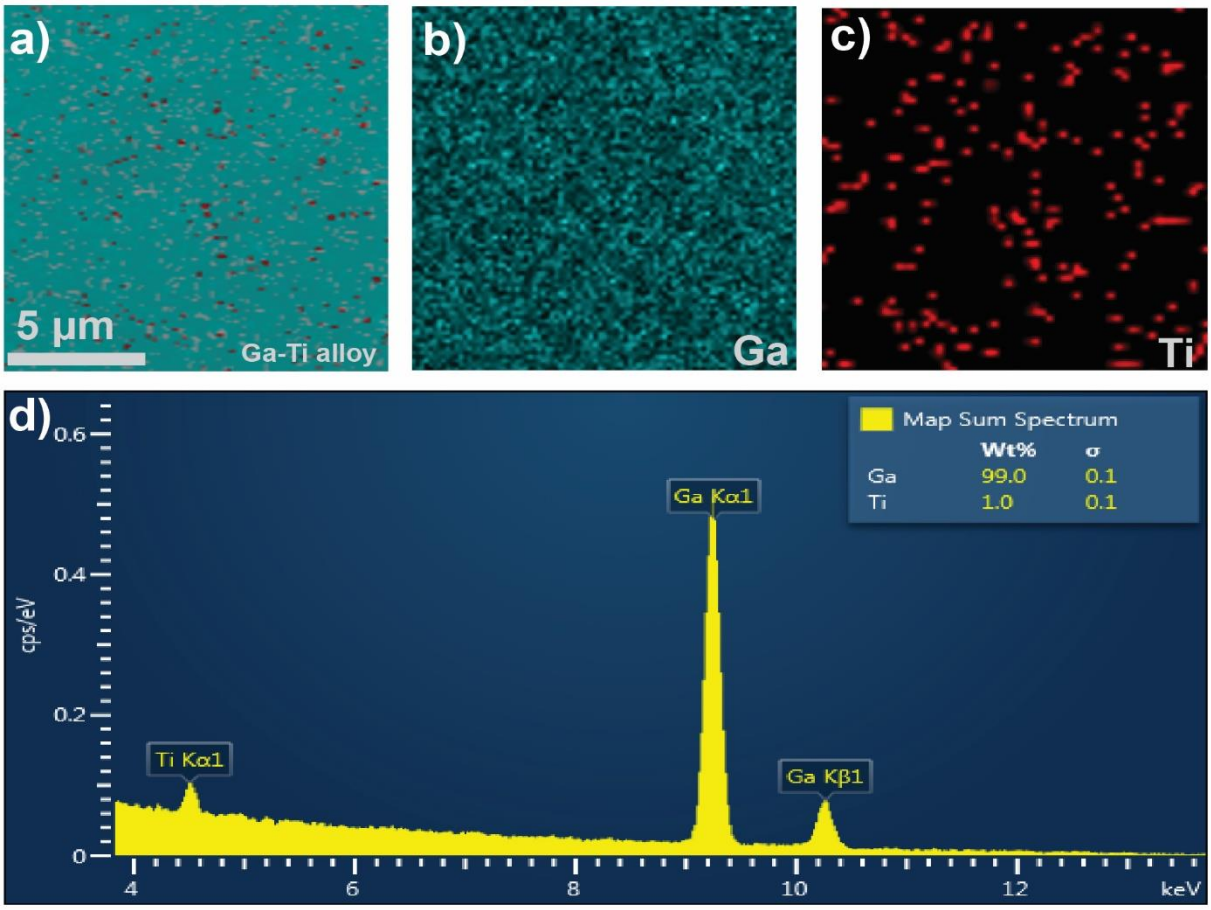

Fig. SI3. Characterization of the dispersion of Ga-Ti alloy after gas injection synthesis using EDXS. a) EDXS layered image of the used Ga-Ti alloy. b) and c) Element maps of Ga and Ti, respectively. d) EDXS spectrum demonstrates that there is no discernible change in the concentration of the alloy.

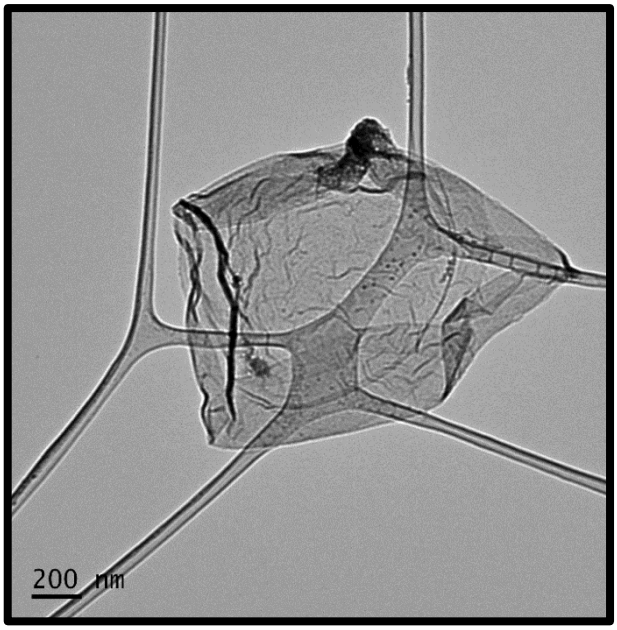

Fig. SI4. TEM characterization of 2D TiO_2 nanosheets

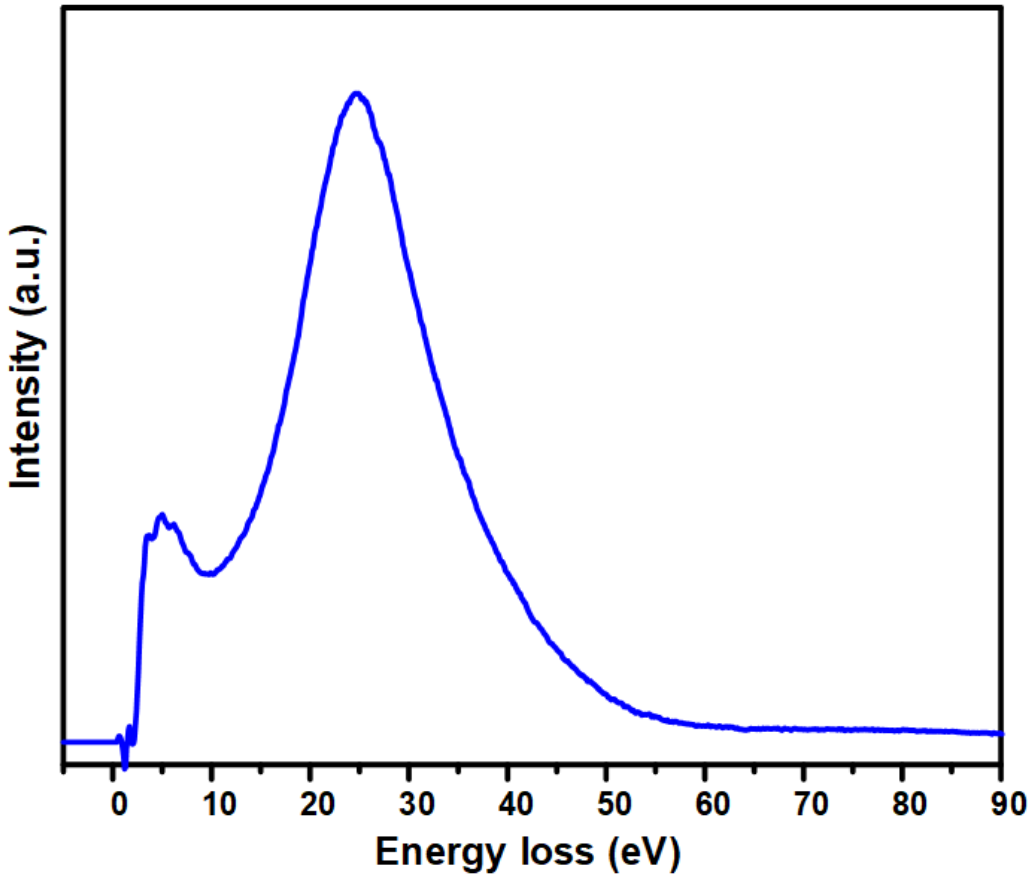

Fig. SI5. The spectrum after using a Fourier-ratio deconvolution and suitable Gaussian function to remove zero loss peak.

4. References:

1. R. Ma, Y. Zhou and J. Liu, *arXiv preprint arXiv:1706.01457*, 2017.