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Liquid metal-mediated fabrication of metalloid nanoarchitectures†

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By overcoming all conventional limitations associated with the synthesis of metalloid micro- and nanoparticles in aqueous media, we present a new one-step approach to the synthesis of highly crystalline metalloid hollow architectures. The liquid metal-mediated synthesis of Ge- and Sb-based hollow structures with satisfactory reaction kinetics at room temperature and normal pressure is presented.

Metalloid and post-transition metals are important materials in various fields, including photovoltaics, optics,[1] catalysis,[2] energy storage[3–5] and bioimaging.[6,7] To meet the demands of these applications, several top-down synthetic techniques such as electrodeposition and vapor deposition have been developed to produce metalloid nanostructures with varying morphologies and dispersities.[1,8] These techniques, however, are often costly, multistage, and require sophisticated equipment.[9,10] In our previous works,[11,12] we showed that a library of bimetallic microcapsules can be obtained in aqueous solutions by a galvanic replacement reaction using liquid gallium hydrocolloid as a template. However, this approach cannot be applied to metalloids since they undergo rapid hydrolysis in water.[13,14] This work presents a method for the preparation of hollow Ge, Sb and Bi particles in a facile and robust manner using galvanic replacement reaction on liquid metal emulsion in the organic solvent media. Overcoming the limitations of metalloid halide reduction, we propose an approach that does not require additional electrolytes, or high temperatures and pressures.

Ga-based liquid metals are easily emulsified upon sonication, making them an ideal sacrificial template for galvanic replacement. The driving force behind galvanic replacement is the difference in standard reduction potential of the metal/

metal ion pairs involved in the redox reaction. Although electrode potentials may differ from those in aqueous solutions, we relied on tabular data to guide our work (Fig. 1A). Metalloid salts can be employed in a synthesis in the form of a chloride, which is more stable than metalloid bromides and iodides and more reactive than metalloid fluorides and alkoxides.[15,16] To demonstrate the potential of the proposed method, GaIn particles galvanically replaced Ge-(hereinafter-Ge-based hollow particles) in non-aqueous media in three different solvents: dimethylsulfoxide (DMSO), dimethylformamide (DMF), and tetrahydrofuran (THF). These solvents were chosen due to their polarities (εDMSO = 47.24; εDMF = 38.25; εTHF = 7.52; εH$_2$O = 80.100),[17] aprotic natures, and abilities to form stable molecular complexes with metals in solution,[18] as well as their abilities to dissolve both reaction precursors (GeCl$_4$) and products (GaCl$_3$ and InCl$_3$). To synthesize hollow particles using Ga-based liquid metals as sacrificial templates, we followed the general procedure depicted in Fig. 1B. First, eutectic GaIn alloy (EGaIn) was dispersed into micro- and nanodroplets in a glass tube with a solvent of choice using ultrasound. Then, a salt solution was prepared in the same solvent and mixed with the EGaIn emulsion in a calculated equimolar ratio (see experimental details in the ESI†). The appearance of a black precipitate indicated the success of the reaction. As obtained hollow particles were washed with isopropyl alcohol and deionized water. It should be noted that THF was unstable in the presence of Lewis acids as catalysts of cationic polymerization;[19,20] therefore, we recommend strict control of the reaction time (no more than 15 min) when using this solvent. The morphologies of the resulting Ge-based hollow particles were examined using scanning electron microscopy coupled with energy dispersive analysis (Fig. 1C). The size and shape of the resulting hollow bimetallic particles were determined by the starting GaIn template particles. Histograms presented in Fig. S1 (ESI†) show the size distribution of the starting GaIn spheres and resulting Ge-based hollow particles obtained in DMSO, DMF, and THF. The particle size and distribution are determined by the interaction of the sample with ultrasound, which depended on factors such as ultrasound frequency and power, vessel material,

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† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d3cc02882h
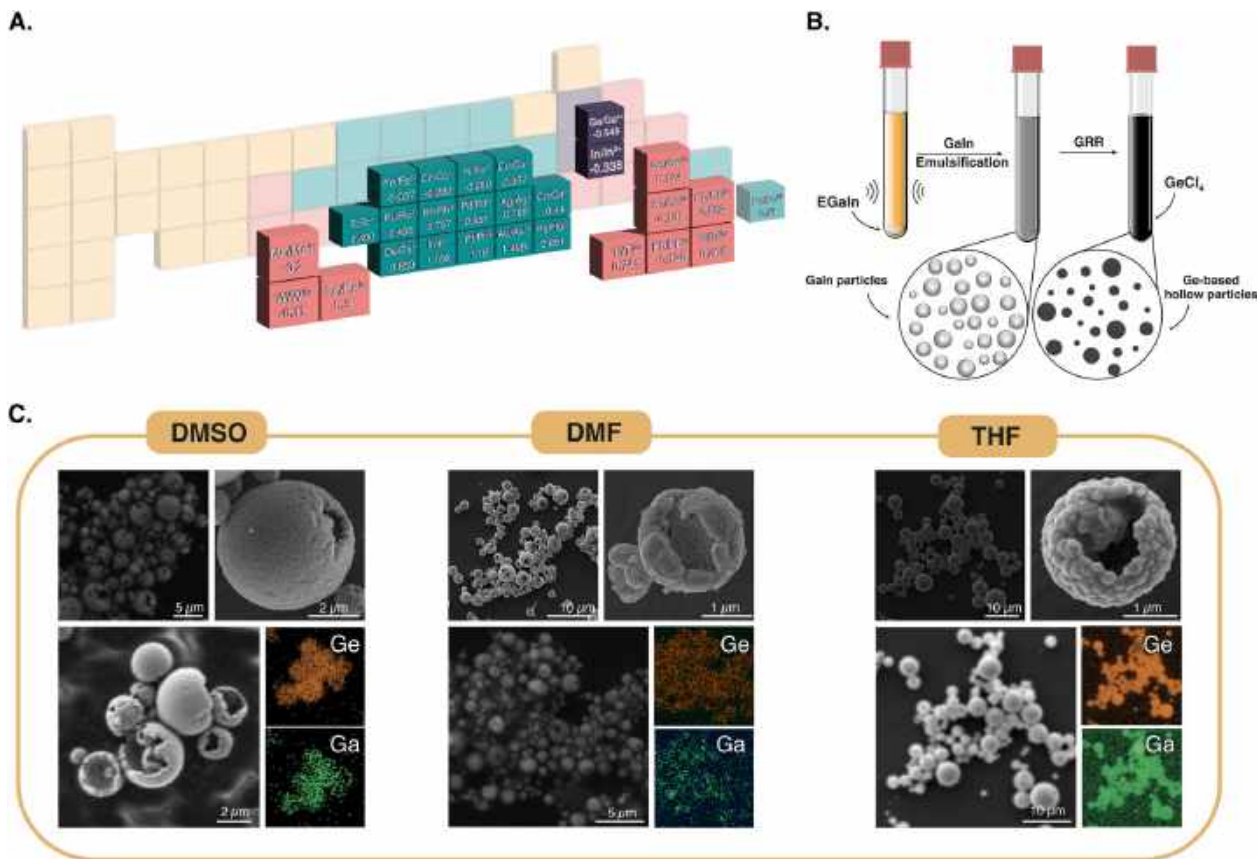
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Fig. 1 Synthesis schematic and main results of the study. (A) Periodic table: elements, suitable for GRR with GaIn particles in water (green) and only in non-aqueous solvent (red); (B) general schematic of the synthesis procedure; (C) SEM and HR-SEM (insets) images and EDS analysis of the resulting hollow Ge-based micro- and nanoparticles in DMSO, DMF, and THF.

and solvent.[21] The velocity of ultrasound in glasses and metals is higher than in plastics, leading to a more intense interaction with the liquid metal drop. As such, the average size may be reduced up to 100 nm.[22] To determine the role of liquid metal in the proposed protocol, we conducted additional experiments on galvanic replacement using aluminium powder. The synthetic procedure was carried out in the same way as in the case of GaIn in DMF media with a $GeCl_4$ concentration of 0.1 mol L^{-1}. Even with the larger potential difference between Al/Al^{3+} (-1.66 E° V) and the used precursor ($Ge/Ge^{4+} = 0.124$ E° V), the reaction did not proceed. Two additional similar experiments were conducted using pure Ga instead of GaIn under the same conditions: at room (20 °C) and elevated temperatures (35 °C, which is slightly higher than the melting point of Ga (29.8 °C)). The results confirmed that at room temperature, where pure Ga is solid, the reaction does not proceed (EDX-spectra of the resulting particles show no Ge signal). However, at the elevated temperature, where Ga is liquid, replacement occurred with a ratio of Ge : Ga = 1 : 1, though it was less effective than in the EGaIn eutectic solution (Fig. S2, ESI†). Additional discussion on this issue as well as on the mechanism details can be found in the ESI† (Fig. S3 and text above it).

The as-obtained germanium powders were analysed using X-ray diffraction (Fig. 2). In all the experiments the dominant phase (up to 100%) is Ga-doped germanium $Ge_{0.987}Ga_{0.013}$. The

material contains up to 20% crystalline indium since it is not consumed during the reaction. Gallium has a lower reduction potential than indium, resulting in a higher difference between reducing and oxidizing agent potentials (-0.53 V for Ga versus -0.34 for In); therefore, gallium is consumed first. Indium only reacts after gallium is completely consumed, as it is the weaker reducing agent in this system. The production of highly crystalline germanium in a single-step wet synthesis without subsequent annealing of the samples is a remarkable feature of the suggested method. Gallium is technologically important in conductive nanomaterials because it is a p-type dopant. Ga diffusion in Ge is consistent with the vacancy mechanism as it has a lower diffusion activation enthalpy than Ge self-diffusion.[23,24] The composition of the synthesised samples is affected by the solvent utilized (Fig. 2G and H). Most of the samples consist of $Ge_{0.987}Ga_{0.013}$ and In crystallites of various sizes (20–60 nm). Meanwhile, no universal dependence of the concentration regime on the phase composition and crystallite size of Ge-based samples was found since the results in different solvents are inconsistent. This apparent lack of correlation may be due to multiple mechanistic routes given all the complicated simultaneous processes occurring during the reaction. The Ge/Ga ratios in the synthesized particles obtained in different solvents were calculated via energy dispersive analysis (Fig. 2D–F). The degree of substitution increases with
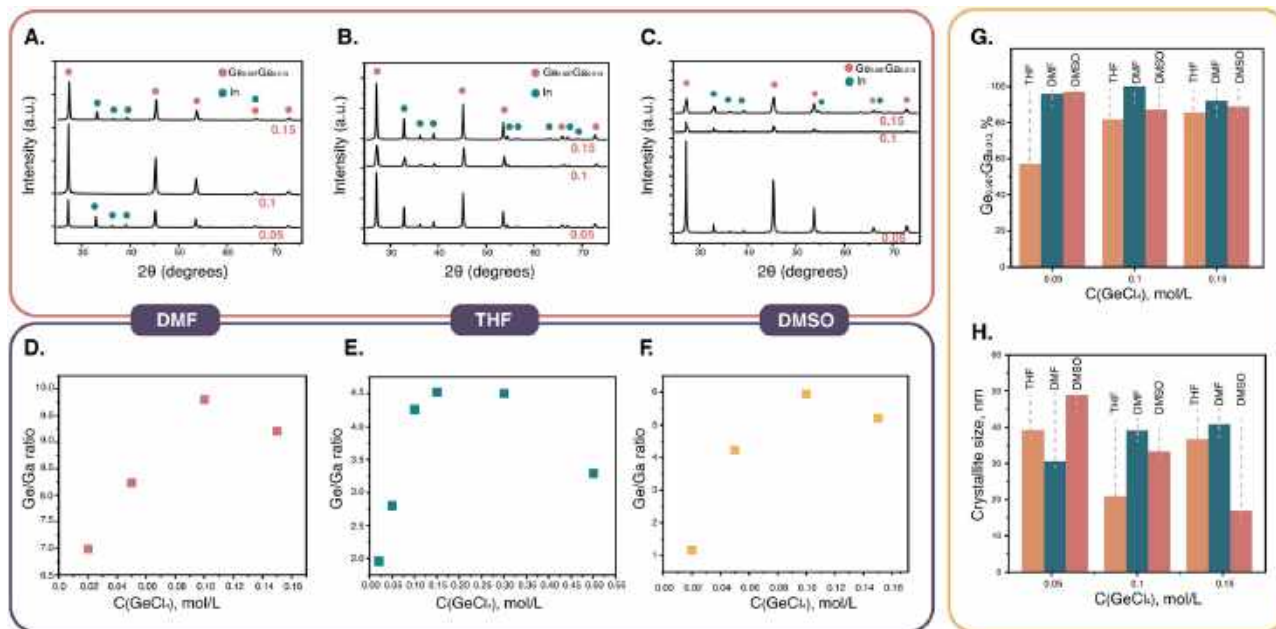
Fig. 2 Structural characteristics of Ge-based hollow particles synthesized in different media. X-ray diffraction patterns for Ge-based capsules at different $GeCl_4$ concentrations (0.05, 0.1 and 0.15 M) synthesized in (A) DMF, (B) THF and (C) DMSO; Ge/Ga ratios according to the EDS semi-quantitative analysis of particles obtained in (D) DMF, (E) THF and (F) DMSO. (G) Ga-doped germanium amount (%) in samples obtained in different media with 3 concentrations of $GeCl_4$ (0.05, 0.1 and 0.15 mol L^{-1}); (H) $Ge_{0.987}Ga_{0.013}$ crystallite sizes of the particles obtained in different media with 3 concentrations of $GeCl_4$ (0.05, 0.1 and 0.15 mol L^{-1}).

increasing concentration; however, when the precursor concentration reaches a particular level (0.1 M for DMF and DMSO and 0.3 M for THF), the degree of replacement plateaus, indicating the limit of the reaction. It is known that Ga tends to oxidise in aqueous media to form Ga_2O_3 and GaOOH on the surface of the liquid metal particle,[25] though it was also shown that this is not the case for organic media.[26] On the other hand, oxygen may have oxidized the Ga during washing and storage, and although it was not visible on the XRD spectra, EDX examination reveals oxygen in some cases (Fig. S4, ESI†). To examine this, we deliberately attempted to oxidize GaIn in two different methods, carrying out tests as usual. GaIn was ultrasonically dispersed in aqueous media, dried, and then redispersed in THF to replace it with $GeCl_4$. The second way involved dispersing GaIn in THF, letting it sit for 24 hours to allow the oxide layer to properly form, and then replacing it as usual. In both cases the reaction took place with the same velocity; a black precipitate was obtained. Scanning electron microscopy coupled with EDX analysis reveals the same Ge-based hollow spheres without any specific differences. At the same time, X-ray diffraction data showed a higher content of indium in the sample (especially for the first experiment), as well as increased amorphous zones, likely provided by unreacted alloy (Fig. S5, ESI†). The samples are also less crystalline. Therefore, it seems that the oxide film does not affect the reaction route and products dramatically. However, we still recommend performing all the experiments on freshly prepared GaIn particles. After successfully synthesising Ge-based hollow particles, we aimed to apply the same protocol to antimony and bismuth systems. DMSO was found to be the most suitable medium for the synthesis of Sb- and Bi-based hollow particles, due to several limitations associated with THF and DMF related

to complex formation and stability in the selected solvents. Highly exothermic formation of Lewis acid complexes occurred during the preparation of antimony pentachloride ($SbCl_5$) and germanium tetrachloride ($GeCl_4$) solutions in DMF[27,28] (Fig. S6, ESI†). The resulting white precipitates were dispersed using ultrasound, and then used in synthesis as a suspension. Contrary to expectations, the synthesis of Sb-based materials in DMF was unsuccessful. A possible explanation for this result is that $SbCl_5$/DMF complexes are more stable and less reactive toward GaIn alloy than with $GeCl_4$/DMF complexes. DMSO is a well-known coordinating solvent (with donor oxygen atoms) that easily forms complexes with both $SbCl_5$ and $GeCl_4$.[29,30] When $SbCl_5$ dissolves in DMSO, the solution becomes yellow, which is visible even to the naked eye. DMSO/metalloid precursor complexes are also completely soluble in the original solvent, unlike DMF/metalloid precursor complexes. The synthesis of Sb-based hollow particles in THF was also unsuccessful compared to Ge (in the presence of Sb^{5+}, THF rapidly polymerizes to form a polyester).[31] Following the same procedures as with $GeCl_4$, we faced the problem of extremely high reaction rates, leading to the formation of unstructured and broken capsules. We improved the reaction system by adding polyvinylpyrrolidone (PVP, K30, 4 wt%). PVP is known as a stabilizing agent in nanostructure synthesis and as a shape control agent.[32] Adding PVP also increases the viscosity of the solution, ensuring a gentler reaction route due to decreased reagent diffusion. Hollow particles obtained with PVP possess more integrity compared to the material obtained without PVP (Fig. S7, ESI†). Moreover, in the case of Sb-based materials, the addition of PVP also prevents the formation of antimony oxide, which may be present in the sample as an undesirable impurity. The same
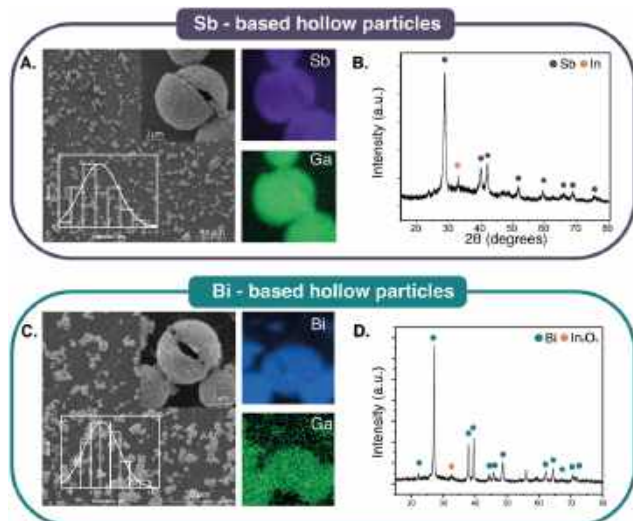
Fig. 3 Structural properties of Sb- and Bi-based hollow particles obtained *via* GRR in DMSO. (A) and (C) Scanning electron microscopy images of Sb- and Bi-based hollow particles obtained with 0.05 mol L^{-1} precursor solutions; (B) and (D) X-ray diffraction spectra of the resulting hollow sphere powders obtained using 0.1 mol L^{-1} salt solutions.

Conflicts of interest

There are no conflicts to declare.

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procedure was carried out with BiCl$_5$. Unfortunately, bismuth chloride is almost insoluble in any aprotic solvents unless small amounts of hydrochloric acid are added. When acid is added, the reaction proceeds in a matter of minutes, resulting in a black precipitate of Bi-based hollow microparticles. Both Sb- and Bi-based hollow particles are spherical with rough surface morphologies. In samples with a concentration of 0.05 mol L^{-1}, the initial gallium remains, which is completely replaced when the concentration is increased to 0.1 mol L^{-1}, as can be seen in the X-ray diffraction patterns (Fig. 3B and D). The dominant crystalline phases are Sb and Bi (91.6% and 100% for Sb- and Bi-based hollow particles, respectively) with minimal inclusions of indium residues. The particles consist of crystallites with sizes of 15.9 nm (Sb) and 31.7 nm (Bi). It should be noted that XRD analysis did not show any signs of gallium in the case of Sb-based material, while EDS mapping clearly indicates gallium in the sample. Together with a noticeable amorphous halo on the spectrum itself, it means that not all the Ga was consumed during the reaction, leaving room for improvement. Unlike the Sb-based samples, Ga is fully replaced on bismuth after the BiCl$_3$ critical concentration (0.1 mol L^{-1}) is reached, which is in accordance both with XRD and EDS analysis.

In summary, an innovative approach to the synthesis of metalloid hollow spheres is presented. Galvanic replacement reaction in aprotic solvents was used to produce high-quality Ge-, Sb-, and Bi-based hollow particles with up to 100% substitution in a one-step solution mediated manner. Liquid metals and selected solvents used to achieve these results are presented. The proposed technique is simple, scalable, and highly reproducible, making it suitable for many applications, including semiconductor material development, anode materials for energy storage, and catalytic systems.