Supporting Information

Liquid metal-mediated fabrication of metalloid nanoarchitectures

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I. Experimental details

Chemicals. Gallium-indium eutectic alloy Galn (CAS 56451-02-6; 75.5 wt. % Ga; 24.5 wt. % In; purity > 99.99 %; Sigma Aldrich; USA); germanium tetrachloride GeCl₄ (CAS 10038-98-9; purity 99.999 %; ABCR Chemie; Germany); antimony pentachloride SbCl₅ (CAS 7647-18-9 purity 99 %;Sigma Aldrich); bismuth trichloride (CAS 7787-60-2, purity 99%, Srichem, India); dimethylformamide (DMF) (CH₃)₂NCHO (CAS 68-12-2; purity > 99%, EKOS-1, Russia); dimethylsulfoxide (DMSO) (CH₃)₂SO (CAS 67-68-5; purity > 99%, EKOS-1, Russia); polyvinylpyrrolidone K 30 (PVP, CAS 9003-39-8, Sigma Aldrich, USA); tetrahydrofuran (THF) C₄H₈O (CAS 109-99-9; purity > 99%, EKOS-1, Russia); isopropyl alcohol (IPS, propanol-2) C₃H₇OH (CAS 67-63-0; purity > 99%, EKOS-1, Russia). High-purity water with a resistivity of 10–15 mΩ*cm was obtained from an Elix Essential 3 water purification system. All solutions were freshly prepared for immediate use in each experiment.

Characterization. Scanning electron microscopy (SEM) images were recorded on Tescan Vega 3 SBH at accelerating voltages of 5 and 20 kV. High-resolution images were recorded on the Scanning electron microscope Merlin Carl Zeiss. Energy dispersive analysis was conducted with the EDX detector X-ACT from Oxford Instruments, Inc., at an accelerating voltage of 20 kV. The materials composition was analysed using AZtec One image processing software. X-ray diffraction data were collected using Bruker D2 PHASER X-ray diffractometer with Cu Ka. Size distribution was determined with ImageJ image analysis software manually.

Fabrication of Galn particles. 250-300 mg of Bulk Galn eutectic alloy (75.5 wt. % Ga and 24.5 wt. % In) was placed in the 18 ml "SCHOTT" DURAN glass tube. Required amount of solvent (DMF, DMSO, THF) was added to the final concentration of liquid metal of 20.0 mg/ml. Metal drop was subjected to ultrasound in the "Elmasonic S30H" ultrasonic bath at a frequency of 37 kHz (double half-wave sound) and a power of 280 W (80 W effective US power) via the following treatment scheme: 5 min in a degassing (alternating) regime, 1 min of manual shaking, 5 min in a degassing regime again, 1 min of manual shaking, 10 min in a standard regime, and then shaking on the rotational shaker (60 rpm) till use the emulsion in a synthesis. Smooth spherical Galn particles of 1-3 μ m mean size were obtained). All subsequent synthetic procedures were performed at room temperature (20 °C) unless otherwise is indicated.

Synthesis of Ge hollow particles. Estimated GaIn molar mass taken for the synthesis calculations: M(GaIn) = 80.77 g/mol (for 75.5 wt.% Ga and 24.5 wt.% In). Molar mass and density of GeCl₄ taken for the calculations: M(GeCl₄) = 80.77 g/mol; ρ (GeCl₄) = 1.88 g/cm³¹. Concentration of GaIn in the prepared emulsion: C(GaIn)emulsion = 20.0 mg/mL = 0.248 mol/L = const (the concentration does not vary in the synthesis).

Synthetic reaction: $4Ga + 3GeCl_4 = 3Ge + 4GaCl_3$. Galn alloy is used in a deficiency (90 % of the stoichiometric amount) in relation to the amount of $GeCl_4$ substance (100 % of the stoichiometric amount). This approach allows to shift the reaction equilibrium to the product side and to achieve a higher degree of germanium substitution.

Concentration of GeCl_4 varied in six ways (**Table S1**) to investigate the effect of the reagent's concentration on the composition and structure of synthesized metal microspheres. Samples number 3 and 4 were synthesized in the similar concentrations for the reproducibility check. The volume of the final synthetic solution is constant for all the concentration regimes V (final solution) = 12.0 mL = const. All the samples were washed 4 times with alcohol and deionized water via centrifugation (6000 rpm, 5 minutes).

Synthetic algorithm:

 Required amount of GaIn is weighted in the analytical scales and put in a glass tube. Then a solvent is added to the tube to produce 20.0 mg/mL GaIn concentration.

- 2. Glass tubes with Galn are put in the US bath to produce an emulsion of liquid metal in the chosen solvent (the procedure is thoroughly described in the "Synthesis of Galn particles" section).
- 3. According to Table S1, six volumes of solvent and GeCl₄ are put in 15 mL plastic tubes. Then these tubes are shaken with a rotating shaker (60 rpm) for 5 min (in DMSO till complete dissolution of GeCl₄; in DMFA till homogeneous whitish suspension formation and partial dissolution; in THF is not required at all).
- 4. Gain emulsion is added to all the tubes with GeCl₄ solutions in the amounts represented in Table S1. The tubes are shaken with a rotational shaker for 1 h (in THF for 15 min to prevent polymerization). Reaction indicator is a change in the colour of the disperse system from grey to black.
- 5. Then solutions with synthesised germanium particles are transferred to 50 mL plastic tubes. 20 mL of solvent is added to each tube, samples are washed and centrifuged at 8000 rpm for 7 min. Next, samples are sequentially washed with 20 mL of the solvent, water, and isopropanol (3 times in total) and centrifuged.
- 6. After washing all the samples are dried for 48 hours under the vacuum at room temperature. The samples are weighted, and yields are evaluated.

Sample number	1	2	3	4	5	6
C(GeCl ₄) in the final solution [mol/L]	0.010	0.020	0.050	0.050	0.10	0.15
n(GeCl₄) used in the synthesis [mmol]	0.12	0.24	0.60	0.60	1.2	1.8
V (GeCl₄) used in the synthesis [mkl]	14	27	68	68	14	21
n(Galn) stoichiometric [mol]	0.00016	0.00032	0.00080	0.00080	0.0016	0.0024
n(Galn) in a deficiency (90 %) [mol]	0.00014	0.00029	0.00072	0.00072	0.0014	0.0022
V (GaIn emulsion) used in the synthesis [mL]	0.58	1.16	2.90	2.90	5.81	8.71
V of the final solution [mL]	11.42	10.84	9.10	9.10	6.19	3.29

Table S1. Concentration regimes of Ge-based hollow particles synthesis

Synthesis of Sb hollow particles. Concentrations of $SbCl_5$ varied in six ways (Table S2) to investigate the effect of the reagent's concentration on the composition and structure of synthesized metal microspheres. Synthetic reaction: 5Ga + $3SbCl_5 = 3Sb + 5GaCl_3$. Galn alloy is used in a deficiency (90 % of the stoichiometric amount) in relation to the amount of $SbCl_5$ substance (100 % of the stoichiometric amount).

GaIn particles were made with the same procedure described above except the concentration regimes (see Table S2). Each sample contained the same amount of GaIn Ps and $SbCl_5$ and only final volumes of the solutions varied to achieve concentration of the salt 0.01, 0.03, 0.05, 0.1 and 0.15.

Five $SbCl_5$ solutions in DMSO were prepared, followed by PVP addition to 4wt% in each sample. At the same time GaIn particles were prepared in the DMSO media the same way as in GaGe hollow spheres synthesis (20 mg/ml). After that

solution was transfused in five plastic tubes and centrifugation (6000 rpm, 5 min) to give wet precipitate. In each tube solutions with SbCl₅ and PVP were added. Within 5 minutes solutions discoloured and black precipitate was formed. All the samples were washed 4 times with alcohol and deionized water via centrifugation (6000 rpm, 5 minutes).

Sample number	1	2	3	4	5
C (SbCl ₅) in the final solution [mol L ⁻¹]	0.01	0.03	0.05	0.1	0.15
m (GaInPs) in the synthesis [mg]	5	5	5	5	5
n (GalnPs) in the synthesis [mmol]	0.0574	0.0574	0.0574	0.0574	0.0574
n(SbCl₅) used in the synthesis [mmol]	0.0412	0.0412	0.0412	0.0412	0.0412
V(SbCl₅) used in the synthesis [mkl]	5.3	5.3	5.3	5.3	5.3
m (PVP) in the solution [g]	0.189	0.1	0.04	0.0189	0.0126
V of the final solution [ml]	4. 13	1.37	0.862	0.413	0.275

Table S2. Concentration regimes of Sb-based hollow particles synthesis

Synthesis of Bi - based hollow particles. GaBi microspheres were synthesised via the same method as GaSb (all the concentration regimes are described in the Table S3). Bismuth chloride is not soluble in DMSO in acceptable amounts, therefore, to each solution hydrochloric acid was added dropwise till the solution became transparent.

Five BiCl₃ solutions in DMSO were prepared, followed by PVP addition to 4wt% in each sample. At the same time GaIn particles were prepared in the DMSO media. After that solution was transfused in five plastic tubes and centrifugation (6000 rpm, 5 min) to give wet precipitate. In each tube solutions with BiCl₃ and PVP were added. Within 15 minutes black precipitate was formed. All the samples were washed 4 times with alcohol and dilute hydrochloric acid via centrifugation (6000 rpm, 5 minutes).

Table S3. Concentration re	egimes of Bi-bas	sed hollow particles	synthesis

Sample number	1	2	3	4	5
C(BiCl ₃) in the final solution [mol L ⁻¹]	0.01	0.03	0.05	0.1	0.15
m (GaInPs) in the synthesis [mg]	5	5	5	5	5
n (GaInPs) in the synthesis [mmol]	0.0574	0.0574	0.0574	0.0574	0.0574
n(BiCl ₃)) used in the synthesis [mmol]	0.0697	0.0697	0.0697	0.0697	0.0697
m(BiCl₃) used in the synthesis [mg]	21.411	21.411	21.411	21.411	21.411

m (PVP) in the solution [g]	0.316	0.105	0.064	0.032	0.012
V of the final solution [ml]	6.9	2.3	1.394	0.697	0.464



Figure S1. (A, B, C) Size distributions of the GaIn particles and Ge-based hollow particles (D, E, F) obtained in DMSO, DMF, and THF respectively.





II. Discussion on the mechanistic details of the Galvanic replacement reaction on the Galn

microparticles

The galvanic replacement reaction on liquid GaIn microparticles is described by the following equation:

$$Ga_{+n}^{0} \stackrel{3}{}_{-M} e^{n} \stackrel{*}{\leftarrow} Ga_{+n}^{3} \stackrel{3}{}_{+n} Me^{0}$$
(1)
Which consists of two half-reactions:

oxidation of gallium:
$$Ga^0 \rightleftharpoons Ga^{3+} + 3e^- (-0.549 V vs SHE)$$
 (2)

reduction of metalloid:
$$Me^{n+} + ne^{-} \Rightarrow Me^{0} (> -0.549 V vs SHE),$$
 (3)

where Me = Ge, Sb, Bi

Electrode potentials of the metalloids used in the study are as follows:

Ga³⁺ + 3e⁻ = Ga⁰ - 0.549 V;

 $Ge^{4+} + 4e^{-} = Ge^{0} + 0.124 V;$

Bi³⁺+ 3e⁻ = Bi⁰ + 0.304 V;

 $Sb_2O_5 + 10H^+ + 10e^- = 2Sb^0 + 5H_2O + 0.592 V$ (estimated by combining two other half-reactions and their standard electrode potentials; E(Sb^{5+/}Sb⁰) is not presented in literature).

In comparison to the frequently used solid templates for GRR, technique in liquid droplets of eutectic composition offers several advantages. The key role of the liquid state is that, at a given temperature, all kinetic processes, such as the diffusion of species in the liquid, proceed significantly faster by orders of magnitude compared to the solid state. This ensures low needed temperatures and high process speeds in comparison to solid-GRR processes. However, it may involve additional complex phenomena, among others, such as the crystallization of different components in a droplet due to different GRR rates for one or another component, mutual diffusion of the components. These differences impose certain features on the course of the GRR in liquids. The possible formation mechanism of hollow spheres from eutectic microdroplets can be represented as follows. As in the solid case², we suppose that the reactions of Ga and In with metal ions proceed right at the droplet surface with the formation of atomic Me⁰ saluted in the droplet and GaCl₃ or InCl₃, soluted in the solvent. Since the solution is stirred during the synthesis process, we assume that there is an effective intermixing of the reagents in the solvent; therefore, a constant concentration of metal chloride at the surface of the droplet is maintained while the reaction product (gallium and indium chlorides) is effectively removed to the bulk solution. It should be noted that, depending on the initial total amount of MeCl_x in the solvent, its concentration may gradually decrease over time. In this approximation, the equilibrium and driving force of the reactions are determined by the activities of the components (Me⁰, In, Ga) at the droplet surface, which in turn depend on their diffusive fluxes to and from the volume of the liquid droplet. The crystallization process of the components in the droplet also depends on its local composition. Therefore, depending on the reaction kinetic rates and diffusivities of all reaction participants in the liquid microdroplet and their phase diagrams, the following cases are possible (Figure S3):

1. If the reaction rate at the surface is high enough (e.g., due to a high concentration/activity of MeCl_x), and the diffusivity of components is relatively low (Figure S3A, iii), the droplet's composition in the subsurface layer changes significantly due to the fast increasing in the concentration of soluted Me⁰ and a decrease in Ga and In. We note that because the reaction of Me ion with Ga proceeds much faster than that with In, the fraction of In rises and, according to the Ga-In phase diagram³ (Figure S1 A), the crystallization of indium in the subsurface layer of some thickness d, where the Ga/In ratio changed sufficiently, should start at room temperature along with Me⁰ crystallization. The nanocrystals growth proceeds until they grow together, forming a dense crust. When the crystallization is completed, diffusion throughout the crystallized boundary layer stops and the process of shell formation finishes. At this stage the GRR of MeCl_x with solid In crystallites at the subsurface layer may still proceed via the standard GRR solid mechanism², but with a very low rate, since the temperature is too low⁴. Note that depending on the driving force of Me⁰ and In crystallization in the subsurface layer the mean size and concentration of Me⁰ and In nuclei may differ. The higher the driving force (the deviation of composition from the Ga/In eutectic ratio), the larger the number of nuclei and the smaller their mean size, according to the nucleation theory⁵. Thus, as can be seen from the experiment, the shell structures have different surface roughness at the end of the process (Figures S4).

2. If the reaction rate is low and the diffusive fluxes in the template droplet have enough time to equalise the concentrations of components inside the droplet (Figure S3A, ii), the Ga/In ratio is preserved throughout the entire particle. In this case, the crystallization of indium occurs much later and in a much broader layer, only after reaction (2) consumes enough Ga from the entire volume of the particle to change the Ga/In ratio. At the same time, while in this regime the Ga/In ratio changes slowly, the accumulation of Me⁰ in the droplet still occurs, and once it exceeds the solubility, nucleation of Me⁰

nanocrystals proceed in a broad subsurface layer. In this regime, shell structures with thick walls are formed with a high replacement degree. It is worth noting that the transition between the two cases mentioned above at a given temperature can be accomplished by altering the activity (concentration) of the Me ions in the solution. A higher concentration leads to a faster reaction rate and depletion of the subsurface layer by Ga. Consequently, increasing the initial Me concentration in the solution above a critical value should result in a reduction in wall thickness. However, in our case the size distribution of GaIn particles is quite broad, leading to uneven reaction routes and wide thickness variations. Therefore, more research on the issue should be done (Figure S8).

In the context of the present study, it was found that the use of different solvents for the reaction had a significant effect on the final product (Figure S6). In the above simple model, we assumed that there is an immediate supply of initial Me chloride to the droplet surface and a fast carryover of the reaction products (gallium and indium chlorides) back to the bulk solution. In real systems, even when stirring is present, there is always a thin boundary diffusion layer between the surface of the liquid or solid particle and the bulk solute. The thickness of this diffusional layer depends on the properties of the solute, such as the viscosity. In turn, the diffusional influx and outflux of reagents depend not only on the thickness, but also on their diffusion coefficients in different types of solvents. Moreover, different solutes not only modify the transport properties but also the surface properties of the droplet, which affect the reaction rate significantly.

Let us additionally discuss the mechanism behind the appearance of the hollow core on the example of Ge hollow particle formation. During the GRR process, the number of Ga and In atoms leaving the droplet is larger than the number of Ge atoms incorporated into it due to the stoichiometry of the reaction (for instance, for every four Ga or In atoms that leave, only three Ge atoms arrive). Therefore, the number of atoms in the particle decreases by 25% in the case of the full replacement of Ga by Ge. The molar volumes of Ga (11.8 cm³/mol) and Ge (13.6 cm³/mol) differ by only ~15%. This means that during GRR, the total volume of the substance in the liquid particle constantly decreases and its radius should also decrease. However, the solidification of the walls starts from the surface of the particle and at some point, a strong crystalline Ge framework (walls) forms on the surface, which prevents further reduction of the particle's radius. At this stage the liquid GaIn, which remains in the core of the particle, is attracted to the formed walls due to capillary forces from the inside upon further reaction, and a void is formed in the centre (Figure S3B, i.).

In certain experiments, the formation of pinholes on the surface of the shell was observed, leading to the formation of a void in the centre. We note that in certain experiments, the formation of pinholes on the surface of the shell was also observed, which is also a common occurrence in solid-state GRR processes, described elsewhere^{2,6}. This





phenomenon is illustrated in Figure S3B, ii.

Figure S3. (A) Schematic representation of Ga, In, Me radial distribution during the synthesis at different conditions: initial droplet (i); when reaction rate is low relative to diffusion (ii); when reaction rate is high (iii); (B) Mechanism of the regular hollow particles fabrication (i) and pinhole formation (ii).



Figure S4. (A) Scanning electron microscopy images of GaGe hollow spheres in different solvent with varying concentrations of germanium chloride (IV); (B) Energy dispersive X-ray spectroscopy spectra for corresponding samples.



Figure S5. Results of galvanic replacement on Galn intentionally oxidised. (A) Galn particles were dispersed in water, dried and the redispersed in THF to conduct the reaction with 0.1 mol L^{-1} GeCl₄; (B) Galn were emulsified in THF as usual, let sit for 24 hours and galvanically replaced with 0.1 mol L^{-1} GeCl₄.

Solvent	Concentration of GeCl ₄		of Yield [%] Phase of		sition [%]	Crystallite size [nm]	
	Nº	[mol L ⁻¹]		Ge _{0.987} Ga _{0.013}	In	Ge _{0.987} Ga _{0.013}	In
DMF	1	0.010	58.7	94.7	5.3	36.8	49.7
	2	0.020	53.8	97.2	2.8	41.9	51.2
	3	0.050	77.3	96.8	3.2	31.8	43.6
	4	0.050	72.4	96.0	4.0	30.6	41.6
	5	0.10	83.8	100	0.0	39.1	-
	6	0.15	95.1	92.2	7.8	40.8	48.5
	Mear	n value	73.5	96.2	3.8	36.8	46.9
DMSO	1	0.010	-	-	-	-	-
	2	0.020	-	-	-	-	-
	3	0.050	53.8	97.5	2.5	50.4	60.1
	4	0.050	57.1	97.2	2.8	48.9	59.5

Table S4. XRD data (crystallinity, crystallite size, composition) for Ge-based samples

	5	0.10	67.6	87.2	12.8	33.3	54.9
	6	0.15	72.8	89.0	11.0	17.0	19.1
	Mear	n value	62.8	92.7	7.3	37.4	48.4
THF	1	0.010	-	-	-	-	-
	2	0.020	-	-	-	-	-
	3	0.050	-	-	-	-	-
	4	0.050	51.0	57.3	42.7	39.2	60.3
	5	0.10	-	81.9	18.1	20.9	24.0
	6	0.15	-	85.7	14.3	36.8	39.5
	Mear	n value	-	83.8	16.2	28.9	31.8



Figure S6. Assumed molecular complex of SbCl₅ with dimethylformamide.

H₃C′

 Table S5. XRD data (crystallinity, crystallite size, composition) for Sb & Bi samples.

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Capsule type	Concentration of MeCl _x ,	Phase comp	osition [%]	Crystallite size [nm]		
	[mol L ⁻¹]	Sb (Bi)	In	Sb (Bi)	In	
Sb	0.1	91.6	8.4	15.9	92.5	
Bi	0.1	100.0	0.0	31.7	-	



Figure S7. Comparison of Sb- (A) and Bi-based (B) hollow particles synthesised in DMSO: particles obtained in DMSO media without PVP (i); particles obtained in DMSO media with addition of PVP (4wt%) (ii); EDS spectra for particles obtained in the presence of PVP (iii).



Figure S8. A Box charts illustration the distribution of Diameter/Wall thickness parameter after the reaction with different concentrations of GeCl₄ in THF.

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