Self-Limiting Galvanic Growth of MnO$_2$ Monolayers on a Liquid Metal—Applied to Photocatalysis

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Liquid metals offer unprecedented chemistry. Here it is shown that they can facilitate self-limiting oxidation processes on their surfaces, which enables the growth of metal oxides that are atomically thin. This claim is exemplified by creating atomically thin hydrated MnO$_2$ using a Galvanic replacement reaction between permanganate ions and a liquid gallium–indium alloy (EGaIn). The “liquid solution”–“liquid metal” process leads to the reduction of the permanganate ions, resulting in the formation of the oxide monolayer at the interface. It is presented that under mechanical agitation liquid metal droplets are established, and simultaneously, hydrated gallium oxides and manganese oxide sheets delaminate themselves from the interfacial boundaries. The produced nanosheets encapsulate a metallic core, which is found to consist of solid indium only, with the full migration of gallium out of the droplets. This process produces core/shell structures, where the shells are made of stacked atomically thin nanosheets. The obtained core/shell structures are found to be an efficient photocatalyst for the degradation of an organic dye under simulated solar irradiation. This study presents a new research direction toward the modification and functionalization of liquid metals through spontaneous interfacial redox reactions, which has implications for many applications beyond photocatalysis.

1. Introduction

Ambient temperature liquid metals demonstrate extraordinary properties that originate from their electron-rich bulk and their unique interfaces, providing chemical reaction media that are fundamentally different from ionic and molecular liquids. Liquid metals can undergo self-limiting Cabrera–Mott oxidation in air, forming atomically thin planar metallic compounds with minimum grain boundaries. This phenomenon has been recently exploited for the synthesis of a variety of functional 2D materials using “gas”–“liquid metal” interfacial reactions. Liquid metals have also been applied as diverse components in microfluidics, actuators, wearable devices, coolants, plasmonics, electronics, and a variety of bio applications. Due to their versatility, liquid nature, and unique surface and bulk characteristics, liquid metals can also offer remarkable capabilities as catalysts, way beyond what has been shown so far, leading to future possibilities that should be explored.

Liquid metals, which mostly constitute the family of post-transition metals, are extraordinarily malleable, providing access to the liquid metallic state at low temperatures in comparison to transition metals. This provides opportunities for their utilization in synthesis and catalysis, thereby enabling the use of their liquid phase during these processes. Within a secondary liquid such as water or an organic solvent, an applied mechanical energy can break down liquid metals into smaller droplets for increasing the...
surface-to-volume ratio, leading to enhanced catalytic activity.\cite{5}
Additionally, by alloying and supersaturating the liquid metal with other metallic elements, the surface activity may be tailored, exploiting the diffusion of atomic and molecular entities across the interface, leading to superior catalytic systems based on liquid metals.\cite{2,6}

We envisage that interfacial reactions such as surface oxidation or interfacial Galvanic replacement reactions can be utilized for synthesizing catalysts in situ at the liquid–metal interface. Catalytic interfacial materials may be grown using liquid metals, allowing active sites to be created and segregated during processes that are facilitated by the dynamic flow of atomic elements within the liquid, leading to rapid surface reactions for materializing Galvanic replacement reactions and crystal growth on the surface of liquid metals.\cite{1b,7} The very low toxicity of gallium based alloys and their low vapor pressure are further favorable properties for developing catalysts.\cite{8}

EGaIn (eutectic gallium–indium binary alloy) and Galinstan (gallium–indium–tin ternary alloy) are the most commonly utilized gallium based eutectic alloys, which EGaIn melts at above 16 °C, while Galinstan melting point is even lower.\cite{9} Consequently, these alloys can be used for synthesizing nanomaterials at room temperature in aqueous solutions. The formation of micro- and nanodroplets is essential for increasing the surface area and enhancing catalytic activity. Besides size control, the behavior of liquid metals is crucially affected by changes to the surface composition and surface functionalization that can be achieved within aqueous solutions, allowing one to selectively enhance the properties of liquid metal droplets toward specific catalytic reactions or induce sensitivity to external stimuli. For example, liquid metal droplets functionalized with graphene or silver have shown high sensitivity to light, leading to shape transformation and rapid oxidation.\cite{10,9}

In addition, the surface of liquid metals with incorporated particles show extraordinary sensitivity and selectivity for heavy metal ion sensing.\cite{34} It is established that gallium based liquid metals in aqueous solutions form interfacial oxide nanosheets that originate from the reactive parent metal. Alternatively, liquid metals can be directly placed into a suitable liquid environment containing desired reactive species to produce specific interfacial oxide materials\cite{11,2,5a,10} as well as other types of nanomaterials.\cite{11} Such metal oxides supported on liquid metal may prevent free carrier recombination, with the aim to enhance photocatalysis.\cite{2,5a} These properties give access to heterogeneous systems with catalytic activities that are otherwise not achievable by the oxide in its pure form, establishing the ground to use the synergistic characteristics of liquid metals and oxide compounds.

One such oxide that is of particular interest is MnO2 which has remarkable light absorbing properties, but is generally a poor photocatalyst due to rapid internal recombination of photogenerated excitons.\cite{10} Due to the physical and chemical properties of MnO2, it has received significant attention for application in supercapacitors, batteries, and sensors\cite{13} but received less interest as a photocatalyst for the aforementioned reasons. Although the bulk forms of MnO2 does not show the desired activity for important reactions such as the photo-oxidation of water,\cite{14} this material has been used in conjunction with other metal oxides or metals as an effective photocatalyst.\cite{15} The rapid exciton recombination rate has been shown to be mitigated by the synergistic impact of added metals or metal oxides, resulting in a catalytic reaction where the manganese oxide engages in oxygen activation through the Mn^3+/Mn^4 redox cycle.\cite{16}

Recently it has been demonstrated that transforming MnO2 into its 2D form, either in its hydrated or stoichiometric crystalline phases, widens its bandgap and also reduces the recombination rate of the photogenerated excitons.\cite{17} These two effects are sought after attributes for photocatalysis. Such sheets are composed of MnO6 octahedra and interlayered cations, featuring large surface-to-volume ratios, which suppresses carrier recombination.\cite{16a,18} Up to now, different methods\cite{19} have been used for preparing 2D MnO2. However, the interfacial Galvanic replacement\cite{2,3b} synthesis of hydrated MnO2 can in principle be implemented on gallium based alloys in an aqueous permanganate solution, due to the highly oxidizing nature of MnO4− and the mildly reducing properties of metallic gallium. We also hypothesize that this process is governed by the self-limiting Cabrera–Mott oxidation of metals to generate atomically thin oxides of manganese. The electrochemical mechanism for the Galvanic replacement reaction is straightforward, where the sacrificial metal template is oxidized in the presence of cations of another metal with a higher standard reduction potential.\cite{20}

In this work, we introduce a "liquid solution”–“liquid metal” reaction process based on the reduction of permanganate ions on the surface of liquid EGaIn metal in an aqueous solution to produce single-layer hydrated manganese dioxide nanosheets. The Galvanic replacement reaction was explored on a bulk scale and the obtained sheets were thoroughly characterized. The nanosheets were then morphed onto EGaIn droplets to form shells, synthesized by ultrasonic agitation to produce heterostructures composing of liquid metal cores and metal oxide shells. We demonstrate the extraordinary migration of gallium from the metallic cores onto the surface of the particles, leaving behind solid metallic indium cores. The photocatalytic performance of the droplets, made from galvanically generated hydrated MnO2 and gallium oxide nanosheets, was investigated as a heterogeneous catalyst for the degradation of a model dye, Congo Red, under simulated solar irradiation.

2. Results and Discussion

The redox reaction between permanganate ions and EGaIn was initially investigated through the direct exposure of bulk EGaIn droplets to aqueous solutions of KMnO4 (Mn7+) at different molar concentrations as described in the Experimental Section. Changes in the appearance of the bulk metal's surface and the color of solutions were monitored continuously and presented in Figure S1 of the Supporting Information and UV–vis instrument was applied to measure the concentration of KMnO4 solution at different times correlated to the solution color as presented in Figure S2 (Supporting Information). An overview of the process is provided in Scheme 1a.

Almost immediately upon the initial contact (t = 0 s) of EGaIn and KMnO4 the shiny metallic surface of EGaIn turned gray-orange. After 24 h, the surface of the EGaIn droplet in
KMnO₄ solutions turned black and was covered with a thick material. The thickness of this black coating increased with time and the intense pink coloration of the KMnO₄ solutions reduced over the course of a week, indicating that the KMnO₄ concentration is the limiting reagent in this reaction (Figure S1, Supporting Information). Subsequently, the outer black layers developed on the surface of EGaIn droplets were collected for detailed characterization. Mechanical detachment of the hydrated oxides is expected to be possible due to the liquid nature of the metal (Scheme 1b), resulting in minimal adhesion between the oxide layers and the metal due to the absence of a solid lattice, which precludes the occurrence of strong van der Waals forces between the grown metal oxides and EGaIn.

The process was repeated with gallium and no indium at room temperature. Gallium at room temperature is solid as its melting point is ≈30 °C. Although very quickly the surface of gallium tuned gray-orange, the layer was not thickened in time and the black coverage was not seen even after several days (Figure S3, Supporting Information), signifying that the process only continues on liquid and not solid metal. A control experiment was carried out with molten gallium only at 32 °C (Figure S4, Supporting Information) to show that the molten nature of pure gallium metal also generates the hydrated MnO₂ to further confirm that self-exfoliation due to the lack of van der Waals force adhesion onto the bulk liquid is essential for the continuation of the process.

The described observations and creation of hydrated MnO₂ on the surface of EGaIn indicated a redox reaction between the liquid metal and permanganate ions. While both gallium and indium as the components of the EGaIn liquid metal can be oxidized in contact with KMnO₄ solution when considering the high standard reduction potential (E⁰[MnO₄⁻/MnO₂] = 1.697 V vs SHE) the greatest thermodynamic driving force arises for the replacement of gallium with a lower standard reduction potential (E⁰[Ga³⁺/Ga⁰] = −0.529 V vs SHE) when compared with indium (E⁰[In³⁺/In⁰] = −0.34 V vs SHE), which leads to the greatest reduction in free energy (ΔG = −2.226 eV).[21] As such, the oxidation of gallium is expected to be the dominant process and not indium. The Galvanic replacement occurs at the interface of the liquid metal and solution, where the surface of EGaIn serves as the sacrificial substrate for the formation of hydrated MnO₂ sheets. The redox reaction between metallic gallium and MnO₄⁻ can be described as follows[21]

\[ \text{MnO}_4^{2-} + 2\text{H}_2\text{O} + 3e^- \rightarrow \text{hydrated MnO}_2(s) + 4\text{OH}^-_{(aq)} \]  \hspace{1cm} (1)

\[ \text{Ga}^{(l)} \rightarrow \text{Ga}^{3+}_{(aq)} + 3e^- \]  \hspace{1cm} (2)

\[ \text{MnO}_4^{2-} + 2\text{H}_2\text{O} + \text{Ga}^{3+}_{(l)} \rightarrow \text{hydrated MnO}_2(s) + \text{Ga}^{3+}_{(aq)} + 4\text{OH}^-_{(aq)} \]  \hspace{1cm} (3)

The possible formation of thin Ga₂O₃, as the self-limiting oxide, on the surface of EGaIn is prohibited due to the
production of soluble [Ga(OH)$_4$]$^-$(gallate) through the reaction of this thin oxide with the released OH$^-$ as below$^{[22]}$

$$\text{Ga}_3\text{OH} + 3\text{OH}_\text{aq}^{-} \rightarrow \text{Ga(OH)}_3(\text{s})$$  \hspace{1cm} (4)

$$\text{Ga(OH)}_3(\text{s}) + \text{OH}_\text{aq}^{-} \rightarrow [\text{Ga(OH)}_4]^-$$ \hspace{1cm} (5)

It is important to use fresh EGaIn for the experiments. If the EGaIn is left in the aqueous solution for a relatively long time, the galvanic reaction does not take place as discussed in the Supporting Information. The reaction only progresses when the surface of EGaIn is clear or just slightly oxidized that can be removed by the produced hydroxide via Equation (1). The prohibitive effect of Ga$_2$O$_3$ on the formation of hydrated MnO$_2$ on the surface of liquid metals was explored by introducing KMnO$_4$ reactant after a stable EGaIn colloidal solution was established, as shown in Figure S5 (Supporting Information).

The reduction of permanganate into MnO$_2$ is expected to occur across the liquid metal surface, which acts as a smooth, stress, and dislocation free substrate due to its liquid state. The gallium is expected to oxidize to form Ga$_2$O$_3$ in a process that resembles Cabrera–Mott metal oxidation, inducing the formation of ultrathin layers. Due to the lack of van der Waals forces between the formed ultrathin layer and surface of the liquid metal, the surface oxides constantly delaminate, leading to the repeated growth of ultrathin layers and the gradual consumption of gallium (the coloration of the solution changes over the course of a week; Figure S1, Supporting Information). As the gallium is consumed, the stoichiometry of the alloy will change, resulting in an increased melting point of the liquid metal. If the metal solidifies, the nature of the oxidation process is expected to be fundamentally altered. This prospect will be discussed in further detail later on. The isolated MnO$_2$ from the surface of liquid metal is expected to be hydrated since the reaction occurs in an aqueous environment, with similar results being observed for many other liquid phase synthesis processes of metal oxides.$^{[23]}$

2.1. The Morphology of Hydrated MnO$_2$ Sheets Grown on Bulk EGaIn

As can be seen from the transmission electron microscopy (TEM) images (Figure 1), the as-synthesized delaminated hydrated MnO$_2$ nanosheets are highly crumbled and folded, which is indicative of nanosheets that are atomically thick and likely to be monolayered. The high-resolution TEM (HRTEM) image (Figure 1b) taken from the edge of the nanosheets exhibits the polycrystalline nature of the hydrated MnO$_2$ monolayers, which are folded everywhere. These sheets show interplanar spacings of 0.21 and 0.25 nm, corresponding to the (301) and (400) planes of hydrated monolayered-type MnO$_2$, respectively.$^{[24]}$ The larger interplanar spacings of $\approx$0.69 nm for the folded nanosheets are seen everywhere, corresponding to the distance between two planes as the characteristic spacing of stacked MnO$_2$ monolayers.$^{[24b]}$ Figure 1d reveals the energy-dispersive spectroscopy (EDS) mapping of the hydrated MnO$_2$ products on the surface of the EGaIn bulk droplet. As can be seen, the elemental mapping of the delaminated agglomeration of sheets is dominated by Mn and O. Very small traces of residual metallic In and Ga are also observed due to the sampling process. Monolayer thickness of the flakes ($\approx$1 nm) is further confirmed by the atomic force microscopy (AFM) assessments as shown in Figure 1c.

The HRTEM and AFM analysis prove that hydrated MnO$_2$ is formed by the Galvanic replacement reaction. The interfacial reaction appears to be self-limiting, leading to the growth of a single monolayer of hydrated MnO$_2$ at a time, with subsequent layers being formed and wrinkled once spontaneous delamination occurred.

Figure S6 of the Supporting Information shows the scanning electron microscopy (SEM) and TEM images of the hydrated MnO$_2$ films that formed on the EGaIn surface in a $5 \times 10^{-3}$ m solution of KMnO$_4$ after 72 h, indicating a typical morphology of strongly folded and crumbled nanosheets that formed through a combined interfacial growth and self-delamination process.$^{[24b,25]}$ These morphologies are also in agreement with TEM and AFM images. Altogether, the MnO$_2$ coatings are made of nanosheets with a flaky appearance where ultrathin

![Figure 1.](attachment:image.png)
interconnected nanosheets produce a porous structure with a large surface area. The broad van der Waals affinity between nanosheets stabilizes the 3D structure. Furthermore, Raman spectroscopy of the detached layers also shows the presence of hydrated MnO₂ nanosheets due to the presence of this material’s characteristic peaks as discussed in Figure S7 of the Supporting Information. A bandgap of 2.1 eV was acquired for these hydrated MnO₂ nanosheets through the UV–vis and Tauc plot measurements as graphed in Figure S8 (Supporting Information).

2.2. Sonication Growth Process

The reactivity of permanganate ions toward the EGaIn droplets was found to increase under sonication due to the fact that liquid metals break apart into distinct smaller particles, resulting in a higher surface area by the applied high-intensity mechanical agitation. The effect of sonication time on gallium alloys has been previously characterized and we refer the readers to the relevant report. The median diameter of EGaIn droplets is in the order of 3.5 µm after 20 min of sonication (an example is shown in Figure 2a). The surfaces of the droplets were smooth and the alloy predominantly adopted spherical morphologies.

It was noticed that the color of the permanganate solution turned visibly lighter within just a few minutes (rather than several days in the bulk case) after the sonication process, while the EGaIn droplets simultaneously became darker. This indicates the fast consumption of KMnO₄ and the formation of MnO₂ sheets on the surface of the EGaIn droplets that liquid metals break apart into distinct smaller particles, resulting in a higher surface area by the applied high-intensity mechanical agitation. The effect of sonication time on gallium alloys has been previously characterized and we refer the readers to the relevant report. The median diameter of EGaIn droplets is in the order of 3.5 µm after 20 min of sonication (an example is shown in Figure 2a). The surfaces of the droplets were smooth and the alloy predominantly adopted spherical morphologies.

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Using SEM imaging, a remarkable change was observed when EGaIn was sonicated in KMnO₄ solutions (1 to 10 × 10⁻³ M). The EGaIn particles’ surface became rough and was covered entirely with nanoflakes. Very thin and crumbled large flakes, similar to those that grew on bulk EGaIn in the absence of sonication, were not observed. Obviously, the sonication process broke down the sheets into smaller flakes and restacking of the nanoflakes also occurred, rendering them more rigid, while minimizing wrinkling.

The MnO₂ nanosheet coverage became thicker with increased KMnO₄ concentration, with larger size flakes beginning to dominate the surface (Figure 2b–d). Nanosheets of hydrated MnO₂ can be seen on the surface EGaIn nanodroplets indicating the quick and effective Galvanic reaction between gallium and permanganate ions during sonication. For high KMnO₄ concentrations, the comparatively thicker outer layer cracked and separated itself from the metallic core on many of the droplets as shown in Figure 2e. Additionally, according to BET measurements, the surface area significantly reduced from 35.5 to 25.6 m² g⁻¹ by increasing the KMnO₄ concentration from 2.5 to 10 × 10⁻³ M, indicating the transformation of MnO₂ into less porous morphologies (refer to Figure S9 of the Supporting Information for details).

The EDS analysis and elemental mapping images of as-sonicated EGaIn are shown in Figure 3a, with In and Ga both present at the core. Interestingly, the EGaIn/Mn-2.5 droplet in Figure 3b reveals the presence of Ga, Mn, and O in the nanoflakes surrounding the indium core. Presence of Ga is in contrast to the stagnant nonsonication case where the large flakes only contained Mn and O elements (Figure 1d). This may be rationalized by the overall slower reaction when sonication is not applied, allowing for the oxidized gallium to enter the solution as solvated ions, while the faster reaction rate in the sonicated experiment may lead to the precipitation of gallium oxide. Furthermore, sonication of liquid gallium containing alloys in aqueous solution is known to produce gallium oxides, which may be occurring as a side reaction.

Interestingly, the nanoflakes were found to be primarily composed of Ga and Mn elements after sonication, while the core of the droplet mainly contained In and no Ga. This confirms that gallium is driven out of the core and preferentially oxidized due to the larger thermodynamic driving force. The observation that the reaction ceased when the gallium was consumed is however counterintuitive, due to the substantial driving force for the oxidation of indium by permanganate ions in aqueous solutions (ΔG = −2.037 eV). A likely mechanism behind this phenomenon may be derived from the different melting points of Ga and In. As the gallium is consumed by the reaction, the composition of the alloy changes, leading to an increasing
melting point. Due to the solid nature of indium, the reaction cannot proceed beyond the formation of an initial surface layer, since sonication may not remove the grown surface oxides due to their firm attachment to the solid metallic surface through van der Waals interactions. The EDS of detached shell fragments provides further evidence, since the produced flakes are only made of elemental gallium, manganese, and oxygen, with no significant amounts of indium being detected (Figure 3c). Considering that EGaIn contains 75.5% Ga, the depletion of the entire gallium content during the sonication process is a remarkable observation. A zoomed in EDS image of this area and a semiquantitative elemental EDS analysis were added to the Supporting Information as Figure S10 and Table S1, respectively, to demonstrate the different chemical composition of the products. The presence of solid indium is also evident in X-ray diffraction (XRD) patterns (presented later in the text), supporting this hypothesis.

Figure 4 presents the bright field image, selected area electron diffraction (SAED) pattern and high-resolution TEM images of the detached shells isolated from an EGaIn/Mn-2.5 droplet. It appears that the thick layers of hydrated MnO$_2$ nanosheets are distributed on the surface of porous gallium oxyhydroxide (GaOOH) flakes (Figure 4b). We have previously analyzed similar gallium oxyhydroxide flakes and have reported their properties. The overall SAED pattern from the surface of EGaIn/Mn-2.5 (Figure 4a) rendered concentric diffraction rings corresponding to planes of GaOOH and hydrated monolayer-type MnO$_2$ phases, indicating the coexistence of these phases on the surface of liquid metal nanodroplets. HRTEM imaging reveals three frequently observed interplanar spacings within one area, where interplanar spacings of 0.25 and 0.29 nm correspond to the (400) and (310) planes of hydrated monolayer MnO$_2$, respectively, and the interplanar spacing of 0.41 nm is assigned to the (110) plane of GaOOH (Figure 4d–f). The existence of both GaOOH and hydrated MnO$_2$ within this area was further confirmed through the fast Fourier transform (FFT) graph as marked in Figure 4g. The majority of the surface consists of overlayers of GOOH and hydrated MnO$_2$, as shown by the FFT analysis. To confirm the hydration of both gallium and manganese oxide sheets, thermogravimetric analysis (TGA) was carried out which will be discussed later.

Powder XRD was utilized to further confirm the HRTEM observations and gain insight into the crystalline properties of the metallic remnants which could not be analyzed using TEM based imaging due to their thickness. Figure 5a shows the XRD pattern for the hydrated manganese oxide layer produced.
on the surface of bulk EGaIn (bottom Figure 5a), followed by the XRD patterns of as-sonicated EGaIn and EGaIn sonicated in KMnO₄ solution. Diffraction peaks of the flakes exfoliated from bulk EGaIn match with hydrated manganese oxide and are indexed to tetragonal α-MnO₂·H₂O (JCPDS 44-0140). The indexation was conducted with care, since α-MnO₂ and α-MnO₂ feature similar patterns which has led to too much confusion in the past. [19g,24a,29] The XRD patterns of sonicated EGaIn in the absence of any reactant indicate that GaOOH is the main phase and have been indexed to the orthorhombic structure.[5b,30] For the EGaIn/MnO₂ samples two major sets of changes are seen with reference to only EGaIn: i) the main peaks related to hydrated MnO₂ around 36° and 43° are seen in EGaIn/Mn-5, while they cannot be found in sonicated EGaIn. More importantly, there is no shift in the peak locations with reference to hydrated MnO₂, suggesting that the sheets retained their initial crystal phase even after sonication. ii) A relatively intense peak associated with metallic indium, centered at 2θ = ~ 33° arises upon sonication, confirming the presence of solid In. This effect is observed for both, EGaIn sonicated in water and aqueous KMnO₄.[31] This observation is in agreement with EDS results (Figure 3), suggesting that the core of liquid metal droplets has transformed into pure indium due to the preferential oxidation of gallium, supporting the hypothesis that a liquid surface is required for the continuous oxidation of the metal template leading to sheet formation.

X-ray photoelectron spectroscopy (XPS) measurements were carried out to attain the chemical bonding states of the synthesized materials. Figure 5b,c shows the outcomes for the samples obtained by sonicated EGaIn and EGaIn/Mn-2.5. The main characteristic peaks of the Ga 3d regions for the sonicated EGaIn and EGaIn/Mn-2.5 are located at slightly different binding energies of ≈19.9 and ≈19.7 eV, respectively. This is an indication that EGaIn/Mn-2.5 is less oxidized as more OH⁻ is produced (Equation (1)) during the galvanic reaction, dissolving a slightly larger amount of gallium oxide during the replacement reaction.[5b] For the In 3d region (Figure 5b,c), the peaks centered at 443.8 (In 3d 5/2) and 451.5 eV (In 3d 3/2) with a separation of spin-orbit components \( \Delta_{\text{metal}} \approx 7.7 \) eV, are attributed to metallic indium in both samples,[32] which signifies that indium oxidation never occurred. The characteristic Mn 2p peak (Figure 5b) for MnO₂ as expected is not observed for sonicated EGaIn (0 × 10⁻⁵ M KMnO₄), while for the EGaIn/Mn-2.5 sample (Figure 5c) shows two peaks centered at 641.8 and 653.5 eV in
the Mn 2p spectral region which are generally associated with the spin orbit doublet of Mn 2p_{1/2} and Mn 2p_{3/2}, respectively. The observed binding energies are in good agreement with the expected Mn 2p region present in MnO_2,[33] demonstrating the stoichiometry of the formed manganese oxide layers. The discussion on the oxygen peak regions is presented in Figure S11 of the Supporting Information.

TGA tests of the sonicated droplets confirmed the hydration, while TGA could not be directly conducted on the material grown on bulk EGaIn due to the small mass produced. TGA analysis was used for assessing the structural stability and the change in water content of the materials. The TGA curves of EGaIn droplets exposed to different KMnO_4 solutions of 0, 2.5, and 10 \times 10^{-3} M concentrations were analyzed in the heating range of 50 to 450 °C (Figure S12, Supporting Information). From 50 to 120 °C similar weight losses of 1.1% were recorded for EGaIn/Mn-2.5 and EGaIn/Mn-10, which is attributed to the removal of surface water and physically adsorbed hydrates.[34] The figure is approximately one-quarter of the magnitude for EGaIn without the hydrated MnO_2 nanosheets, which is related to the dehydration of GaOOH.[35] For EGaIn/Mn-2.5 and EGaIn/Mn-10 samples, the large weight loss between 120 and 380 °C can be associated with the removal of occluded water in the structural framework of hydrated MnO_2 nanosheets.[26a] Heating of the droplet covered with shells to 450 °C resulted in further weight loss, possibly indicating the loss of oxygen and a phase transition and crystallization into substoichiometric Mn_2O_3.[26b,35]

Fourier transform infrared spectroscopy (FTIR) was used for further characterization of EGaIn/MnO_2 samples to define the hydration properties. The main absorption bands were detected around 1368, 1635, 2940, and 3433 cm\(^{-1}\) as shown in Figure 5d. The band at 1368 cm\(^{-1}\) is assigned to the –OH bending vibrations attached to Mn atoms.[16] The presence of troves at 1368 and 1635 cm\(^{-1}\) provides evidence that the materials are layered hydrated MnO_2.[37] The weak band around 1635 cm\(^{-1}\) is attributed to bending vibrations of O–H groups of adsorbed water, while the broad band at 3433 cm\(^{-1}\) presents the O–H stretching of interlayer water molecules.[24b] The broad band between 2750 and 3750 cm\(^{-1}\) became more intense upon increasing the concentration of KMnO_4 during the sonication process, as can be seen in Figure 5d. The O–H stretching band of GaOOH is known around 3200 cm\(^{-1}\), while H–O–H stretching band appears at 3400 cm\(^{-1}.[10]\)

Raman spectroscopy was also conducted on the samples. Two different series of peaks corresponding to GaOOH and hydrated MnO_2 were found in the Raman spectra as shown in Figure 5e. Peaks located at ~415, ~470, and ~710 cm\(^{-1}\) are associated with GaOOH[38] and peaks at 567 and 632 cm\(^{-1}\) are known as the characteristic signature of hydrated MnO_2.[39] At 1 and 5 \times 10^{-3} M, MnO_2 nanosheets grew around the metallic particles and a peak centered at ~632 cm\(^{-1}\), which is associated with hydrated sheets of MnO and is assigned to Mn–O vibrations perpendicular to the orientation of MnO octahedral double chains of hydrated MnO_2.[37,40] By increasing the molar ratio of KMnO_4, the peaks at 567 and 632 cm\(^{-1}\) grew gradually in intensity and evolved as two distinct peaks when the concentration of KMnO_4 increased to 10 \times 10^{-3} M. The peaks attributed to GaOOH, however, were gradually masked by the intense hydrated MnO_2 peaks when the shell became thicker.

In order to establish the electronic band structure of the core/shell structures Kelvin probe force microscopy (KPFM), UV–vis), and XPS valence band measurements were conducted. For KPFM measurements, the contact potential difference (CPD) between tip and sample was imaged as shown in Figure 6c for the example of a core/shell EGaIn/Mn-2.5 droplet on a silicon substrate. A higher potential was detected all over the silicon surface,[41] while significant contrasts appeared across the scan area on the top of the rough EGaIn/Mn-2.5 droplet. A CPD variation from ~135 to 380 mV was obtained for a 175 nm step height, as demonstrated in Figure 6c. The CPD is defined as \(\Phi_{\text{sample}} - \Phi_{\text{tip}}\), where \(\Phi_{\text{sample}}\) and \(\Phi_{\text{tip}}\) are the work function of sample and tip, respectively.[42] Since \(\Phi_{\text{tip}}\) is ~4.7 eV for the silicon tip,[43] the work function of EGaIn/Mn-2.5 can be estimated to be ~4.45 eV, which is similar to values reported for hydrated layered MnO_2.[13a,44] The Fermi energy levels of droplets from other samples were also very close to this number.

The UV–vis spectroscopy tests were carried out to study the optical bandgaps of the materials. These samples were suspended in ethanol and drop casted on quartz slides. The resulting UV–vis spectra, shown in Figure S13 of the Supporting Information, were used for calculating the Tauc plots to measure the optical bandgaps of individual samples. The bandgap (\(E_g\)) values are estimated from Figure 6a and are presented in Table 1.

EGaIn/Mn-10 showed a bandgap of 2.33 eV which is dominated by the hydrated nanosheets of MnO_2, while sonicated EGaIn presented the largest bandgap of 3.80 eV, dominated by the sole presence of GaOOH. The value of 2.33 eV for EGaIn/Mn-10 is slightly larger than the bandgap for monolayer MnO_2 nanosheets (2.23 eV)[17] and is in agreement with a previous report, indicating that MnO_2 slightly widens its bandgap when it has a hydrated layer structure.[45] Conversely, this bandgap can also be attributed to the establishment of hydrated MnO_2 nanosheets on EGaIn droplets due to the presence of the wider bandgap material GaOOH. In this case, the value is an average for the bandgap of bulk MnO_2, known to be ~1.3 eV[46] and sonicated EGaIn which was measured as 3.80 eV.

For assessing the location of the valence band edges, XPS valence band assessment was conducted. The measurements are shown in Figure 6b and the value for different samples are presented in Table 1. As can be seen, by increasing the shell thickness this value decreases until an anomaly for EGaIn/Mn-10 where the shell delaminates itself from the core.

Energy band diagrams are established for sonicated EGaIn, EGaIn/Mn-1, and EGaIn/Mn-2.5, as shown in Figure 6d. As the shell becomes thicker, the conduction and valence band edges move closer to each other. This in principle should enhance the photocatalytic properties, which will be discussed in the next section.

2.3. Photocatalysis

The photocatalytic performances of the synthesized nanoparticles were tested by decomposition of an organic dye. Congo Red (CR) dye with a complex chemical structure was selected...
as a popular and commonly used material in previous photocatalytic activity investigations of MnO₂ to enable a direct comparison of performance. The characteristic absorbance spectrum of CR was monitored during the gradual decomposition and degradation under simulated solar light irradiation. Fixed values of 0.09 mg mL⁻¹ and 7.8 × 10⁻⁶ m, respectively, for the catalysts and dye were used for all experiments. Solutions were stirred (400 rpm) and illuminated under simulated 1 sun AM 1.5 light (Abet Technologies’ model 11 002 SunLite Solar Simulators, ASTM Class A with 100 W Xe arc lamp). The photocatalytic degradation of CR was carried out for 2 h while the absorbance of the CR solution was measured every 20 min to calculate the photodegradation rates. Figure 7a summarizes the relative absorbance change (Aₜ/A₀) during the photocatalytic reaction where A₀ and Aₜ are the initial absorption of CR without irradiation and the absorption of CR at a particular time (t), respectively. CR degradation occurs as hydroxyl radicals (•OH) generated for all samples affect the photocatalytic degradation of CR. Hydroxyl radicals are mostly produced through H₂O oxidation by photogenerated holes (h⁺) and O₂ reduction by photogenerated electrons (e⁻).[48]

The optimum photocatalysis was obtained for samples synthesized with the KMnO₄ concentrations of 2.5 and 5 × 10⁻³ m as can be seen in Figure 7a. For more information, the absorption spectra of the reaction solution containing EGaIn/Mn-2.5 droplets and CR dye before and during photocatalysis experiments are graphed in Figure 7b. The intense CR absorption peak centered around 500 nm reduced significantly during the first 20 min of exposure (70% degradation) and almost disappeared after 120 min (97% degradation). In comparison, EGaIn sonicated in the solution of KMnO₄ at 1 × 10⁻³ m showed a degradation rate of 35% after 20 min and nearly 85% after 2 h. This was similar to the sonicated EGaIn sample, indicating that there is the insufficient formation of MnO₂ on the surface of EGaIn to drive the reaction as also evidenced by the SEM image.

**Table 1.** Bandgaps and difference between Fermi energy levels and valence band edges of the values of the samples.

| Sample          | Bandgap (eV) | Fermi level–Valence band edge (eV) |
|-----------------|--------------|------------------------------------|
| Sonicated EGaIn | 3.80         | 2.75                               |
| EGaIn/Mn-1      | 3.11         | 2.45                               |
| EGaIn/Mn-2.5    | 2.62         | 2.05                               |
| EGaIn/Mn-5      | 2.79         | 2.02                               |
| EGaIn/Mn-10     | 2.33         | 2.12                               |
in Figure 2b. The repeatability of the EGaIn/Mn-2.5 samples was tested, and the outcomes are presented in Figure S14 of the Supporting Information. Samples showed strong stability and recyclability after multiple usages.

For EGaIn/Mn-10 the photocatalytic activity was significantly reduced and the material showed a photocatalytic activity similar to that of sonicated EGaIn. As shown in the SEM images (Figure 2e), by increasing the concentration of KMnO₄ in solution the morphology of droplets changed dramatically. The further increase of KMnO₄ produced shells that detached themselves from the metallic core, reducing the heterojunction effect. Additionally, BET shows that the surface area was also reduced for this sample (Figure S9, Supporting Information).

Several phenomena may contribute to the enhancement of the photocatalytic activity for the synthesized core/shell droplets in comparison to EGaIn only droplets: i) the high surface porosity of 3D hydrated monolayered MnO₂ nanosheets placed on the large area GaOOH nanoflakes, ii) the altered energy band structure of modified core/shell droplets (the band structure of as-sonicated EGaIn, EGaIn/Mn-1, and EGaIn/Mn-2.5 samples, are presented in Figure 6d), and iii) the increase in the trap state density within the area between the Fermi level and valence band (as can be seen in XPS valence band graphs in Figure 6b).

In comparison to sonicated EGaIn and EGaIn/Mn-1, the bandgap of EGaIn/Mn-2.5 was significantly decreased leading to the expansion of photocatalytic reaction toward the visible-light range and higher rate of exciton photogeneration. The conduction band, which also moved closer to the Fermi level for EGaIn/Mn-2.5, possesses a highly reducing potential introducing sufficient driving force for the catalytic reactions. Consequently, superoxide radicals (O₂⁻) which play a significant role in the decomposition of CR were produced more effectively by photogenerated electrons through the reduction process. The presence of trap states can also improve photoabsorption by reducing the effective bandgap. It is also a sign of the formation of more quasi-metallic sites, facilitating free carrier transfer and improving catalysis efficiency.

A table comparing the photocatalytic efficiency of EGaIn/Mn-2.5 and previous reports on photocatalysis of either MnO₂ nanosheets or MnO₂ nanostructures with other nanomaterials is presented in Table S2 (Supporting Information). As can be seen, under Sun simulated conditions, EGaIn/Mn-2.5 is a superior photocatalyst in comparison to these previous state-of-the-art reports for MnO₂. As such, the process presented in this paper provides a viable pathway that can be expanded for creating other photocatalysts using liquid metal synthesis and templating processes.

3. Conclusion

We showed that monolayers of hydrated MnO₂ can be produced on the surface of EGaIn in a process that exploits Galvanic replacement reactions on smooth liquid metal surfaces, leading to monolayer growth. The reaction took advantage of the reduction of KMnO₄ on the surface of gallium-containing alloys, leading to the rapid growth of very large 2D sheets of hydrated MnO₂ on the liquid metal template. The reaction was found to be self-limiting due to the prevailing oxidation mechanism of the liquid metal template that is akin to the Cabrera–Mott process. The generated oxides were found to self-exfoliate on the liquid metal surface, leading to the continuous production of ultrathin metal oxide sheets. When mechanical agitation was utilized to facilitate oxide delamination, core/shell nanostructures consisting of a porous shell composed of hydrated manganese and gallium oxide sheets, surrounding a solid indium core, were generated. Interestingly, sonication led to the migration of the gallium fraction of the liquid alloy to the surface, leaving a solid metallic indium core behind. This phenomenon highlights the necessity of providing a liquid metallic surface during the Galvanic growth of 2D nanosheets, which is believed to enable oxide delamination from the metal, thereby enabling the continuous growth of nanosheets. The obtained core/shell structures were employed for the photocatalytic degradation of CR with unprecedented efficiency in...
comparison to MnO₂ sheets or MnO₂ composites with other materials.

This work demonstrates a novel pathway to many possible procedures for creating 2D materials and core/shell structures from liquid metals. The methodology should enable the growth of 2D sheets composed of other transition metals, provided that the electrochemical driving force is sufficient for the reaction. This should be explored in future studies, leading to possible applications in energy storage and conversation, sensing, optics, and electronics. The unique surface of liquid metals offers extraordinary possibilities for synthesis and should be thoroughly explored for creating future functional materials.

4. Experimental Section

Analytical grade chemicals (Sigma-Aldrich) and Milli-Q water were used in all experiments. The liquid metal, EGaIn, was prepared at room temperature by mixing and grinding 75.5% gallium and 24.5% indium by weight. The core/shell EGaIn–hydrated manganese oxide droplets were synthesized by sonication of EGaIn in aqueous solutions of KMnO₄.

Hydrated MnO₂ Sheets on Bulk EGaIn: For the synthesis of hydrated manganese oxide sheets, bulk EGaIn liquid metal droplets (0.5 g) were placed in aqueous solutions (4 mL) of KMnO₄ (1 to 5 × 10⁻³ M) as the reaction media for up to one week. The produced hydrated MnO₂ samples were isolated from the reaction mixture for further characterization.

Sonication Process: Sonication experiments were carried out in a common ultrasonic bath (Unisonics Australia). Sonication of liquid metal drops in solution produced micro/nanodroplets within 20 min. For this experiment, EGaIn droplets (0.2 g) were sonicated in 20 mL aqueous solutions of KMnO₄ with different concentrations of 0, 1, 2.5, 5, and 10 × 10⁻³ M for 20 min. The obtained materials were separated from the supernatant by centrifugation (at 5000 rpm) followed by drying at 60 °C overnight. The materials obtained with this approach were denoted as EGaIn/Mn-1 to EGaIn/Mn-10, respectively.

Material Characterization: The surface and morphology of the isolated nanostructures were imaged by a Nova Nano SEM 450 while denoted as EGaIn/Mn-1 to EGaIn/Mn-10, respectively.

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.

Keywords

2D, galvanic replacement, liquid metals, low melting point, MnO₂

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