Unlocking the Electrocatalytic Activity of Antimony for CO₂ Reduction by Two-Dimensional Engineering of the Bulk Material

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Abstract: Two-dimensional (2D) materials are known to be useful in catalysis. Engineering 3D bulk materials into the 2D form can enhance the exposure of the active edge sites, which are believed to be the origin of the high catalytic activity. Reported herein is the production of 2D “few-layer” antimony (Sb) nanosheets by cathodic exfoliation. Application of this 2D engineering method turns Sb, an inactive material for CO₂ reduction in its bulk form, into an active 2D electrocatalyst for reduction of CO₂ to formate with high efficiency. The high activity is attributed to the exposure of a large number of catalytically active edge sites. Moreover, this cathodic exfoliation process can be coupled with the anodic exfoliation of graphite in a single-compartment cell for in situ production of a few-layer Sb nanosheets and graphene composite. The observed increased activity of this composite is attributed to the strong electronic interaction between graphene and Sb.

The electrocatalytic CO₂ reduction reaction (CO₂RR) is of considerable interest because of its potential for both the storage of intermittent renewable energy from wind and solar, and the conversion into value-added fuels and other chemicals in a sustainable manner.[1] However, a great number of possible products, including CO, formic acid (or formate, depending on pH, “formate” is used hereafter to represent both forms), hydrocarbons, and oxygenates, can be generated with poor product selectivity [i.e., low faradaic efficiency (FE) for each product], energy efficiency (i.e., large overpotential, η), and durability.[2] In addition, the hydrogen evolution reaction (HER) is a prevalent competing reaction because the equilibrium potentials for the CO₂RRs are close to that of the HER [0 V vs. the reversible hydrogen electrode (RHE); all potentials reported in this work are with respect to this reference unless otherwise noted], and the kinetics for the HER is relatively facile.[3] Thus, significant advances in the development of effective and selective catalysts for the CO₂RR are required to tackle these issues.

Among the various products from CO₂RR, formate is a liquid fuel with high-energy density, and regarded as a useful hydrogen carrier for fuel cell applications.[4] Several post-transition metals, such as Pb, Sn, In, and Bi, have been shown to catalyze the reduction of CO₂ to formate.[5] However, antimony (Sb) has received much less attention as an electrocatalyst for the CO₂RR, despite it being adjacent to Sn and Bi in the periodic table. This lack of attention is probably due to the fact that the catalytically active sites are not highly exposed in the bulk material.[5] It is of great interest to exploit the application of Sb for the electrocatalytic CO₂RR.

Several nanostructural engineering strategies have been identified to optimize the performance of metal catalysts for the CO₂RR, such as nanoparticle size and morphology modulation, alloying, surface modification, core–shell structuring, meso-structuring, and integrating molecular catalysts with covalent organic frameworks.[6] Recently, two-dimensional (2D) engineering of materials has emerged as an effective approach to increase the catalytic activities of materials for which the catalytic activities are either essentially absent or considerably inferior in their bulk forms.[7] For example, nanostructured transition-metal dichalcogenides (TMDCs), such as MoS₂, have been demonstrated as promising alternatives to Pt for catalyzing the HER.[8] The activity of MoS₂ nanoflakes scales linearly with the length of the edge, rather than surface area, thus indicating that the edge is the catalytically active site.[9] MoS₂ and WSe₂ have also been identified as effective catalysts for the CO₂RR in ionic-liquid media using water as a proton source, and the edges are mainly responsible for the catalytic performance.[10] The group of Xie[11] reported a partially oxidized cobalt catalyst, with a 2D layered structure, for the electrocatalytic reduction of CO₂ into formate at low overpotentials. The distinctive catalytic property, which is absent in bulk cobalt, is likely due to both the 2D structure and the oxidation state.[12] All the above-mentioned research, as well as that of many others,[13] indicate that reducing the thickness of bulk crystals to a few layers or even one layer can promote the catalytic activity, which is attributed to the dramatic increase of active edge
sites and defects, the enhanced hopping of electrons, and/or the enlarged surface areas.

The Sb crystal adopts a rhombohedral layered structure (terms as β-phase) with a space group of R3m (Figure 1). Theoretical studies have predicted that Sb could exist in a 2D form (antimonene) with high stability and interesting properties. However, there are only a few reports of the experimental preparation of antimonene, and it severely restricts the exploration of its fundamental properties and further applications.

Herein, for the first time, we demonstrate the preparation of few-layer Sb nanosheets (SbNSs) from bulk crystal by a cathodic exfoliation method. This method has been proven to be a simple, economic, and environmentally friendly, yet efficient approach for the mass production of classic 2D materials, such as graphene and TMDCs. Detailed characterizations confirm the nanosheet features of the obtained few-layer Sb. In contrast to the bulk counterpart, SbNSs were found to selectively and efficiently catalyze the reduction of CO2 to formate. This catalytic activity of Sb is ascribed to the increased number of active edge sites in the SbNSs. Furthermore, when coupled with the anodic exfoliation of graphite, the few-layer Sb nanosheet-graphene (SbNS-G) composite can be readily formed in an in situ manner. This composite showed an enhanced performance towards the CO2RR, compared to the SbNSs, because of a synergistic effect resulting from the strong electronic interaction between graphene and the SbNSs.

Bulk Sb crystals can be viewed as the ABC stacking of monolayer Sb along the c-axis direction and adjacent layers interact through van der Waals interactions. This arrangement implies the possibility of exfoliating bulk Sb to 2D nanosheets using either liquid-phase exfoliation or electrochemical exfoliation methods established previously for other 2D materials. The electrochemical exfoliation of Sb was carried out in a two-electrode system with 0.5 M Na2SO4 as the supporting electrolyte. A small Sb crystal (of good purity and crystallinity; see Figure S1 in the Supporting Information) connected to a copper wire and a Pt foil were used as the cathode and anode, respectively. A direct current (DC) potential of 10 V was applied between the Sb and Pt electrodes to drive the electrochemical exfoliation (see the Supporting Information for details). After washing and mild sonoication, well-dispersed SbNSs were obtained, thus showing a typical Tyndall effect (see Figure S2).

The anion of the supporting electrolyte has little influence on the exfoliation process, while cations with sizes that are either too large (i.e., Cs+) or too small (i.e., Li+), compared to the interplanar spacing of the Sb crystal, decrease the exfoliation rate (see Table S1). From these observations, and previous reports on electrochemical exfoliation of graphite to graphene, a mechanism of electrochemical exfoliation is proposed as follows (Figure 1): application of a potential, which is more negative than the point of zero charge results in negatively charged Sb layers, to drive the intercalation of cations (e.g., Na+) for charge screening. This intercalation leads to the expansion and eventual exfoliation of the Sb crystal. It is worth noting that cathodic exfoliation intrinsically possesses the advantage of not introducing any oxidation to the as-prepared materials, an unavoidable aspect for anodic exfoliation which is particularly problematic for Sb because of its electrochemical instability.

Figure 2a depicts a typical TEM image of the SbNSs, and clearly outlines the nanosheet structure. Energy-dispersive X-ray spectroscopic analysis of the sheets shows that the major elemental composition of the nanosheets is Sb, while only a small peak of O is present (see Figure S3). The average lateral size is 350 nm (see Figure S3). As displayed in the high-resolution TEM (HRTEM) image in Figure 2b, lattice fringes with a distance of 0.31 nm are clearly observed, and can be assigned to the (012) crystal plane of rhombohedral Sb. Atomic force microscopy (AFM) characterizations (see Figure S3) reveal that the mean thickness of the nanosheets is about 3.5 nm, corresponding to four layers of Sb sheets, and about 60% of the exfoliated product comprises nanosheets of no more than four layers.

The majority of SbNSs was exfoliated along the c-axis during the electrochemical exfoliation process. As evidence, compared to the bulk crystal (see Figure S1), the (003) and (006) diffraction peaks are absent in the powder X-ray diffraction (XRD) patterns of the SbNSs (Figure 2c). The remaining strong peaks, such as (012), are consistent with the HRTEM results, and confirm the good crystallinity of the SbNSs, along with the Raman spectrum (see Figure S3). X-ray photoelectron spectroscopy (XPS) was utilized to analyze the oxidation state of the elements, and the high-resolution XPS
spectrum of the Sb 3d and O 1s is deconvoluted as shown in Figure 2d. The Sb 3d<sub>5/2</sub> and Sb 3d<sub>3/2</sub> peaks clearly demonstrate that the SbNSs are mostly Sb<sup>5+</sup> (binding energy of 537.7 and 528.3 eV) and only a slight amount can be assigned to Sb<sup>3+</sup> (binding energy of 540.0 and 530.6 eV).<sup>[13]</sup> The oxide is probably formed in the storage period before XPS analysis.

By virtue of its nanosheet morphology, the SbNSs expose a greater number of edges than the bulk counterpart, and is expected to be more active in electrocatalysis. To assess the possibility of using the SbNS as a catalyst for the CO<sub>2</sub>RR, linear-sweep voltammetric curves (LSVs) were recorded in N<sub>2</sub>- and CO<sub>2</sub>-saturated 0.5 M NaHCO<sub>3</sub> solutions using bulk Sb and SbNS-modified glassy carbon electrode (GCE) as working electrodes. As shown in Figure 3a, both electrodes show a larger catalytic current under a CO<sub>2</sub> atmosphere than that under an N<sub>2</sub> atmosphere, while the SbNSs exhibit a lower onset potential and significantly increased catalytic current density (normalized by the geometric surface area) compared to bulk Sb. The SbNS electrode also shows a broad peak centred at ~1.06 V under the CO<sub>2</sub> atmosphere, a process which is absent under the N<sub>2</sub> atmosphere. A similar process was also observed by our group<sup>[18]</sup> and others<sup>[9]</sup> for different electrocatalysts, and has been assigned to the reduction of CO<sub>2</sub>.

Potentiostatic electrolysis was conducted over the potential range of ~0.56 to ~1.36 V and the FE data for the products versus applied potential are presented in Figure 3b. These data demonstrate that H<sub>2</sub>, CO, and formate are the reduction products with a combined FE value of around 100% over the whole potential range. The gaseous and liquid products were quantified by gas chromatography (GC) and <sup>1</sup>H NMR spectroscopy, respectively, and no other products were detected. The selectivity towards formate and H<sub>2</sub> is dependent on the applied potential while FE for CO does not vary significantly with applied potentials (ca. 5%). The FE for formate reaches a maximum of about 84% at ~1.06 V (overpotential of 0.97 V for formate).<sup>[20]</sup>

We speculate that the enhanced activity of SbNSs arises from the edge sites exposed after electrochemical exfoliation, similar to the case of MoS<sub>2</sub> for catalyzing the HER,<sup>[9]</sup> and Ag nanoplates for catalyzing the CO<sub>2</sub>RR.<sup>[20]</sup> In addition, SbNSs produced by the shear exfoliation method showed moderate HER activity because of the edge sites.<sup>[19]</sup> To test our hypothesis, SbNSs with different sizes (see Figure S4) were separated by centrifugation at certain rotation speeds and cast on a GCE to obtain the current response in a CO<sub>2</sub>-saturated 0.5 M NaHCO<sub>3</sub> solution. As shown in Figure 3c, the peak I<sub>max</sub> (current normalized by the mass loading of Sb on the electrode) at ~0.96 V associated with the smaller SbNSs (average lateral size of 170 nm) is 3.6 times as large as that found for the larger SbNSs (average lateral size of 485 nm). I<sub>max</sub> instead of I was used to take into account the difference in the surface area (see detailed explanation/justification in the Supplementary Note in the Supporting Information). The positive correlation between I<sub>max</sub> and the lateral size of the SbNSs (hence the length of its edge) confirms that edge sites are indeed more active.

The structural and electronic interaction of the catalyst with a support, such as graphene or a metal surface, has been widely proven to be critical in electrocatalysis, and leads to the synergetic enhancement of the reactant adsorption and reaction kinetics<sup>[6,7,12b,21]</sup> Using the electrochemical exfoliation method, we can readily produce Sb-graphene composite materials in a single-compartment electrochemical cell to probe the effect of the interaction on the electrocatalytic performance of the CO<sub>2</sub>RR.

As illustrated in Figure 4a, when the Pt anode is replaced by a graphite rod during the exfoliation of Sb at the cathode, the graphite can be electrochemically exfoliated into graphene, and has been used by several groups to produce high-quality graphene<sup>[15c–e]</sup> As a result of the electrostatic interaction between the freshly exfoliated graphene and the Sb flakes, a graphene-Sb composite can be readily prepared. After washing and sonication, the composite can be redispersed in water (see Figure S5). The SbNSs adopt a face-to-face structure to couple with graphene sheets (see Figure S5) to maximize the interaction between these two components, and is expected to lead to strong electronic coupling. The produced graphene is of high quality (see Figure S5).
The SbNS-G-modified GCE exhibits a higher $I_{\text{max}}$ compared to that of SbNSs (see Figure S6). Moreover, the SbNS-G presents a higher selectivity towards formate at lower overpotentials compared to bulk Sb and SbNSs (Figure 4b). At a potential of $-0.96$ V (overpotential of $0.87$ V), it delivers the maximum FE for formate of $88.5\%$, whereas SbNS gives its maximum FE of $84\%$ at $-1.06$ V. Other products were confirmed to be H$_2$ and CO. The partial current density for formate of the SbNS-G is considerably larger than that of bulk Sb and SbNSs (Figure 4c). For example, the value of SbNS-G at $-1.07$ V is $1.5$ and $16$ times higher than that of SbNSs and bulk Sb, respectively. Collectively, these results prove that, by 2D engineering of the structure and further compositing with graphene, we can transform Sb from a catalytically inactive material into an active form.

When SbNSs are compositied with graphene, $I_{\text{max}}$ is not expected to change significantly if the number of edge sites is the only factor that determines the catalytic activity. The enhanced catalytic ability of SbNS-G could be attributed to the synergetic effect between SbNSs and graphene. This effect is likely to arise from a strong electronic coupling between SbNSs and graphene, as proven by the Raman spectrum (Figure 4d) and Sb 3d$_{5/2}$ XPS spectrum (see Figure S7). A red shift of both $E_g$ and $A_g$ peaks, especially the $A_g$ peak ($7.8$ cm$^{-1}$), was observed in the SbNS-G sample. The red-shift of the Raman spectrum has been observed in other 2D composites[28] and was attributed to the n-type doping from graphene to the other material. The Sb 3d$_{5/2}$ XPS spectrum of SbNS-G also presents a negative shift in binding energy (ca. $0.5$ eV) compared to that of SbNSs. A similar negative shift has been reported in the graphene-supported SnO$_2$ nanoparticles and was attributed to the electron donation from graphene.[86] In the SbNS-G composite, electrons from the lower work function graphene (ca. $4.43$ eV)[23] tend to migrate across the Sb-G boundary to the higher work function SbNS ($4.55$–$4.70$ eV)[24] thus increasing the electron density at the surface of SbNS. No Raman or XPS spectrum shift was found in the physical mixture of exfoliated SbNS and graphene, and indicates this electronic interaction only occurs in the in situ formed composite.

The strong electronic interaction of metal nanoparticles with graphene is capable of tuning the adsorption energies of reactant and/or intermediates on the nanoparticle surface, hence modulating the reaction kinetics of, for example, CO$_2$RR, HER, and CO oxidation.[10,21a,23] Tafel analysis was conducted to probe the influence of such electronic interaction on the CO$_2$RR mechanism of our materials. A large Tafel slope associated with bulk Sb suggests that CO$_2$ adsorption is likely to contribute to the rate-determining step(s).[3] The continuous decrease of the Tafel slope in going from bulk Sb to SbNS-G (see Figure S8) indicates an enhanced CO$_2$ adsorption ability and therefore improved catalytic activity. This electronic interaction induced performance enhancement is also evidenced by the positive shift of onset potential (Figure 3a; see Figure S6), in agreement with previous finding on enhanced CO$_2$RR activity from Au nanoparticles embedded in graphene.[20] Furthermore, a Tafel slope of $110$ mV dec$^{-1}$ for SbNS-G is in an excellent agreement with the expected value of $117$ mV dec$^{-1}$, thus suggesting that the $^\prime$CO$_2/^\prime$CO$_2$ ($^\prime$ stands for an adsorbed species) step becomes rate-limiting.[3,9,11] Additionally, the SbNS-G also shows great stability with imperceptible activity or selectivity loss over 12 hours (see Figure S9).

In summary, we have demonstrated the preparation of few-layer SbNSs by cathodically exfoliating bulk Sb crystals for the first time, and it represents a facile, environmentally friendly, and efficient route to the production of few-layer, 2D materials, and is intrinsically suitable for large-scale processing. The few-layer structure was confirmed by microscopic and spectroscopic characteristics. More importantly, the electrochemical exfoliation approach also enables the in situ production of SbNS-G composites in a single electrochemical cell when coupled with the anodic exfoliation of graphite. This composite material shows the capability to catalyze the electroreduction of CO$_2$ to formate selectively and efficiently, and is in stark contrast to the inactivity of bulk Sb. The enhanced performance is attributed to more catalytically active edge sites brought about by exfoliation and the strong electronic interaction between graphene and Sb enabled by the in situ preparation method.

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Conflict of interest

The authors declare no conflict of interest.

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