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The beneficial impact of surface oxidation on electrochemical reactions with GaSe nanosheets

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Summary. — Gallium selenide (GaSe) is a van der Waals semiconductor widely used for optoelectronic devices, whose performances are dictated by bulk properties, including band-gap energy. However, recent experimental observations that the exfoliation of GaSe into atomically thin layers enhances performances in electrochemistry and photocatalysis have apparently opened new avenues for its applications in the fields of energy and catalysis. Here, with surface-science experiments and density functional theory (DFT) we study the oxidation of GaSe into β-Ga_2O_3. The oxidation driven by Se vacancies, created in the exfoliation process, plays a pivotal role in the catalytic process.

1. – Introduction

Layered semiconductors offer application capabilities often complementary to those of graphene [1-3]. Specifically, the presence of a bulk band gap, absent in graphene [4], makes them suitable candidates for optoelectronic devices [5], gas sensing [6] and photocatalysis [7]. Among semiconductors with weak interlayer van der Waals interactions, III-VI semiconductors, such as GaSe and InSe, have attracted significant attention, in consideration of the band-gap energy matching the visible range of the electromagnetic spectrum and the possibility of room-temperature single-photon emission [8].

GaSe exist in nature in four polytypes, the most diffuse are hexagonal ϵ-GaSe (space group P6̄m2), exhibiting a Se-Ga-Ga-Se sequence. Recently, exfoliation of GaSe in nanosheets has been shown to be beneficial for improving the performance of hydrogen evolution reaction (HER) [9] and gas sensing [10].

However, GaSe undergoes oxidation in ambient air with the formation of Ga_2O_3 [11-13]. Furthermore, another important issue is related to the impact of chemical reactivity of Se vacancies [14]. Currently, most single crystals of GaSe are far from being stoichiometric [15, 16]. Subsequently, the abundant amount of Se-vacancy sites could play an important role in electrocatalytic and photocatalytic performances.

Here, by means of surface-sensitive experimental techniques and density functional theory, we demonstrate that the surface transformation of GaSe in Ga_2O_3 in ambient conditions is the main responsible for the enhancement of performances in electrochemistry and photocatalysis. Therefore, contrary to the common picture, exfoliation in nanosheets does not improve HER kinetics in consideration of higher surface-to-volume ratio, but rather for the enhancement of oxidation rate, which plays an unexpectedly beneficial

role. Accordingly, the self-assembled $Ga_2O_3/GaSe$ heterostructure represents an ideal platform for electrocatalysis.

2. – Experimental

2˙1. *Single-crystal growth*. – GaSe single crystals were grown by modified Bridgman-Stockbarger method using quartz ampoules. Stoichiometric ratios of Ga and Se were put to the ampoule to grow 50 g of GaSe and sealed under a vacuum of 10^{-6} mbar. Then, the crucible was placed into a two-zone horizontal furnace.

2˙2. *XPS*. – XPS spectra for oxidized GaSe nanosheets were acquired using Al Kα with a VG-Scienta R3000 hemispherical analyzer.

3. – Results and discussion

Exfoliated nanosheets of GaSe should be more reactive because of the higher number of edge sites and surface defects in comparison to the pristine crystal. The morphology of exfoliated nanosheets of GaSe was characterized by atomic force microscopy (AFM) in order to evaluate their lateral dimension and thickness. Statistical AFM analysis indicates that the lateral size and thickness of the nanosheets follow a log-normal distribution peaked at $\sim$ 45nm and $\sim$ 2.5 nm. To prove the inevitable oxidation of GaSe nanosheets, we performed X-ray photoelectron spectroscopy (XPS). We measured Ga-3d (fig. 1(a)) and Se-3d (fig. 1(b)) core levels in exfoliated flakes obtained by liquid-phase exfoliation [17]. In Ga-3d of GaSe nanosheets (fig. 1(a)), the hydroxylated components are predominant together with Ga_2O_3 (45% and 27% of the total spectral area, respectively). Notably, we did not observe any trace of SeO_2 in Se-3d (fig. 1(b)) even in air-exposed GaSe nanosheets, as demonstrated by the absence of the related spectral component at BE of 59–60 eV [18]. However, the formation of Se-Se aggregates (38%) and $Se(0)/Ga_2Se_3$ phases (28%) was detected in Se-3d core level of exfoliated GaSe flakes. From quantitative XPS we estimated the thickness of gallium-oxide phase in GaSe nanosheets to be 1.8 ± 0.3 nm.

To assess the impact of oxidation of GaSe in electrocatalysis, we modelled HER and oxygen evolution reaction (OER) for pristine, defective and oxidized bulk and monolayer GaSe. (For the sake of comparison, we also considered InSe.) Exceptionally, calculated values of free energies for HER (fig. 1(c)) evidence unsuitability of both bulk GaSe and InSe for this reaction, with energy barriers as high as 1.9 and 1.5 eV/H$^+$, respectively. The presence of Se vacancies in both GaSe and InSe significantly decreases the energy cost of the process (1.5 and 0.7 eV/H$^+$, respectively), but the magnitude is still significantly larger than that of the Pt(111) surface (0.1 eV/H$^+$), usually taken as standard reference (fig. 1(c)) [19]. In the case of free-standing monolayers, the values of the energy cost of HER are even larger, *i.e.*, 2.2 and 1.8 eV for GaSe and InSe, respectively. Therefore, the common picture that liquid-phase exfoliation of GaSe and InSe favours the improvement of HER performance on the basis of the higher amounts of edges behaving as active sites, recently proposed in ref. [20], should be revised. On the contrary, calculated values for Ga_2O_3 and the sub-stoichiometric oxide $Ga_2O_{2.97}$ are 1.1 and -0.3 eV/H$^+$. Therefore, for $Ga_2O_{2.97}$ the Heyrovsky step ($H_{ads} + H^+ + e^- \rightarrow H_2$) of HER is exothermic.

In the case of OER, in both acidic and alkali media, we find large negative values of free energy (-7.4 and -5.7 eV in acidic and alkali media, respectively) for pristine GaSe, making third step energetically unfavorable (fig. 1(d), (e)), owing to the favorability of
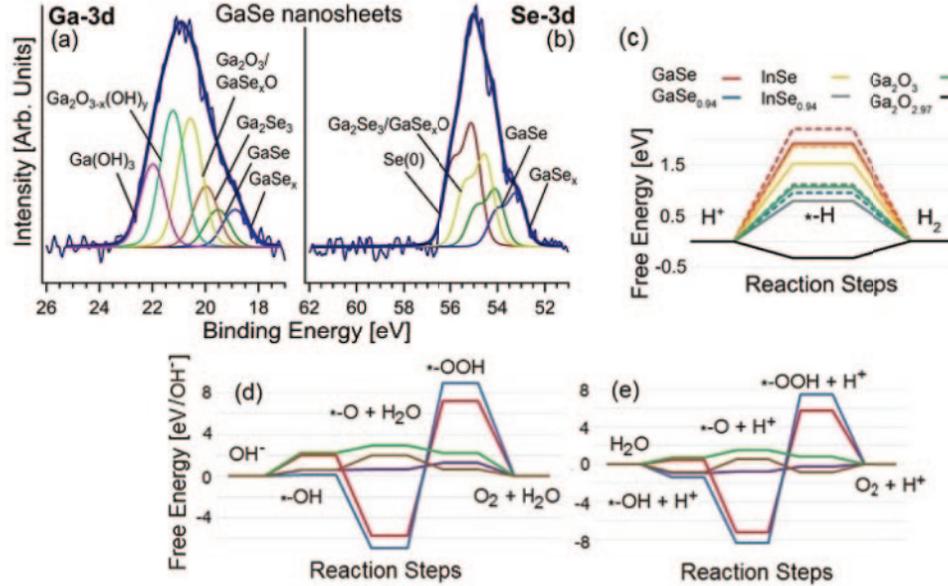
Fig. 1. – (a), (b) Ga-3d and Se-3d core levels for exfoliated sample of GaSe. The photon energy is 1486.6 eV (Al Kα). (c) Free energy diagram for the HER in acidic media over the surface of bulk and monolayer GaSe, GaSe$_{0.94}$, InSe and InSe$_{0.94}$ and forthe HER over the surface of Ga$_2$O$_3$ and Ga$_2$O$_{2.97}$. Results for monolayers are depicted by dashed lines. Note that the line for the free energy for GaSe$_{0.94}$ is overlapped with that associated with InSe$_{0.94}$. (d), (e) Free energy diagrams for OER in (d) acidic and (e) alkali media over the surface of bulk GaSe, GaSe$_{0.94}$, Ga$_2$O$_3$ and Ga$_2$O$_{2.97}$.

GaSe oxidation. Thus, the surface of bulk GaSe will be irreversibly oxidized during OER in both acidic and alkali environments. Considering the inevitable formation of Ga$_2$O$_3$-skin over GaSe substrate exposed to oxidative environments, we modelled OER over the (001) surface of Ga$_2$O$_3$ (fig. 1(d), (e)), We find that the Ga$_2$O$_3$ skin has reduced energy barriers for OER in both acidic and alkali environments, *i.e.*, 1.5 and 2.9 eV, respectively. The presence of oxygen vacancies additionally decreases energy cost of OER in both environments to 0.5 and 2.0 eV, respectively. Our results are consistent with previous theoretical [21] and experimental [22] results for water-gas shift reactions catalyzed by defective Ga$_2$O$_3$.

Particularly, we note that, in the survey of electrochemical properties of GaSe by Tan *et al.* [9], authors assume from XPS analysis that surface composition of GaSe is more complex respect to the theoretical one, considering the non-stoichiometric [Ga]:[Se] ratio and the presence of oxygen contaminants. The lowest Tafel slope (150 mV dec^{-1}) in HER was found in nominally reduced GaSe, for which authors claimed the removal of the passivation layer of Ga$_2$O$_3$, supposed to poison active sites of GaSe surface. However, surface treatments as those in ref. [9] are expected to promote the formation of sub-stoichiometric Ga$_2$O$_{3-x}$ phases, which indeed we demonstrate to represent a suitable platform for HER, according to our model depicted in fig. 1(c).

Likewise, recently, it has been reported that the HER-activity of InSe flakes increases when the thickness is reduced into atomically thin layers [20]. This size effect led to the identification of the active sites for HER at the edges of the InSe nanosheets. The absence of In$_2$O$_3$ and SeO$_2$ was inferred from missing related contributions in Raman

spectroscopy and X-ray diffraction, inappropriate technique for detecting a nanometric amorphous oxide layers. Conversely, the presence of In_2O_3 and SeO_2 surface phases in liquid-phase exfoliated InSe nanosheets is well evident from XPS spectra in ref. [17].

4. – Conclusions

We have demonstrated that recent results reporting enhanced performance of electrochemical and photocatalytic reactions upon exfoliation of GaSe in atomically thin layers should not be explained by the activation of quantum size effects or higher surface-to-volume ratio. Unexpectedly, oxidation of GaSe into Ga_2O_3 plays a beneficial role in catalytic processes. Explicitly, both HER and OER are energetically unfavourable in pristine GaSe, due to energy barriers of 1.9 and 5.7–7.4 eV, respectively. Exfoliation in nanosheets even increases the energy barrier for HER up to 2.2 eV. On the contrary, the Heyrovsky step $(H_{ads} + H^+ + e^- \rightarrow H_2)$ of HER is energetically favorable in substoichiometric $Ga_2O_{2.97}$ $(-0.3 \, eV/H^+)$. We also show the validity of this model for the parental compound InSe. Therefore, these results elucidate the role of surface oxides in electrocatalysis and photocatalysis based on nanosheets of III-VI layered semiconductors. These findings open a new way for the creation of a novel efficient and cost-effective (photo-) electrocatalysts, based on self-assembled heterostructures formed by the natural interaction of sub-stoichiometric van der Waals semiconductors with air.

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REFERENCES

[1]   Hu Jue *et al.*, *Adv. Funct. Mater.*, **30** (2020) 1908520.
[2]   Lihter Martina *et al.*, *Adv. Funct. Mater.*, **30** (2020) 1907860.
[3]   Guo Cheng *et al.*, *2D Mater.*, **7** (2020) 035026.
[4]   Novoselov Kostya, *Nat. Mater.*, **6** (2007) 720.
[5]   Viti Leonardo *et al.*, *Nanoscale*, **11** (2019) 1995.
[6]   Paolucci Valentina *et al.*, *ACS Appl. Mater. Interfaces*, **12** (2020) 34362.
[7]   Zhang Qingzhe *et al.*, *Adv. Funct. Mater.*, **29** (2019) 1902486.
[8]   Tonndorf Philipp *et al.*, *2D Mater.*, **4** (2017) 021010.
[9]   Tan Shu min *et al.*, *Phys. Chem. Chem. Phys.*, **18** (2016) 1699.
[10] Wu Yecun *et al.*, *Adv. Mater. Technol.*, **2** (2017) 1600197.
[11] Tovstyuk N. K., *J. Phys Stud.*, **8** (2004) 47.
[12] Balitskii O. A., Savchyn V. P. and Yukhymchuk V. O., *Semicond. Sci. Technol.*, **17** (2002) L1.
[13] Bergeron Alaric *et al.*, *Appl. Phys. Lett.*, **110** (2017) 241901.
[14] Shi Li *et al.*, *J. Phys. Chem. Lett.*, **8** (2017) 4368.
[15] Ni Youbao *et al.*, *J. Cryst. Growth*, **381** (2013) 10.
[16] Zappia Marilena Isabella *et al.*, *Adv. Funct. Mater.*, **30** (2020) 1909572.
[17] D'Olimpio Gianluca *et al.*, *Adv. Funct. Mater.*, **30** (2020) 2005466.
[18] Fan Yaming, Zhuo Yuqun, and Li Liangliang, *Appl. Surf. Sci.*, **420** (2017) 465.
[19] Greeley Jeff *et al.*, *Nat. Mater.*, **5** (2006) 909.
[20] Petroni Elisa *et al.*, *Small*, **14** (2018) 1800749.
[21] Liu Taifeng *et al.*, *Chem. Mater.*, **30** (2018) 7714.
[22] Jochum Wilfrid *et al.*, *J. Catal.*, **256** (2008) 278.