



# Methods to Improve Lithium Metal Anode for Li-S Batteries

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The lithium-sulfur (Li-S) battery has received a lot of attention because it is characterized by high theoretical energy density (2,600 Wh/kg) and low cost. Though many works on the “shuttle effect” of polysulfide have been investigated, lithium metal anode is a more challenging problem, which leads to a short life, low coulombic efficiency, and safety issues related to dendrites. As a result, the amelioration of lithium metal anode is an important means to improve the performance of lithium sulfur battery. In this paper, improvement methods on lithium metal anode for lithium sulfur batteries, including adding electrolyte additives, using solid, and/or gel polymer electrolyte, modifying separators, applying a protective coating, and providing host materials for lithium deposition, are mainly reviewed. In addition, some challenging problems, and further promising directions are also pointed out for future research and development of lithium metal for Li-S batteries.

**Keywords:** lithium-sulfur battery, anode, dendrite, safety, gel polymer electrolyte, coating

## INTRODUCTION

As a kind of lithium metal secondary battery, lithium-sulfur battery is very likely to be another energy storage device for its high theoretical energy density (2,600 Wh kg<sup>-1</sup>) and specific capacity (1,675 mAh g<sup>-1</sup>) (Lu et al., 2013; Tao T. et al., 2017; Li J. H. et al., 2019). Meanwhile, using sulfur as cathodic material makes it cheaper and more environmentally friendly (Yin et al., 2013). However, the shuttle effect and uneven deposition of lithium limit the practical application of lithium-sulfur batteries (Li et al., 2014; Manthiram et al., 2014). Other problems such as poor electrical conductivity and severe volume change of sulfur also limit the performance of batteries to a certain extent (Evers and Nazar, 2013). At present, the improvement of lithium sulfur battery mainly focuses on the cathode, while much less research has been done on lithium metal anodes.

In Li-S batteries, the metallic lithium is oxidized to produce lithium ion firstly. Unfortunately, the stripping of lithium is uneven commonly, which affects the uniform deposition of lithium in the next step. The uneven and porous lithium deposition layer leads to a large change in its volume, fracturing the fragile solid electrolyte interface (SEI) and then consuming the inner fresh lithium to form a new SEI after reacting with the electrolyte. Polysulfides formed during the charging process transfer to the Li metal anode via the electrolyte, react with lithium irreversibly. At the same time, the uneven deposition of lithium leads to the enrichment of lithium ions in the tip region, and aggravating the growth of lithium dendrites. When the dendrite grows to a certain extent, the electrical contact with the substrate will be broken to produce the unreactive “dead” lithium, which increases the internal resistance and attenuates the capacity of the battery. To make matters worse, dendrites can even pierce through separator, posing a safety hazard. These challenges lead to the drawbacks of Li-S batteries.

So, the improvement of lithium metal anode could be classified into two aspects: protecting active lithium from side reactions and guiding uniform deposition of lithium. Since gain/loss of one electron especially that in 2s orbit should be very fast, the solutions to Li metal are not fully addressed, and there are few reviews on Li metal anode (Cheng et al., 2017; Yan et al., 2019). As a result, here we summarized some promising methods: (1) Adding additives to the electrolyte. (2) Using solid electrolytes or gel polymer electrolytes (Marom et al., 2011). (3) Modifying the separators. (4) Coating protective layers on the surface of lithium directly. (5) Providing host materials for lithium deposition. We summarized the above five directions in the recent 5 years; challenges and further directions are also pointed out.

## ADDING ADDITIVES TO THE ELECTROLYTE

Organic liquid electrolyte, especially ether-based electrolyte, is commonly used in lithium-sulfur batteries for its high ionic conductivity, good interface contact with electrodes, and less side reaction with lithium. However, issues originating from the dissolution of intermediate polysulfides make it necessary to add suitable additives to protect the lithium metal anode. So far, the additives include nitrates, iodides, sulfur-containing compounds, and various organic compounds, and their functions are listed in **Table S1**.

It is well-known that  $\text{LiNO}_3$  has the ability to protect the lithium metal anode effectively by participating in forming a robust SEI layer *in situ* on the metal surface (Liang et al., 2011). The composition of SEI was investigated by *Operando* X-ray absorption spectroscopy (XAS); results showed that during the initial discharge process,  $\text{LiNO}_3$  reacted with polysulfides to form  $\text{Li}_2\text{SO}_4$ ,  $\text{Li}_2\text{SO}_3$ , and  $\text{LiNO}_2$ , which composed a stable SEI on the surface of anode to hamper the side reactions between polysulfides and lithium (Zhang et al., 2018). Other types of nitrates such as  $\text{La}(\text{NO}_3)_3$  and  $\text{KNO}_3$  were also studied in particular. Both the cation and nitrate can participate in improving the stability of SEI on anode (**Figure 1A**) (Liu S. et al., 2016), and a Li-S full battery using 1 M LiTFSI (DME:DOL = 1:1 v:v) electrolyte added with 0.1 M  $\text{KNO}_3$  exhibited an average discharging capacity of 687 mAh/g within 100 cycles, which was higher than the one with 0.1 M  $\text{LiNO}_3$  (average 637 mAh/g) (Jia et al., 2016).

Iodide, such as  $\text{LiI}$  and  $\text{InI}_3$ , had also acquired outstanding breakthrough (Eo et al., 2009; Liu et al., 2017). Quantum chemistry calculations showed that the  $\text{I}^\cdot$  radicals reacted with DME to form comb-branched polyether in solution (**Figure 1B**), which suppress the dissolution of polysulfides and then protect the Li metal anode simultaneously (Wu et al., 2015a). Poly(sulfur-random-triallylamine) (PST) (**Figure 1C**) (Li G. et al., 2017),  $\text{SOCl}_2$  (Li S. et al., 2019), 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) (Qian et al., 2018), and magnesium oxide nanoparticles (Ponraj et al., 2016) were also proven to be effectual.

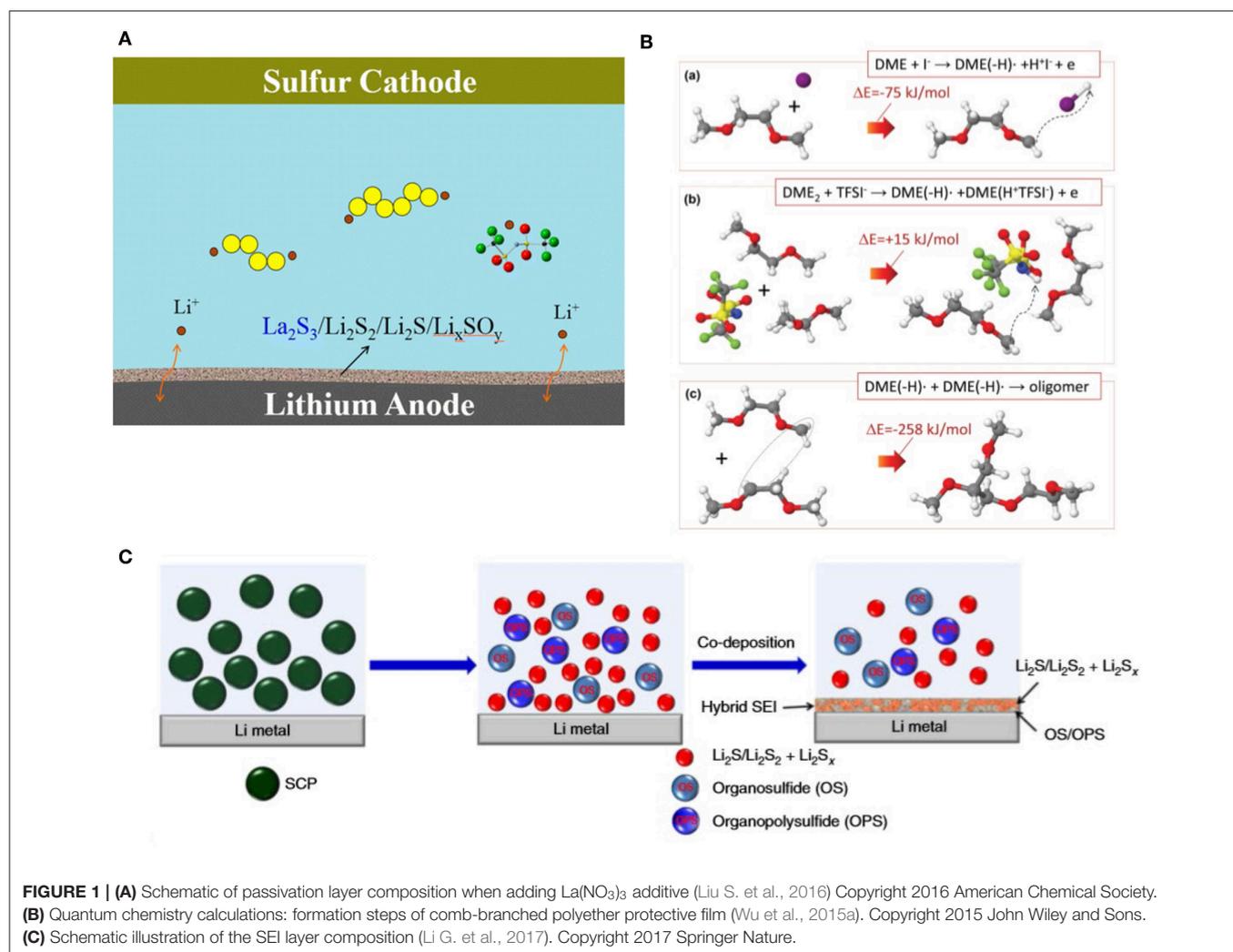
In order to reduce the polysulfides in electrolyte during the cycling of Li-S battery, additives such as dithiothreitol (DTT), which can slice the S-S bond to accelerate the conversion from polysulfides to  $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$  (Liu M. et al., 2019), biphenyl-4,4'-dithiol (BPD) (Wu H. L. et al., 2017) and carbon disulfide ( $\text{CS}_2$ ) (Gu et al., 2016), which could react with polysulfides to reduce the chance of contact with the anode, were developed.

## USING OTHER TYPES OF ELECTROLYTE

Ionic liquid electrolyte is an electrolyte composed entirely of anion and cation, which determines its high safety, excellent stability, and strong solubility to lithium salt (Ghandi, 2014). Moreover, the weak solvation of ionic liquids can reduce the solubility of polysulfides. However, ionic liquids usually have high viscosity, which leads to low ionic conductivity. Adding an appropriate amount of solvents such as DME and DOL to achieve a balance between ionic conductivity and solubility of polysulfides is a suitable choice (Yang et al., 2017). For example, the room temperature ionic conductivity of *N*-methoxyethyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)-imide ( $\text{P}_{1,2\text{O}1}\text{TFSI}$ ) with 30 wt.% TEGDME as the diluent was increased to  $4.303 \text{ mS cm}^{-1}$ , the Li-S full battery using the electrolyte showed an initial discharge capacity of 1,264 and 911.4 mAh  $\text{g}^{-1}$  was retained after 50 cycles (Wu et al., 2015b).

Solid electrolyte is also an important direction to improve lithium metal anode by blocking the polysulfides physically. Generally, it can be classified into inorganic solid electrolyte and polymer solid electrolyte. Inorganic solid electrolytes are mainly composed of sulfides, oxides, and phosphates. Examples of sulfides are  $\text{Li}_6\text{PS}_5\text{Cl}$  (**Figure S1A**),  $\text{Li}_3\text{PS}_4$ , and  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  (Yamada et al., 2015; Han et al., 2016; Yao et al., 2017). Oxides include  $\text{Li}_{3.3}\text{La}_{0.56}\text{TiO}_3$ ,  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ , and  $\text{Li}_{14}\text{ZnGe}_4\text{O}_{16}$  (Zheng et al., 2014; Yu et al., 2015).  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ge}_{1.7}(\text{PO}_4)_3$ ,  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ , and  $\text{Li}_2\text{P}_5\text{O}_6\text{N}_5$  (Monchak et al., 2016; Meesala et al., 2017) are typical representatives of phosphates. Polymer solid electrolytes are based on polymer matrix such as PEO, PMMA, PVDF, and PAN without liquid phase. It is characterized by chemical stability, mechanical persistence (durability), and flexibility. However, the low room temperature ionic conductivity plagues the direct application of them (Lin et al., 2016a), and methods such as doping (Monchak et al., 2016), blending, and cross-linking are applied to improve the performance of solid electrolyte. Among them, adding fillers may be the most effective route. Fillers such as  $\text{LiN}_3$  (Eshetu et al., 2017),  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) (**Figure S1B**) (Tao X. et al., 2017),  $\text{MoS}_2$  (Xu et al., 2017), food grade starch (Lin Y. et al., 2016), and halloysite (Lin et al., 2017) were proven to be effectual. Besides, constructing multilayer solid electrolyte by coupling a dense layer that provides supporting function and hosts for electrolytes with a thin layer to block the polysulfides and inhibit the growth of dendrites (**Figure S1C**) (Fu et al., 2017) was another promising solution.

As an intermediate of liquid electrolyte and all-solid electrolyte, the gel-polymer electrolyte (GPE) therefore has



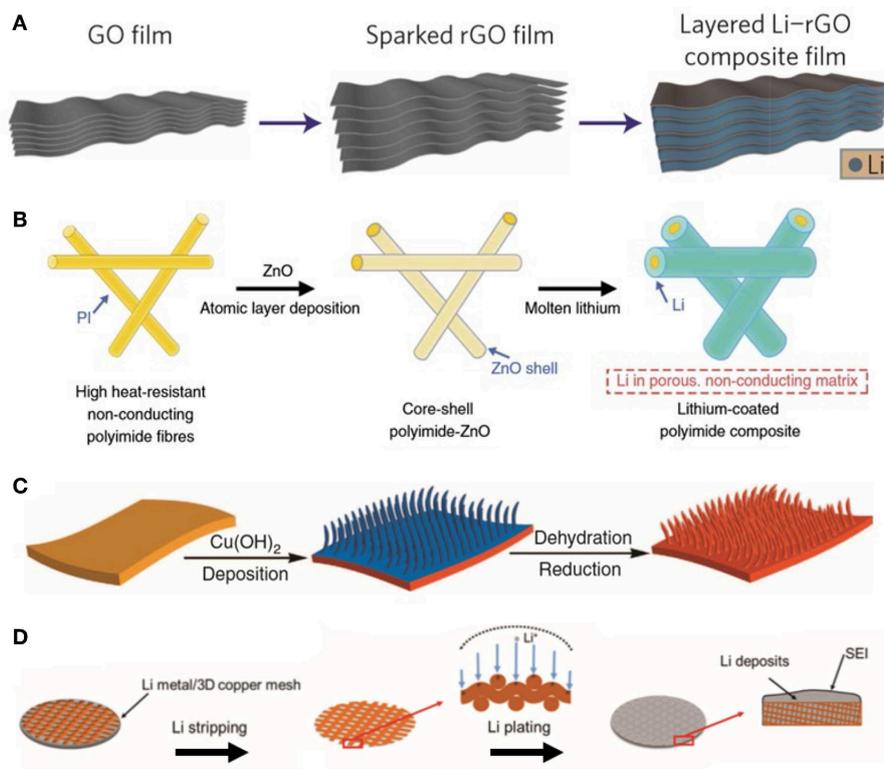
relatively high ionic conductivity and the ability to inhibit polysulfide shuttle (**Figure S1D**) (Choi et al., 2017). But this GPE is not perfect since its mechanical properties are poor and the ionic conductivity still has room for improvement. The main improvement methods are adding nano-fillers, compounding with plasticizers, and so on (**Figure S1E**) (Cheng et al., 2018). Specific examples of nano-fillers include ZnO, MgO,  $\text{Al}_2\text{O}_3$ , polyethylene, and polystyrene (Kim, 2017; Wu N. et al., 2017; Tripathi and Kumar, 2018).

## MODIFICATION ON SEPARATORS

Coating functional layers that can block polysulfides and modify lithium metal anode on the surface of common separator is also an important way, the actions of which are summarized in **Table S2**. A layer of porous carbon material on the surface of the separator not only can immobilize polysulfides but also can be used as an upper current collector to improve the utilization rate of active materials. Hence, various carbon materials are used to modified the separator,

such as mesoporous carbon (Balach et al., 2015), porous graphene (Zhai et al., 2017), super-P (Zhu et al., 2016), microporous carbon nanofiber (**Figure S2A**) (Chung et al., 2015), and acetylene black (**Figure S2B**) (Yang et al., 2019). A multifunctional separator integrated with one or more layers is also a popular improvement direction. Utilizing the synergy effect of carbon and BN on the two sides of a membrane, the performance of the Li-S battery using 1M LiTFSI in DIOX and DME electrolyte (v:v = 1:1) had been significantly improved; there was still  $702 \text{ mAh g}^{-1}$  specific capacity at a rate of 4C (**Figure S2C**) (Kim et al., 2017). On the same principle, a modified separator with compounds of Ketjen Black and MnO coated on Celgard 2400 membrane was developed (Qian et al., 2016).

MXenes are a kind of ultrathin two-dimensional materials that have very high conductivity and surface homogeneity (**Figure S2D**) (Anasori et al., 2017). By coating  $\text{Ti}_3\text{C}_2\text{T}_x$  (T is -O, -OH, or -F) on commercial Celgard 2400 separator, a superior composite membrane can be obtained (**Figure S2E**). At a rate of 0.5C, the capacity of the Li-S battery after 500 cycles was



**FIGURE 2 | (A)** Schematic of the preparation process of a layered Li-rGO composite film (Lin et al., 2016b). Copyright 2016 Springer Nature. **(B)** Composite Li anode based on electrospun polyimide PI coated with a layer of lithiophilic ZnO (Liu Z. C. et al., 2019). **(C)** Preparation of a 3D porous copper (Yang et al., 2015). **(D)** The surface of Li anode modified with copper mesh exhibits uniform Li deposition (Li Q. et al., 2017). Copyright 2017 John Wiley and Sons.

550 mAh g<sup>-1</sup>, and the capacity attenuation per cycle was only 0.063% in an electrolyte of 1 M LiTFSI in DME and DOL (v:v = 1:1) (Song et al., 2016).

## COATING ON THE SURFACE OF LITHIUM

Applying a protective layer directly on the surface of the Li anode is also a facile and effective means. The main method is coating some protective layers such as carbon-based materials, polymer, alloy, and ceramic layer, whose actions are summarized in Table S3.

Without question, the protective layer should have sufficient lithium ionic conductivity, chemical inertness, and superior stability. Various carbon materials such as carbon nanofiber (CNF) (Figure S3A) (Zhang A. Y. et al., 2016), nitrogen-doped few-layer graphene (N-FLG) sheets (Figures S3B, S4A) (Kang et al., 2016), artificial graphite particles (Sun et al., 2016), multi-walled carbon nanotube (Deng et al., 2019), and ladderlike carbon nanoarrays (Figure S4B) (Liu L. et al., 2018) were used to homogenize the current density and promote the even deposition of lithium.

Various polymers also provide a wide range of options for surface modification because of the unique characters (Liu Z. C. et al., 2019). For example, Li-S battery using a

lithium metal anode modified with a soft, viscous polymer layer showed excellent cycling stability (Figure S3C), with 737 mAh g<sup>-1</sup> specific capacity after 300 cycles at 0.2C when using an electrolyte of 0.6 M LiTFSI in DOL/DME (v:v, 1/1) with 0.4 M LiNO<sub>3</sub> as an additive (Zheng et al., 2016). This novel protective layer owned characteristic of slow flow, so it can homogenize the flow of lithium ions and then inhibit dendrite growth (Figure S4C); another advantage is that the process for modifying a polymer protective layer is relatively simple. A 4-μm-thick β-PVDF coating on lithium metal anode made the coulombic efficiency of Cu-Li cells remain 98% in 200 cycles at 1 mA/cm<sup>2</sup> when using an electrolyte of 1 M LiTFSI in DOL and DME (v:v = 1:1) with 3 wt.% LiNO<sub>3</sub> additive (Figure S4D) (Luo et al., 2018).

## PROVIDING HOST MATERIALS FOR LITHIUM DEPOSITION

Layered or three-dimensional frame structure compound has been considered as an effective route to avoid the issues such as the uneven lithium deposition, severe volume change, and safety risks. The frame structure materials include carbon-based materials, polymer materials, metallic materials, and so on, and their actions are summarized in Table S4.

Reduced graphene oxide (**Figure 2A** and **Figure S5A**) (Lin et al., 2016b) and three-dimensional non-stacked framework graphene (**Figure S5B**) (Zhang R. et al., 2016) are good illustrations of carbon-based materials. Adding lithiophilic component such as ZnO could further improve the lithiophilicity and reduce the lithium nucleation overpotential (**Figure S5C**) (Liang et al., 2016).

Highly cross-linked polymeric substrates have abundant pore channels where the  $\text{Li}^+$  can transport rapidly. By electrospinning technique, a polyimide (PI) mesh with a lithiophilic ZnO shell was obtained (**Figure 2B**), then molten metal lithium was infused into the matrix to prepare a composite Li anode (**Figure S5D**) (Liu Y. et al., 2016). Copper is well-suited as an anode current collector for its high conductivity and stability at low potential. Hence, numerous studies were focused on 3D Cu; notable examples of it are 3D Cu/Li (**Figure 2C** and **Figure S5F**) (Yang et al., 2015) and copper mesh /Li composite anode (**Figure 2D** and **Figure S5E**) (Li Q. et al., 2017).

In addition, lithium alloy is also a simple and scalable way to improve the Li-S battery. For example, a Li-Mg (mass ratio: 18.6:81.4) alloy anode was developed. The Mg matrix provided host for the lithium to acquire an even deposition. Also, Mg element participated in the formation of a robust SEI (Kong et al., 2019). Other types of lithium alloys such as Li/Sn (Qiu et al., 2019) and Li/Al (Zhong et al., 2018) had also been proven effective though more studies are still needed.

## SUMMARY

Due to various methods, the performance of lithium-sulfur battery has been greatly improved. However, batteries tested in the experiment are all coin cells, the relatively low current density and the excess amount of lithium underestimate the problems of lithium metal anode to some extent. It is necessary to test the electrochemical performance under the conditions of high current density ( $>3.0 \text{ mA/cm}^2$ ) (Yan et al., 2019) and matching the amount of lithium with the cathodic active materials, so as to meet the needs of practical application.

In addition, problems in lithium-sulfur batteries are various and correlated. Meanwhile, superior comprehensive performance rather than single performance improvement

is more urgently needed. Considering that the gel polymer electrolyte has good compatibility with the electrodes, which is favorable for the uniform deposition and stripping of lithium physically. At the same time, the migration of polysulfides can also be suppressed to some extent. More importantly, the gel polymer electrolyte is simple in manufacturing process and low in cost, which is advantageous for mass production. Therefore, we believe that gel electrolyte, which improved by adding fillers, blending, cross-linking and so on, is a very promising direction.

Lastly, the use of more advanced technology to study the mechanism of lithium metal anodes in lithium-sulfur batteries is also of great help in guiding the improvement strategies. All in all, the understanding and researches on the lithium metal anode in lithium-sulfur batteries are still less, and in order to solve the practical application of lithium-sulfur batteries, more work needs to be done.

## AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

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## SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fchem.2019.00827/full#supplementary-material>

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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