Pyrite-Type CoS$_2$ Nanoparticles Supported on Nitrogen-Doped Graphene for Enhanced Water Splitting

Wei Zhang$^1$, Xiaoya Ma$^1$, Cheng Zhong$^{1,2}$, Tianyi Ma$^{3,*}$, Yida Deng$^{1,2}$, Wenbin Hu$^{1,2}$ and Xiaopeng Han$^{1,4,5,*}$

$^1$ Tianjin Key Laboratory of Composite and Functional Materials, School of Materials Science and Engineering, Tianjin, China, $^2$ Key Laboratory of Advanced Ceramics and Machining Technology (Ministry of Education), Tianjin University, Tianjin, China, $^3$ Discipline of Chemistry, University of Newcastle, Callaghan, Newcastle, NSW, Australia, $^4$ Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin, China, $^5$ Research Institute of Tsinghua University in Shenzhen, Guangdong, China

It is extremely meaningful to develop cheap, highly efficient, and stable bifunctional electrocatalysts for both hydrogen and oxygen evolution reactions (HER and OER) to promote large-scale application of water splitting technology. Herein, we reported the preparation of CoS$_2$ nanoparticles supported on nitrogen-doped graphene (CoS$_2$@N-GN) by one-step hydrothermal method and the enhanced electrochemical efficacy for catalyzing hydrogen and oxygen in water electrolysis. The CoS$_2$@N-GN composites are composed of nitrogen-doped graphene and CoS$_2$ nanocrystals with the average size of 73.5 nm. Benefitting from the improved electronic transfer and synergistic effect, the as-prepared CoS$_2$@N-GN exhibits remarkable OER and HER performance in 1.0 M KOH, with overpotentials of 243 mV for OER and 204 mV for HER at 10 mA cm$^{-2}$, and the corresponding Tafel slopes of 51.8 and 108 mV dec$^{-1}$, respectively. Otherwise, the CoS$_2$@N-GN hybrid also presents superior long-term catalytic durability. Moreover, an alkaline water splitting device assembled by CoS$_2$@N-GN as both anode and cathode can achieve a low cell voltage of 1.53 V at 60 °C with a high faraday efficiency of 100% for overall water splitting. The tremendously enhanced electrochemical behaviors arise from favorable factors including small sized, homogenously dispersed novel CoS$_2$ nanocrystals and coupling interaction with the underlying conductive nitrogen-doped graphene, which would provide insight into the rational design of transition metal chalcogenides for highly efficient and durable hydrogen and oxygen-involved electrocatalysis.

Keywords: water splitting, cobalt sulfide, nanoparticle, graphene, HER/OER, composite

INTRODUCTION

The large demand of clean and sustainable energy stimulated intensive research on the development of efficient and robust electrochemical energy conversion systems such as water splitting that can produce hydrogen and oxygen (Wang J. et al., 2016; Jia et al., 2017; Li H. et al., 2017; Zheng et al., 2017). It consists of two half reactions: the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) (Dong et al., 2015; Menezes et al., 2015; Sun et al., 2017; Han et al., 2018). However, slow reaction dynamics...
and high overpotential limit the wide application of water electrolyzer (Cheng et al., 2017a; Ma et al., 2017; Huang et al., 2018). High-performance electrocatalysts are urgently needed to reduce the overpotential and improve the energy efficiency (Fang et al., 2017; Yin et al., 2017; Shit et al., 2018). Currently, Pt-based materials and noble metal oxides (RuO2, IrO2) are the best catalysts for HER and OER (Han et al., 2014; Lee et al., 2015; Wang et al., 2015), respectively. However, high price and limited reserves restrict the wide application of these noble metal-based materials (Cheng et al., 2017b; Su et al., 2017). Moreover, these catalysts are still faced the problems of inferior long-term stability and unsatisfied bifunctional activity. Therefore, it is of great significance to design and develop high-abundant, high active and stable precious metal-free electrocatalysts (Forgie et al., 2010; McCrory et al., 2015).

Recently, transition metal sulfides, especially cobalt sulfide, have attracted much research attention because of their earth-abundance, environmentally green, and significant chemical/electrochemical stability (Wang et al., 2009; Zheng et al., 2015; Han et al., 2017; Liu et al., 2017; Wu et al., 2017). However, the limited active sites and intrinsically low conductivity of traditional cobalt sulfide materials hinder their activity enhancement for catalyzing HER and OER (Liu et al., 2013). Therefore, the combination of metal sulfides and conductive materials is supposed to increase the electrical conductivity and meanwhile synergistically promoting the catalytic activity (Zhou et al., 2019). For example, Zn–Co–mixed sulfide nanostructure on carbon fiber paper has been synthesized for efficient rechargeable zinc–air batteries and water electrolysis (Wu et al., 2017); CoS8 nanoparticles were anchored on nitrogen and sulfur dual-doped carbon nanosheets for bifunctional oxygen evolution and reduction reactions (Gulzar et al., 2017), CoS4/CoS8 heterostructure supported on nickel foam was developed as an efficient catalytic electrode for accelerating HER and OER (Wang et al., 2018). Previous investigations demonstrated that, among various cobalt sulfides (i.e., CoS4, CoS8, CoS2, etc.), the pyrite-type CoS2 exhibited the superior intrinsic performance owning to the abundant cobalt active sites and more proton-acceptor centers as a result of the unique crystal structure and S-rich nature (Kumar et al., 2018). Accordingly, it appears to be a smart strategy to design CoS2 nanostructure/conductive supported hybrid material to further optimize the HER and OER capability to replace the precious metal-based catalysts, thereby promoting the large-scale implementation of overall water splitting technologies (Wang J. et al., 2016; Xia et al., 2017).

In this work, we prepared the composite material of CoS2 uniformly supported on nitrogen-doped graphene (CoS2@N-GN) by one-step hydrothermal method and its application as bifunctional electrocatalyst for OER/HER and overall water-splitting in alkaline media. The average size of CoS2 is about 73.5 nm, homogeneously dispersed on the N-doped reduced graphene oxide nanosheet. Electrochemical tests reveal that the CoS2@N-GN hybrid exhibits superior catalytic performance than bare CoS2 and physically mixture sample (CoS2/N-GN), delivering low overpotentials of 243 and 204 mV at current density of 10 mA cm−2 for OER and HER, respectively. The in-situ grown composite electrode also presents remarkable long-term catalytic durability with negligible activity decay after 12 h period. Furthermore, the alkaline electrolyzer using CoS2@N-GN loaded on carbon fiber paper as both anode and cathode electrodes can achieve 10 mA cm−2 at a low cell voltage of 1.53 V at 60°C with a faradaic efficiency of 100% for overall water splitting. Our research will provide insights on the development of low cost and efficient hybrid electrocatalysts for next-generation energy conversion devices.

EXPERIMENTAL SECTION

Regents and Materials
Nitrogen doped graphene was purchased from Aladdin. Cobalt (II) acetate tetrahydrate (Co(OH)2·4H2O, 99.5%) and Potassium hydroxide (KOH, 99.99%) were purchased from Beijing Chemicals (Beijing, China). Carbon disulfide (CS2, 99%) and ethylenediamine (EN, 99%) were obtained from Tianjin Yuanli Chemical Co. Ltd. (Tianjin, China). The carbon paper (CP) was purchased from Pzechemi Company Limited and used as the substrate of active substance. The deionized water (18.2 MΩ·cm−1) was obtained via Millipore, an ultrapure water system. High purity nitrogen (Air Product, purity 99.995%) gas was used to deaerate the 1 M KOH solution. All the reagents were of analytical grade and used as received without further purification.

Materials Synthesis
The CoS2@N-GN hybrid was synthesized by one step hydrothermal method. Typically, 30 mg of nitrogen doped graphene was put into a beaker with 100 mL and then 35 mL of deionized water was added followed by 30 min of ultrasonic agitation. Then, 0.4 mmol of Co(CH3COO)2·4H2O was added into the above mixed solution, followed by magnetic stirring under 800 rounds per minute (rpm) for 10 min. Then 0.16 mL of EN was added into the solution with magnetic stirring for 20 min. Afterwards, 0.16 mL of CS2 was dropped into the solution to form a uniform mixture after magnetic stirring for another 20 min. The above aqueous solution was then transferred into a 50 mL Teflon-lined stainless autoclave and then maintained at 200°C for 9 h. After cooling naturally to room temperature, the product was separated by centrifugal force, washed by distilled water for three times, and then lyophilized. The preparation of pure CoS2 was the same as the above route without adding 30 mg nitrogen doped graphene. The synthesis of physical mixture of CoS2 and N-doped graphene was achieved by mechanically mixed two components at mass ratio of 1:1.

Materials Characterization
The phase purity of the as-prepared samples was characterized by X-ray diffraction (XRD, Bruker/D8 Advanced with Cu Kα radiation) at a scanning rate of 2° min−1. The morphological micro-nanostructures were characterized by field-emission scanning electron microscopy (SEM, Hitachi S4800, 30 kV) and transmission electron microscopy (TEM, JEOL JEM-2100F, 200 kV) equipped with an energy-dispersive spectrometer (EDS). The Brunauer-Emmett-Teller (BET) specific surface area was...
determined by N\textsubscript{2} adsorption/desorption isotherms at 77 K using the AutosoriQ instrument (Quantachrome U.S.) with a 6 h outgas at 80\degree C. X-ray photoelectron spectroscopy (XPS) was conducted by using a Perkin Elmer PHI 1600 ECSA system.

**Electrocatalytic Measurements**

The electrocatalytic properties of the synthesized catalysts were tested on an IviumStat workstation using a three-electrode configuration. All the electrochemical data was performed in 1.0 M KOH electrolyte, which was saturated with high-purity N\textsubscript{2} (Air Product, purity 99.995 \%) for OER and HER for at least 30 min before each test and maintained under the corresponding atmosphere during the whole experiment. In addition, a saturated calomel electrode (SCE), and a platinum foil electrode were employed as reference electrode, and counter electrode. The linear sweeping voltammetry (LSV) of ORR and OER were scanning at a same scan rate of 5 mV s\textsuperscript{-1}. The HER and OER potentials were corrected to the reversible hydrogen electrode (RHE) on the basis of following equation:

\[
E(\text{vs. RHE}) = E(\text{vs. SCE}) + 0.059 \times pH + 0.241V \tag{1}
\]

The electrochemical data of HER and OER was measured from \(-0.8\) to \(-1.6\) V vs. SCE, and 0.2 to 1.0 V vs. SCE, respectively. Electrochemical impedance spectra was carried out in a frequency range of from 100 to 100 mHz at a potential of 0.6 V vs. RHE. The obtained HER and OER linear sweeping voltammetry (LSV) data was treated with iR-compensation according to the equation: \(E_c = E_m - I_m \times R_s\), where \(E_c\), \(E_m\), \(I_m\), and \(R_s\) stand for compensated voltage, measured voltage, measured voltage and electrolyte resistance, respectively. The mass loading of synthesized electrocatalysts was about 1.5 mg cm\textsuperscript{-2}. The RuO\textsubscript{2} and Pt/C electrodes were also prepared for comparison with the same mass loading.

**RESULTS AND DISCUSSION**

The synthetic procedure of the composite materials follows a facile, one-step, and hydrothermal method. As shown in **Figure 1a**, the power X-ray diffraction (XRD) pattern of CoS\textsubscript{2}@N-GN can be assigned to cubic CoS\textsubscript{2} (JCPDS no. 41-1471), suggesting the successful formation of pyrite CoS\textsubscript{2} phase
in the hybrid. The morphological structures were characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM) techniques. SEM image in Figure 1b revealed that CoS$_2$ nanoparticles were uniformly anchored on nitrogen-doped graphene nanosheets. The average crystallize size is around 73.5 nm (Figure S1), which coincides with the Scherrer analysis based on the XRD pattern. The homogeneous distribution of CoS$_2$ nanocrystals on graphene is further confirmed by the TEM imaging (Figure 1c). Moreover, in the high-resolution TEM (HRTEM) of inset in Figure 1c, an observed lattice spacing of 0.28 nm matches the (200) lattice plane of CoS$_2$ (Ma et al., 2018), further proving the XRD analysis. Otherwise, the elemental mapping reveal the homogeneous dispersion of Co, S, C and N in the composite (Figure 1d), indicating the uniform distribution of CoS$_2$ nanoparticles on the N-doping graphene substance. These observations collectively demonstrate the successful synthesis of CoS$_2$@N-GN hybrid through stepwise controlled strategies. The Brunner–Emmet–Teller (BET) surface area of CoS$_2$@N-GN hybrid was characterized to be 79.8 m$^2$ g$^{-1}$ (Figure S2). Thus, the CoS$_2$@N-GN shows a significantly high BET area, which can provide more electroactive sites and facilitate electrolyte infiltration during the catalytic process (Li et al., 2018). The content of CoS$_2$ in the hybrid is determined to be around 51 wt% (Figure S3) by thermal gravimetric analysis (TGA) (Liang et al., 2012).

| Catalysts | Reaction tafel slope (mA dec$^{-1}$) | Overpotential @10 mA cm$^{-2}$ (mV) | R$_{ct}$ (Ω) | C$_{dl}$ (mF cm$^{-2}$) |
|-----------|-----------------------------------|----------------------------------|-------------|-----------------|
| CoS$_2$@N-GN | OER | 51.8 | 243 | 1.85 | 76.7 |
| | HER | 108.5 | 204 | | |
| CoS$_2$/N-GN | OER | 71.6 | 307 | 3.2 | 20.1 |
| | HER | 139.1 | 278 | | |
| pure CoS$_2$ | OER | 81.4 | 327 | 4.02 | 13.6 |
| | HER | 144.7 | 297 | | |

TABLE 1 | Summary of the electrochemical activities of CoS$_2$@N-GN, CoS$_2$/N-GN and pure CoS$_2$ electrodes.

FIGURE 2 | (A) XPS survey, (B) N 1s, (C) Co 2p, and (D) S 2p XPS spectra of the CoS$_2$@N-GN hybrid.
The chemical valence states of N, Co, O and S in CoS$_2$@N-GN were characterized by X-ray photoelectron spectroscopy (XPS, Figure 2). The XPS survey spectrum in Figure 2A shows the existence of C, N, Co, S, as well as O. The determined stoichiometric ratio is consistent with the result from energy-dispersive spectroscopy (Figure S4). The existence of O is due to exposure to air (Zhang et al., 2017). Additionally, the high-resolution N 1s spectrum (Figure 2B) can be deconvoluted into three sub-peaks located at 400.30 eV (pyridinic N), 402.20 eV (pyrrolic N), and 403.38 eV (graphitic N) (Fu et al., 2016; Li G.)
et al., 2016; Wang Z. et al., 2016). It is well known that doped N into carbon framework can potentially increase the active sites and thereby benefit the electrochemical catalytic activity enhancement (Ma et al., 2014; Li et al., 2018). The Co 2p spectra (Figure 2C) can be de-convoluted into six species, including pairs of fitting peaks for Co$^{2+}$ and Co$^{3+}$, and their shakeup satellites (Xiao et al., 2013; Ma et al., 2016; Zhu et al., 2016). The Co 2p$_{3/2}$ peaks at 778.9 and 782.4 eV can be assigned to Co atoms in CoS$_2$@N-GN and surface oxidized cobalt species coordinated with oxide or hydroxyl groups, respectively (Li C. et al., 2017). The main peak centered at 798.9 eV corresponds to spin–orbit characteristic peak of Co 2p$_{1/2}$ in CoS$_2$ compounds. For the high-resolution S 2p spectrum (Figure 2D), a weak doublet situated at 163.3 eV corresponds to S 2p. The peak located at 163.7 eV is assigned to the S 2p$_{1/2}$ of S$^{2-}$ ions that matched with metal ions (Du et al., 2015). The peak at 169.7 eV indicates the presence of an oxygen-sulfur (O-S) bond in the CoS$_2$@N-GN compound, which may be ascribed to the surface oxidation, as confirmed by previous observations (Sivanantham et al., 2016).

The electrocatalytic OER performance of synthesized CoS$_2$@N-GN, together with CoS$_2$/N-GN (the mechanical mixtures of pure CoS$_2$ and nitrogen-doped graphene) and pure CoS$_2$, was assessed by a three-electrode configuration in 1.0 M KOH. As shown in the polarization curves (Figure 3A and Table 1), CoS$_2$@N-GN hybrid displays an overpotential of 204 mV to achieve an OER current density of 10 mA cm$^{-2}$, which is much lower than those of CoS$_2$/N-GN (278 mV) and pure CoS$_2$ (297 mV), highlighting the superior OER activity of in-situ fabricated CoS$_2$@N-GN. The fitted Tafel value of the CoS$_2$@N-GN catalyst is 51.8 mV dec$^{-1}$, which is lower than those of CoS$_2$/N-GN (71.6 mV dec$^{-1}$) and pure CoS$_2$ (81.4 mV dec$^{-1}$) (Figure 3B), indicating more favorable OER kinetics over the CoS$_2$@N-GN surface. Otherwise, the corresponding charge transfer resistance ($R_{ct}$) values of CoS$_2$@N-GN, CoS$_2$/N-GN and pure CoS$_2$ are fitted to be 1.85, 3.2, 4.02 Ω, respectively (Figure 3C), suggesting that the efficient charge transfer contributes the superior activity of CoS$_2$@N-GN electrode (Li P. et al., 2016). The presented OER performance parameters here are among the non-noble metal-based OER
electrocatalysts reported in literatures (Table S1). In addition to good catalytic activity, long-term stability is also a critical factor in evaluating its practical performance. As we can see, the OER polarization curve of CoS$_2$@N-GN after 1000 OER cycles at a scanning rate of 200 mV s$^{-1}$ almost overlays the initial one (Figure 3D), evidencing that the activity is considerably maintained after the long-term continuous cycles. This is also corroborated by the chronopotentiometric response (Figure 3E), in which that the overpotential does not increase after 12 h period at an anodic current density of 10 mA cm$^{-2}$. The SEM image of CoS$_2$@N-GN further shows that the morphology is substantially unchanged after the 500 and 1000 OER cycles (Figure S5 and Figure 3f), signaling the remarkable structure durability of the composite catalyst. This may be mainly ascribed to the intrinsic crystal stability of CoS$_2$ and firm attachment between the in situ grown sulfide nanostructures and the graphene support. The possible reaction mechanism of Co-based materials for catalyzing OER in alkaline media follows the sequence (Chen et al., 2015; Ma et al., 2018):

\begin{align}
\text{Co} + 2\text{OH}^- & \rightarrow \text{Co(OH)}_2 + 2e^- \quad (2) \\
3\text{Co(OH)}_2 + 2\text{OH}^- & \rightarrow \text{Co}_3\text{O}_4 + 4\text{H}_2\text{O} \quad (3) \\
\text{Co}_3\text{O}_4 + \text{H}_2\text{O} + \text{OH}^- & \rightarrow 3\text{CoOOH} + \text{e}^- \quad (4) \\
\text{CoOOH} + \text{OH}^- & \rightarrow \text{CoO}_2 + \text{H}_2\text{O} + \text{e}^- \quad (5) \\
\text{Overall:} 4\text{OH}^- & \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \quad (6)
\end{align}

As shown in Figure S6a, after 1000 OER cycles, it can be clearly seen that the proportion of Co$^{3+}$ is significantly increased. Meanwhile, the proportion of S-O is also significantly increased (Figure S6b), suggesting the considerable oxidation, consistent with previous observations (Han et al., 2018; Ma et al., 2018).

In the context of developing bifunctional catalysts for overall water oxidation, the HER performance of synthesized samples was tested in the same electrolyte. All the linear sweeping voltammetry (LSVs) measurements were collected at a scan rate of 5 mV s$^{-1}$ while the electrolyte is saturated with N$_2$ during the experiment. From the HER LSVs in Figure 4A, it is clear that the pure CoS$_2$ shows weak electrocatalytic HER activity. The in-situ fabricated CoS$_2$@N-GN achieves a current density of
10 mA cm$^{-2}$ at an overpotential of 204 mV, which is much lower than that of physical mixture of CoS$_2$/N-GN (278 mV) and pure CoS$_2$ (297 mV).

The corresponding Tafel slopes of N-GP@CoS$_2$, N-GP/CoS$_2$, and pure CoS$_2$ are 108.5, 139.1, and 144.7 mV dec$^{-1}$, respectively, which is comparable to those of transition metal sulfides catalysts reported recently (Figure 4B) (Liang et al., 2016; Sivanantham et al., 2016). In particular, N-GP@CoS$_2$ shows the lowest Tafel slope of 108.5 mV dec$^{-1}$ among three synthesized catalysts. The disparity in Tafel slopes further corroborates the advantage of the synergistic effect between N-GN and CoS$_2$. The double-layer capacitance ($C_{dl}$) values are determined to be 76.7, 20.1 and 13.6 mF cm$^{-2}$ for CoS$_2$/N-GN, CoS$_2$/N-GN, and pure CoS$_2$ (Figure S7), demonstrated that the CoS$_2$/N-GN could provide larger electrochemical active area for electrolyte soaking and water adsorption, which is another favorable factor in enhancing the electrocatalytic capability. The HER typically occurs through two reactions in alkaline solution (Li H. et al., 2017; Ma et al., 2018) Volmer reaction ($\text{H}_2\text{O} + e^- + M \rightarrow M\text{-H}^{\text{ad}} + \text{OH}^-$, where $M\text{-H}^{\text{ad}}$ is a reactive intermediate and M is the catalytically active site) and Heyrovsky reaction ($\text{H}_2\text{O} + M\text{-H}^{\text{ad}} + e^- \rightarrow M + \text{H}_2 + \text{OH}^-$). The key HER performance parameters presented here are among the best non-noble metal HER electrocatalysts reported in literatures (Table S2). Moreover, after 1000 CV cycles, the polarization curve of CoS$_2$/N-GN is remarkably maintained in comparison with the initial state (Figure 4C). The morphology of CoS$_2$/N-GN electrode was still essentially preserved (Figure S8), further confirming the structural durability, which is mainly due to the intrinsic stability of CoS$_2$ and the strong chemical interaction between two components. In a continuous polarization period of 12 h (Figure 4D), the HER current retention of CoS$_2$/N-GN again confirms its remarkable long-term stability for catalyzing the HER in alkaline media.

As shown in Figure 5A, to further investigate its practical application for overall water-splitting, CoS$_2$/N-GN electrode was applied as both anode and cathode to assemble an electrochemical device, which presents low cell voltages of 1.70 V at 25°C and 1.53 V at 60°C to achieve 10 mA cm$^{-2}$ in 1 M KOH. The generated oxygen and hydrogen bubbles on both anode and cathode surface can be obviously seen at 10 mA cm$^{-2}$ (Figure 5B). In addition, the stability of the electrolyzer device was tested with sustained polarization for 12 h at 1.90 V. The activity degradation of CoS$_2$/N-GN (8.1%) is even lower than that of the combined catalyst of precious Pt/C + RuO$_2$ (17.6%, Figure 5C), further demonstrating the considerable durability of the CoS$_2$/N-GN electrode in a practical water splitting device. As displayed in Figure 5D, the amounts of collected H$_2$ and O$_2$ match well with the calculated values at a constant current density of 10 mA cm$^{-2}$, which shows advanced concept of efficient energy conversion from electric energy to chemical fuel gas. The relationship between time and gas quantity is calculated according to the following formula:

$$I \times t = V \times N_A \times 22.4$$

$I$, $t$, $e$, $V$ and $N_A$ are current (mA), time (s), 1.6 × 10$^{-19}$ C, volume (L) and avogadro constant (6.02 × 10$^{23}$).

**CONCLUSION**

In summary, a novel CoS$_2$/N-GN hybrid was successfully prepared through a facile and one-step hydrothermal strategy. Compared with CoS$_2$/N-GN and pure CoS$_2$ catalyst, CoS$_2$/N-GN hybrid exhibits remarkable overall electrocatalytic activity toward OER and HER in alkaline electrolyte as well as the enhanced long-term stability. Moreover, the CoS$_2$/N-GN enables the assembled water splitting device with low cell voltage, high efficiency and prolonged operational life. The remarkable electrochemical properties are attributed to the high intrinsic activity of CoS$_2$, efficient electron transfer provided by N-doped graphene and the synergetic coupling interaction between two components. This work establishes the low cost and earth-abundant metal sulfide-based composite catalyst as a promising and high performance functional electrode for promoting large-scale water electrolyzer technologies.

**AUTHOR CONTRIBUTIONS**

WZ conducted the experiments and helped write the manuscript. XM helped with operating the experiments and data analysis. CZ and YD interpreted the results. XH, TM, and WH supervised the research. All authors read and approved the final manuscript.

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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.2018.00569/full#supplementary-material

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**Conflict of Interest Statement:** 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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