Backstory

Toward Clean Energy Devices: From a Fundamental Understanding to Practical Applications

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Xueliang (Andy) Sun is a Tier 1 Canada Research Chair, Fellow of the Royal Society of Canada and Canadian Academy of Engineering, and Professor in the Department of Mechanical and Materials Engineering at the University of Western Ontario (Western), Canada. Sun received his Ph.D. in materials chemistry in 1999 from the University of Manchester, UK. Following his graduate studies, Sun moved to Canada for his postdoctoral training at the University of British Columbia, Canada and L'Institut National de la Recherche Scientifique (INRS), Canada. From his Ph.D. studies to postdoctoral training, Sun was able to expand his research across different fields, including electrochemical corrosion, nanostructured materials, and PEM fuel cells. Sun joined Western as an assistant professor in 2004 and was promoted to full professor in 2012. At Western, Sun has dedicated his research toward the development of advanced materials for clean energy storage and conversion. Currently, Sun's research is based on three interrelated aspects, as shown in Figure 1, including material fabrication, energy device design, and advanced characterization techniques.

Materials: From Nano to Single Atom

Since 2007, Sun has dedicated his group to the development and application of atomic layer deposition (ALD) for energy storage and conversion applications. ALD is an advanced gas-phase thin film deposition technology that is based on self-limiting surface reactions to form materials with atomic precision. ALD shows unique properties, including uniform and conformal coatings, stoichiometric reaction chemistry, and low growth temperatures. The ALD technique was initially developed and widely promoted for the electronic and semiconductor industries. However, the unique properties also caught the eyes of researchers in the energy storage and conversion communities. Over more than one decade, Sun and his group became one of the most well-known labs for the application of ALD techniques for energy applications. In the initial stage, various recipes of metal oxide by ALD with controllable structures were intensively developed by Sun and his group members, such as Al_2O_3, TiO_2, ZrO_2, SnO_2, Fe_2O_3, et al. The synthesized ALD metal oxides were further used as electrodes or coatings in Li-ion batteries. Inspired from the unique properties of ALD, Sun developed SnO_2 on graphene nanosheets by ALD and used them as an anode material for LIBs (Li et al., Adv. Funct. Mater. *22*, 1647). This work successfully demonstrated the advantages of ALD in that not only could the thickness of the coatings be controlled, but also, the structures of SnO_2 were finely tuned. Both crystalline and amorphous SnO_2 were deposited by controlling the deposition temperature during the ALD process. More importantly, it was found that the amorphous SnO_2 can effectively buffer the huge volume change and shrinkage of the Sn lattice during electrochemical cycling. Besides the fabrication of binary metal oxide compounds by ALD, Sun started to develop more complicated recipes for ternary complexes, particularly for Li-containing solid-state electrolyte

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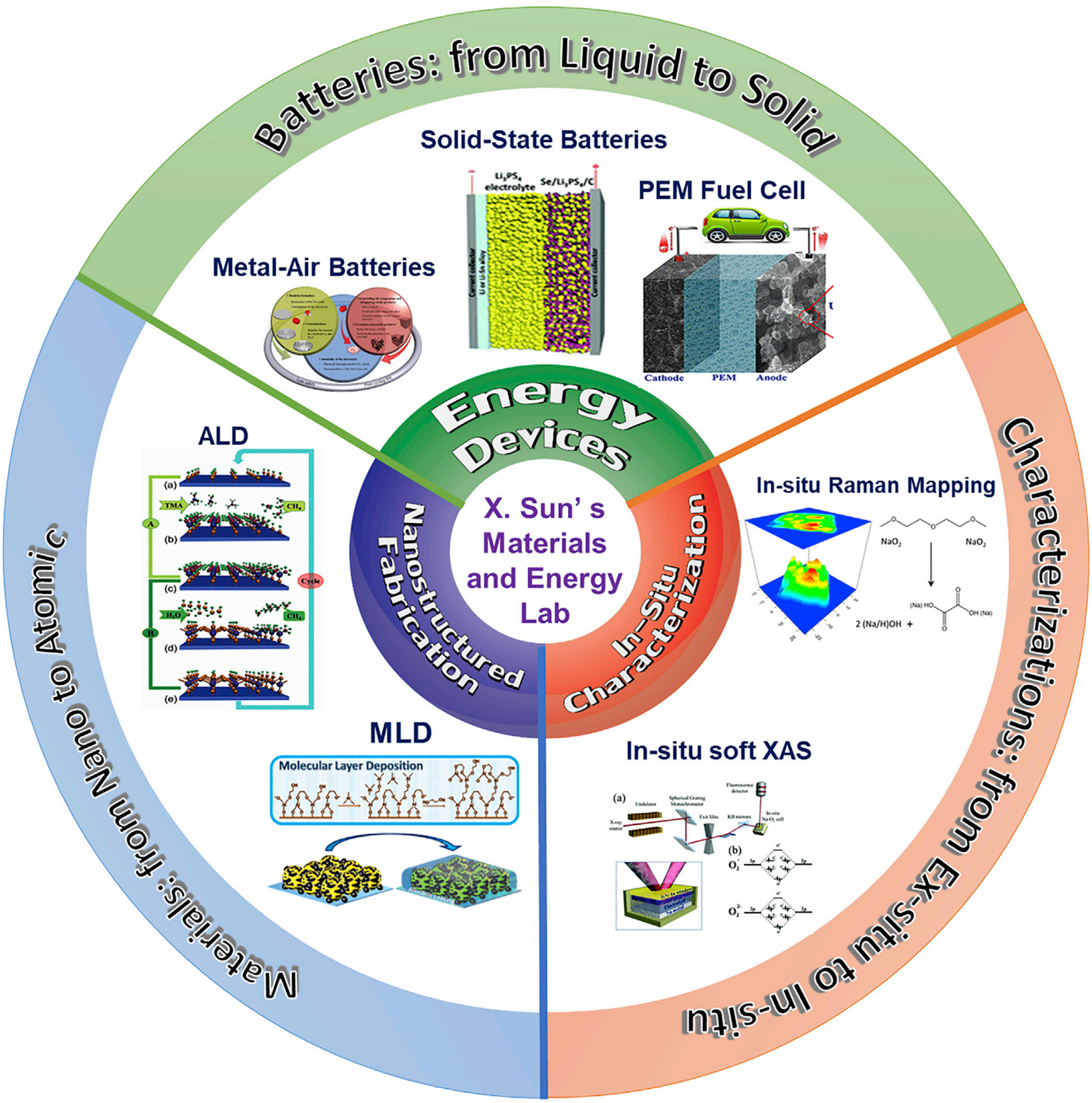

Figure 1. Research Focus in Sun's Group

thin-films. With the significant efforts and continuous dedication of several group members, five types of thin-film solid-state electrolytes had been fabricated by the ALD process, including $Li_4Ti_5O_{12}$, $LiTaO_3$, $LiNbO_3$, Li_2SiO_3, and Li_3PO_4. All these compounds have been proven as potential interfacial materials to stabilize the cathode/electrolyte interface due to their electrochemical stability windows. Furthermore, Sun was able to develop more challenging ALD processes such as $LiFePO_4$, which is one of the most popular cathode materials for LIBs (Liu et al., Adv. Mater. *26*, 6472). This example is the first report using ALD techniques to deposit complicated compounds with four elements. Besides ALD, molecular layer deposition (MLD) has received increasing attention in this community for energy applications. MLD not only inherits all the advantages of ALD but also possesses other unique properties due to the organic chains in the films. Sun was keenly aware of the importance of the MLD technology and dedicated more time on the development of MLD coatings. Up to now, Sun has been able to fabricate and apply several MLD thin films in his lab, such as different metalcone (alucone, zincone, zircone et al.) and pure polymers (polyurea, PEDOT et al.).

Sun focused on not only the development of different ALD and MLD chemistries but also the application of ALD/MLD for battery systems. In 2014, Sun first reported the use of ALD solid-state electrolyte of $LiTaO_3$ as a coating for $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NMC) cathode materials (Li et al., Energy Environ. Sci. *7*, 768). It was the first time a solid-state electrolyte was used as a coating for the cathode, in which the Li-ion conductivity of the artificial layer was shown to play a critical role. Subsequently, Sun designed various approaches to address the challenges for cathode materials with ALD, such as $AlPO_4$, TiO_2, and $LiPO_3$-TiO_2 hybrid coatings. More recently, through collaboration with Dr. Chongming Wang and Dr. Ji-Guang Zhang in Pacific Northwest National Laboratory, they proposed a new concept of infusing ALD Li_3PO_4 into the grain boundaries of cathode secondary particles, which leads to dramatically improved capacity retention and voltage stability (Yan et al., Nat. Energy *3*, 600). Beyond Li-ion batteries, Sun also extended the application of ALD/MLD into next-generation batteries. For example, Sun found that the conventional cyclo-S_8-based sulfur cathodes with MLD alucone coating were completely reversible in carbonate electrolyte and exhibit a safe and stable cycle life at high temperature (Li et al., Nano Lett. *16*, 3545). They further provided insight to the mechanism of the electrochemical reaction, which is a solid-phase lithium-sulfur reaction where the sulfur is directly converted to Li_2S without the formation of linear polysulfides (Li et al., Nat. Commun. *9*, 4059). This finding revealed a facile approach to the direct use of cyclo-S_8-based sulfur cathodes in carbonate electrolyte with excellent cycling performances. In addition, Sun expanded the application of ALD/MLD to protection of alkali metal anodes, which are considered as the ''Holy Grail'' anode materials for the future batteries. In 2017, Sun first reported ALD Al_2O_3 (Zhao et al., Adv. Mater. *29*, 1606663) and MLD alucone (Zhao et al., Nano Lett. *17*, 5653–5659) as coatings for Na metal anodes. They also provided a comprehensive comparison between ALD and MLD films as protective layers for alkali metal and proposed the potential mechanisms. In a more recent paper (Zhao et al., Matter *1*, 10.1016/j.matt.2019.06.020), Sun and his members, inspired by the natural-formed solid electrolyte interface (SEI) layers, created a dual-protective layer by ALD and MLD for the Li metal anode. This work provides a remarkable demonstration of the unique properties of ALD/MLD techniques, in which the thicknesses, compositions, structures, and even the mechanical properties can be precisely controlled.

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Other than the application of thin film coatings for energy storage, Sun has also dedicated his work to the application of ALD/MLD for energy conversion systems, particularly PEM fuel cells. His early studies on fuel cells focused on the design of different catalysts, which attracted high citations. For example, the nitrogen-doped graphene (Geng et al., Energy Environ. Sci. *4*, 760) and star-like Pt nanowires catalysis (Sun et al., Angew. Chem. Int. Ed. *50*, 422) were shown to possess high oxygen-reduction activity and durability. Sun also used ALD techniques for fuel cell applications and collaborated with Ballard Power Systems. In 2013, Sun creatively synthesized the isolated single Pt atoms anchored to graphene nanosheet via ALD deposition (Sun et al., Sci. Rep. *3*, 1775), which is the pioneering work for the development of ALD for single-atom catalysis. Furthermore, Sun reported precise control of Pt catalysts on N-doped graphene with sizes ranging from single atoms, subnanometer clusters, to nanoparticles (Cheng et al., Nat. Commun. *7*, 13638). These works successfully extended the methods of synthesizing single atomcatalysts by gas-phase ALD methods. The main contributors for single-atom catalysis are Dr. Shuhui Sun and Dr. Niancai Cheng, who are currently full professors at the Institut National de la Recherche Scientifique (INRS), Canada, and professor at Fuzhou University, China, respectively. More recently, a postdoctoral researcher in Sun's lab, Dr. Lei Zhang, successfully prepared bimetallic dimer structures (Pt-Ru dimers) through an ALD process (Zheng et al., Nat. Commun., 2019). His most recent work provides more opportunities for ALD to control the size and composition of catalysts for fuel cell applications.

The ALD/MLD group plays a key role in Sun's lab and several generations of ALD members have made significant contributions to its development. Several comprehensive and high impact review papers have been summarized by Sun and his ALD group members over the years. (Meng et al., Adv. Mater. *24*, 1017; Liu et al., Nanotechnol. *26*, 024001; Zhao et al., ACS Energy Lett. *3*, 899; Zhao et al., Joule *2*, 2583). The previous ALD group members have had great success in their careers. Dr. Xiangbo (Henry) Meng, one of the first ALD members in Sun's group, is currently PI in the Department of Mechanical Engineering, University of Arkansas, USA. Subsequent developers, Dr. Jian Liu, has a professorship in the School of Engineering at The University of British Columbia, Canada. Among the most recently graduated ALD members, Dr. Biqiong Wang and Dr. Andrew Lushington continue their efforts on ALD in industry at General Motors and Arradiance, respectively.

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The continuous development of new ALD/MLD chemistry and the corresponding application in batteries and fuel cells are continuously ongoing in Sun' group. The new generation of ALD members is exploring new compounds by ALD/MLD and bigger possibilities for the use of ALD/MLD for energy applications.

Batteries: From Liquid to Solid

Sun started his research on electrochemical energy storage systems with conventional Li-ion batteries. For example, Sun collaborated with Johnson Matthey to deeply understand the carbon-coating process for $LiFePO_4$, which was also practical to the partnership for optimizing their mass production process. A former group member, Dr. Jiajun Wang (currently a professor at Harbin Institute of Technology), dedicated more than three years for this project. They found a size-dependent surface phase change occurring in $LiFePO_4$ during the carbon coating process, in which nanoscale particles exhibit extremely high stability (Wang et al., Nat. Commun. *5*, 3415). Subsequently, they had a detailed study on the composition of the new phase and the influence of size, temperature, and annealing atmosphere on the new phase formations (Liu et al., Nat. Commun. *9*, 929). This finding can give guidance to phase composition during the carbon coating process for $LiFePO_4$ and to tune its quality during the manufacturing process.

Metal air batteries, including Li-O_2 and Na-O_2 batteries, are another highlight from Sun's group. His work started from the early electrode design for Li-O_2 batteries, moving toward the chemical and electrochemical fundamentals of Na-O_2 batteries.

The previous account (Yadegari et al., Acc. Chem. Res. *51*, 1532) and review (Yadegari et al., Adv. Mater *28*, 7065) gave a detailed summary of our contributions to the research of Na-air batteries. Sun has devoted significant efforts on the regulation of the surface and structure of air electrodes to control the discharge products of NaO_2 (Yadegari et al., J. Phys. Chem. Lett. *8*, 4794). They also explored other factors in the Na-O_2 cells, including the discharge-charge mechanism, side reactions at the cathode, solid-state catalysts, and O_2/O_2^-, a crossover to the metal anode, which can significantly affect the cycling performances of Na-O_2 batteries. The research and development of Na-O_2 batteries is still in a state of infancy, and challenges arising from the cathode, anode, and electrodes require a deeper fundamental understanding for better battery design.

More recently, Sun moved his group from conventional liquid-based batteries to the next-generation solid-state batteries (SSBs), which is considered as the future of energy storage devices due to their improved safety and energy density. Currently, over 80% of the members in Sun's group are dedicated to the study of SSBs and his group is becoming one of the most active groups around the world working on this area. Sun created several collaborations with the industrial partners to accelerate the practical application of SSBs. Sun's industrial partners for SSBs include General Motors, 3M Canada, China Automotive Battery Research Institute, Ltd (China), and GLABAT Solid-State Battery (Canada). Their collaboration further attracted funding support from government agencies, such as the Ontario Research Fund and Mitacs.

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Sun's research on SSBs has focused on several components of the battery system, ranging from the synthesis of the solid-state electrolytes (SSEs) to the design and modification of the interface between electrodes and electrolytes, and engineering of novel electrode fabrication processes. Moreover, Sun and his group members have developed procedures for the fabrication of four types of SSEs, such as polymer, oxide, sulfide, and halide SSEs. One of the targets of Sun's group is the synthesis of new SSEs with high ionic conductivity and high air stability for practical applications. With this in mind, the postdoctoral fellows in Sun's lab, Dr. Xiaona Li and Dr. Jianwen Liang, designed the halide-based Li_3InCl_6 SSEs with a high ionic conductivity of 1.49×10^{-3} S cm^{-1} and high stability in dry air. The electrolyte was also found to possess good ionic conductivity retention after a reheating process (Li et al., Energy Environ. Sci. *12*, 2665). These researchers further developed another H_2O-mediated synthesis method for Li_3InCl_6 SSEs with a superior ionic conductivity of 2.04×10^{-3} S cm^{-1} at room temperature (Li et al., Angew. Chem. Int. Ed., 10.1002/ange.201909805). This method is a facile and scalable process, which is highly favorable for practical manufacturing. Moreover, larger efforts have been put forward by Sun to address the interfacial challenges between the electrodes and SSEs. ALD/MLD, as shown above, are the key tools in Sun's lab for interface engineering. For example, on the anode/SSEs interface, MLD alucone-coated Li was used for sulfide-based SSEs to reduce side reactions and dendrite growth, resulting in improved electrochemical performances (Wang et al., Nano Energy *53*, 168). On the cathode/SSEs interface, ALD $LiNbO_3$ was used as a buffer layer to stabilize the electrochemical window gap between $LiCoO_2$ and sulfide-based SSEs (Wang et al., Small Methods,

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1900261). The application of ALD/MLD has not only been shown to be effective for sulfide-type electrolytes but is also effective for other SSB systems, including polymers and oxides. In addition, other approaches have also been developed for this purpose. For example, a solution-based method was developed by Sun to fabricate Li_3PS_4 and air-stable Li_xSiS_y protective layers for sulfide-based SSBs (Liang et al., Adv. Energy Mater., 2019, 1902125), in which the protection layers could prevent Li dendrite formation. With the continuous development of electrolyte and interface design, the electrochemical performances of SSBs in Sun's group are among the best in the world. Besides the solid-state Li-ion batteries, Sun is also planning the fabrication of higher energy density solid-state Li-S and solid-state metal-air batteries. Sun first demonstrated an all-solid-state Li-Se battery (Li et al., Energy Environ. Sci. *11*, 2828) and all-solid-state Li-SeSx battery (Li et al., Adv. Mater. *31*, 1808100) with higher capacity and potentially high energy density. Currently, Sun and his industrial partners are looking for more opportunities to realize the commercialization of all-solid-state batteries.

Advanced Characterizations: From *Ex Situ* to *In Situ*

The development of new materials and understanding of electrochemical reaction mechanisms requires in-depth understanding of material structure and chemical reactions. Sun's lab has access to various facilities for regular characterization techniques as well as established connections within the university campus and across the world for more advanced analytical characterization methods. Traditional characterization of battery materials is carried out in an ''ex-situ'' format, which cannot directly reflect the true physicochemical states of materials during electrochemical operation. Based on this, several *in situ* and in-operando characterization techniques have been developed in Sun's lab to monitor the chemical and physical evolution of various battery systems in a real working environment. Up to now, techniques such as *in situ* X-ray diffraction, *in situ* scanning electron microscopy, and *in situ* Raman have been demonstrated by his group. For example, Sun employed a Raman imaging technique to reveal the chemical mechanism behind the decomposition reaction of NaO_2 in the presence of diglyme-based electrolyte, illustrating the side reactions of the discharge products in Na-air batteries (Yadegari et al., Chem. Mater. *30*, 5156).

Synchrotron radiation-based techniques quickly gained Sun's attention when he joined Western University. The synchrotron techniques demonstrate great potential for the energy devices, especially for the investigation of the physical and chemical properties of electrochemical systems. Sun found his collaborator from the Department of Chemistry at Western, Dr. Tsun-Kong Sham, whom together have continued to collaborate over the decades. Sham is a pioneer on the developments of synchrotron-based techniques and has dedicated a large portion of his life to the establishment of the Canadian Light Source. Sun and Sham have co-published over 80 papers and co-supervised more than 12 students/researchers. Sun is now expanding his connections with the scientists in different light sources around the world, such as Canadian Light Source, Advanced Photon Source, Advanced Light Source, and Taiwan Photon Source. Sun's research using synchrotron techniques eventually evolved from ex-situ to *in situ*. For example, Sun reported the use of *in situ* soft X-ray absorption spectroscopy (XAS) for Na-O_2 cells to study the formation and decomposition of the discharge products during battery cycling (Banis et al., Energy Environ. Sci. *11*, 2073). This work illustrated that *in situ* soft XAS is an efficient probe to study the electrochemical mechanism of alkali metal-O_2 batteries. More recently, in-operando X-ray absorption near-edge structure (XANES) was employed to investigate the interfacial phenomena between the

Ni-rich layered cathodes and sulfide solid-state electrolyte, which provided detailed information on the surface structural reconstruction of Ni-rich cathodes in SSBs (Li et al., ACS Energy Lett. *4*, 2480).

Through these collaborations, the students and postdoctoral fellows in Sun's group have many opportunities to travel around the world to different light sources to carry out their experiments. They have also devoted themselves to the design of different *in situ* cell configurations, which is very challenging in its own right. Sun and his group are still making efforts to explore more techniques from synchrotron radiation, not limited to X-ray absorption spectroscopy, but also synchrotron X-ray diffraction (SXRD), and synchrotron X-ray microscopy. These techniques will provide a comprehensive understanding of the battery mechanisms and guide the design of next-generation high-performance batteries.

As one of the leaders in the fields of ALD/MLD and energy applications, Sun has co-authored more than 400 refereed papers, 18 patents (filed or issued), and has held over 120 plenary and keynote talks in international conferences. His work has accumulated more than 24,000 citations with a H-index of 80. Sun's group was listed in

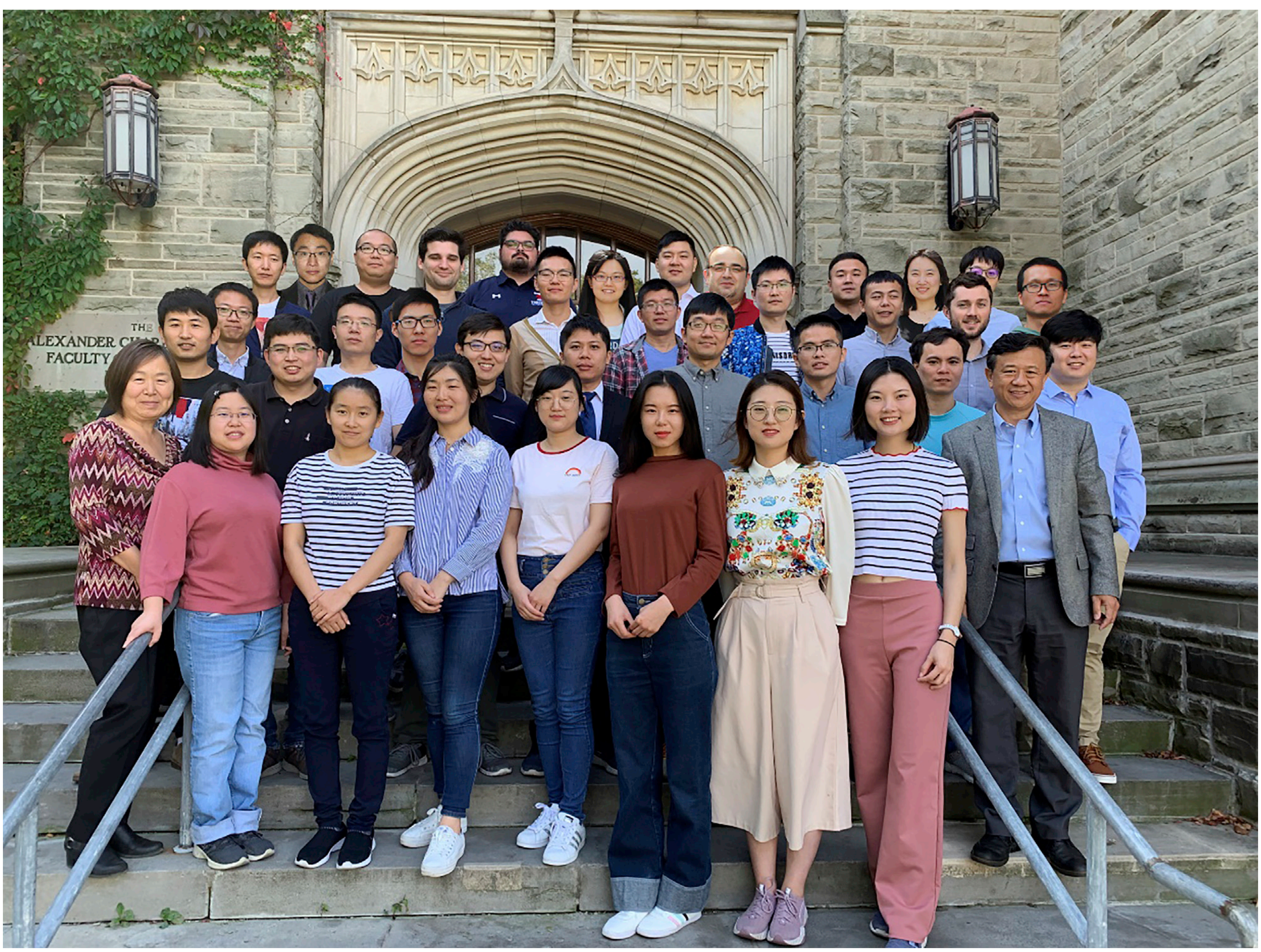

Figure 2. Group Photo of Sun's Group, Taken on September 25, 2019, in the Front of Spencer Engineering Building at the University of Western Ontario

the Highly Cited Researchers 2018 and 2019 by Clarivate. Sun was also selected as the Research Excellence in Materials Chemistry winner from Canada Chemistry Society (2018) and as the 2019 Hellmuth Prize winner, which is the highest honor for research at Western.

Since Sun joined Western as a PI in 2004, he has trained more than 38 Ph.D., 12 visiting Ph.D students, 15 MSc. students and 32 postdoctoral researchers. 11 of the alumni have already obtained professorships in the North American and China. The current group includes near 40 members in total, as shown in Figure 2. Besides the alumni cited above in the text, other professorships supervised by Sun include Dr. Xifei Li (Professor at Xi'an University of Technology, China), Dr. Dongsheng Geng (Professor at University of Science and Technology Beijing, China), Dr. Liang Li (Professor at Soochow University, China), Dr. Biwei Xiao (Materials Scientist at Pacific Northwest National Laboratory, USA).

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