PERSPECTIVES

MATERIALS SCIENCE

Special Topic: Single-Atom Catalysts

Single-atom catalysts by the atomic layer deposition technique

Lei Zhang, Mohammad Norouzi Banis and Xueliang Sun*

Noble metal nanocatalysts have been widely applied in the petrochemical industry, medicine, environmental protection and energy sectors. To decrease the cost and maximize the utilization efficiency, single-atom catalysts (SACs), as a new frontier in heterogeneous catalysis, have attracted considerable attention due to their unique catalytic properties. Unlike traditional nanocatalysts, the catalytic performance of single-atom catalysts is highly dependent on their low-coordination environment, quantum size effects and metal–support interaction. Recently, several methods have been developed for the preparation of single-atom catalysts, including the impregnation method [1], co-precipitation method [2], photo-reduction method [3] and atomic layer deposition (ALD) method [4–6]. Among these, the ALD process is a powerful approach for studying the relationship between the catalysts' structure and their catalytic performances, as it has a great capability to precisely control the deposition of single atoms and nanoclusters. In this perspective, we will briefly discuss the recent progress in the rational design of single-atom catalysts through atomic layer deposition. In addition, we will summarize the key issues for the development of ALD methods and the outlook for future research trends.

Generally, one complete ALD cycle contains two main processes (Fig. 1a) [7]. Taking the deposition of single Pt atoms on graphene as an example, the first step is the reaction of the Pt precursor with the adsorbed oxygen on the surface of the graphene. The second step is an oxygen pulse to convert the precursor ligands to Pt–O species to form a new adsorbed oxygen layer on the Pt surface (Fig. 1b). During the ALD process, Pt catalysts with atomically precise design and control can be synthesized by adjusting the ALD cycles. In 2013, Sun and co-workers fabricated single Pt atoms on graphene nanosheets by ALD for the first time [3]. The graphene substrate exhibited many carbon vacancies and defects, which were favorable for anchoring Pt precursors. Up to now, single-atom Pt catalysts have also been achieved on nitrogen-doped graphene and CeO_2 supports [4,5]. When single Pt atoms are deposited on CeO_2, the atoms tend to deposit on the Ce rows of the $CeO_2(110)$ and (100) facets, instead of the (111) facet [5]. In addition to single Pt atoms, single Pd atom catalysts have also been successfully deposited on graphene by alternately exposing $Pd(hfac)_2$ and formalin at $150°C$ [6]. Although several types of single-atom catalysts have been obtained through the ALD method, large-scale production of single-atom catalysts using the ALD process is still challenging, and optimization of the ALD process is required. For example, the use of the spatial atomic layer deposition technique could greatly improve the industrialization process [8].

Atomic-resolution transmission electron microscopy (TEM), scanning tunneling microscopy (STM) and radiation-ray absorption spectroscopy investigations are three typical characterization methods for detecting SACs. We can directly observe the single atoms through atomic-resolution TEM and STM images while the synchrotron-based X-ray absorption spectrum can provide information on the overall structure of the catalysts. The formation of SACs can be concluded by studying the extended X-ray-absorption fine-structure (EXAFS) spectrum of the corresponding catalysts. Local atomic structure information including coordination number and atomic distances can be derived from the fitted EXAFS spectra in R space. The reduction of peak intensity of metal–metal peaks in these spectra can be a good indicator for the formation of SACs. Though we can conclude the formation of single-atomic catalysts through these methods, it remains a great challenge to identify the accurate binding site between the single atoms and the support. As a result, the development of advanced characterization methods is essential for widespread synthesis and application of SACs. In addition, to attain physical insights into the reactions, advanced *in situ/operando* characterization techniques would be necessary. A systematic understanding of the reaction mechanisms will be crucial for discovering the growth behavior of single atoms on different substrates and its practical applications.

The SACs obtained through ALD have extremely high atom-utilization efficiency, which makes them highly active catalysts for several catalytic reactions. The SACs have been proven to be highly efficient catalysts for several electrochemical reactions, including methanol oxidation, the hydrogen evolution reaction and the oxygen reduction reaction (ORR) [3,4,9,10]. Sun and
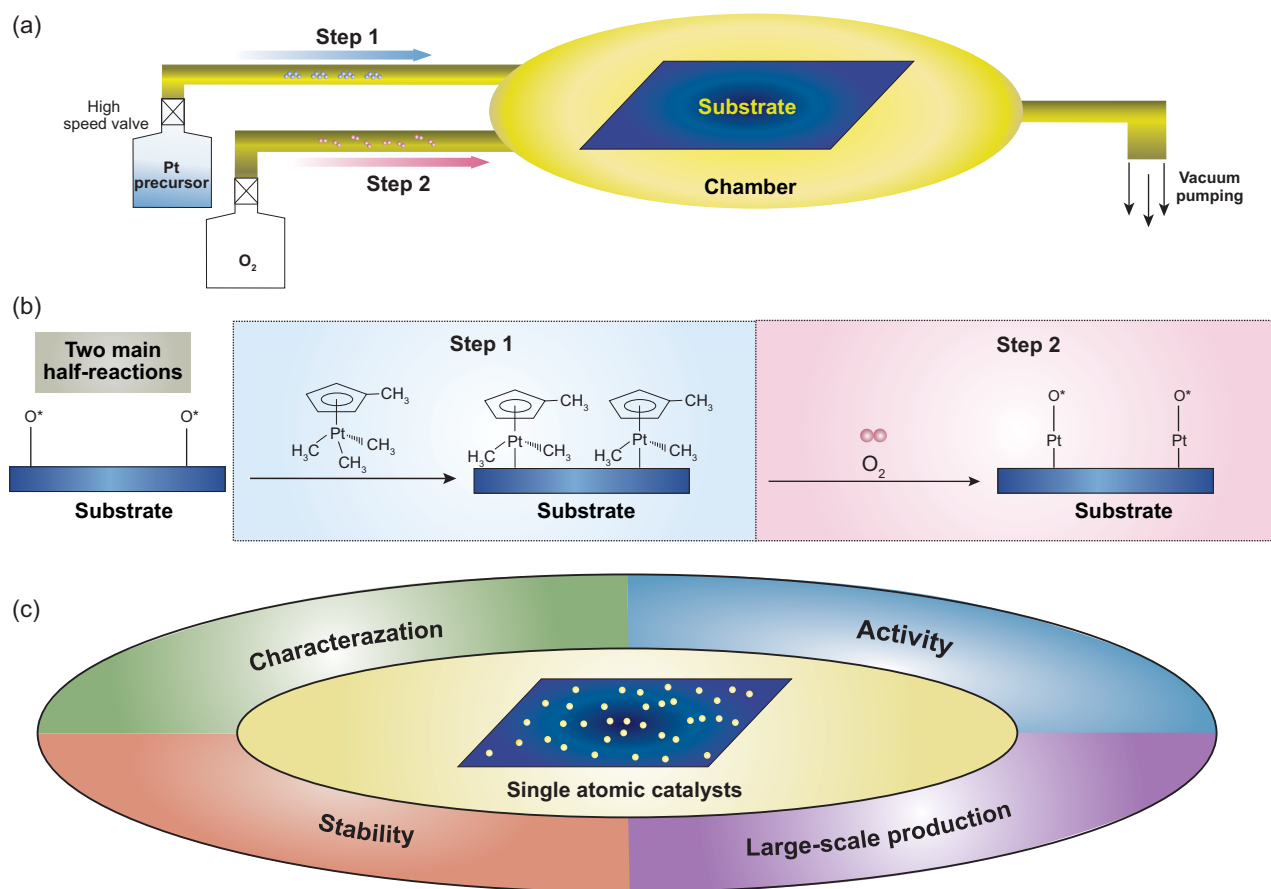
Figure 1. (a) Schematic illustrations of the deposition of single-atomic Pt on substrates through the ALD method. (b) The detailed two main half-reactions during a whole ALD cycle. (c) Four key research areas for the development of the ALD technique for single-atom catalysts.

co-workers reported that the single-atom Pt catalysts on graphene showed 10 times higher activity for methanol oxidation and superior CO tolerance compared to conventional Pt/C catalysts [3]. In addition, they found that the mass activity of single-atom Pt catalysts on nitrogen-doped graphene was around 37.4 times greater than that of the Pt/C catalyst [4]. Thanks to the strong bonding energy between Pt and nitrogen-doped graphene, the activity of the catalysts dropped only 4% after 1 000 cycles, indicating a high durability. For the oxygen reduction reaction, two different pathways were demonstrated on single-atom Pt catalysts [9,10]. The support plays a significant role in the selective catalytic reaction route and final product. For instance, single Pt atoms on a sulfur-doped zeolite-templated carbon support could selectively transfer the O_2 to H_2O_2 through a two-electron pathway [9], while single Pt atoms on nitrogen-doped carbon black exhibited

great performance for highly efficient four-electron ORR [10]. Up till now, the initial active sites for the enhanced mechanism are still unclear. More fundamental studies should focus on the influence of the support on the performance of single-atom catalysts, which might provide a systematic understanding of the interactions between the SAC and substrates. In addition to electrochemical catalytic reactions, the SACs also exhibited superior performance as heterogeneous catalysts in several traditional catalytic reactions. For example, Pt/FeOx and Pt/CeO_2 catalysts exhibited a remarkable activity towards both CO oxidation and preferential oxidation of CO in H_2 [2,5]. The single-atom Pd/graphene catalysts obtained through ALD showed 100% butene selectivity in selective hydrogenation of 1,3-butadiene [6]. The adsorption mode of 1,3-butadiene and the enhanced steric effect induced by single Pd atoms played key roles in improv-

ing the butene selectivity. To further increase the activity, the rational design of SACs with multiple compositions should be explored in the future, because bimetallic catalysts can exhibit improved performance compared to pure metals. The area-selective ALD method provides an effective way to fabricate catalysts with multi-compositions. Elam and co-workers synthesized several types of bimetallic nanoparticles by precisely controlling the ALD conditions [11]. Recently, Pt_2 dimers have been fabricated through selective deposition of a secondary Pt atom onto the preliminary one [12]. Based on the above points, we can infer that, under certain ALD conditions, the fabrication of bimetallic dimers is feasible through deposition of the secondary metal atom on the first single-atomic metal. With the formation of dimer structures, the electronic structure of SACs could be tuned, which would further increase the activity of SACs to a new level.

However, the metal loading is usually very low due to the problems associated with agglomeration during the preparation process. Further Pt deposition during the ALD process tends to adsorb on the existing Pt atoms, which will also result in the formation of clusters. As a result, the development of ALD techniques to achieve high loading of SACs is still a challenge for their future commercial application. Furthermore, the selectivity of substrates is important for the dispersion of singe atoms [3,11]. Recently, Zeng *et al.* found that the mass loading of single Pt atom catalysts can reach up to 7.5% on MoS_2 [13]. In addition to the low loading issues, another key parameter for the SACs is the durability of the catalysts during the catalytic reactions. Single-atom catalysts are highly mobile and tend to aggregate during the catalytic reactions due to the high surface energy of SACs. The interaction between SAC and substrate plays an important role in their stability. Several studies have shown that nitrogen-doped carbon black, graphene and nitrogen-doped graphene can form strong coordination sites with metal, thus observably improving their stability [3,4,10]. However, the single atoms still tend to aggregate on traditional substrates. More studies should focus on the development of effective routes to stabilize the catalysts. The ALD deposition of metal oxide around Pt catalysts has been proven to be an effective way to stabilize the Pt clusters. For example, the ORR stability of Pt clusters was significantly increased by selective deposition of ZrO_2 around Pt clusters to form a cage structure [14]. This method of stabilization may also be applied in single-atom systems. In addition, the fabrication of porous structures to pin the atoms in the hole might also increase the stability of single-atom catalysts. We believe that the ALD method might open up new opportunities in fabrication and optimization of SACs for improved activity and durability in heterogeneous reactions.

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Lei Zhang, Mohammad Norouzi Banis and Xueliang Sun*
Department of Mechanical and Materials Engineering, The University of Western Ontario, Canada
*Corresponding author.
E-mail: xsun@eng.uwo.ca

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