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Single atom catalyst by atomic layer deposition technique

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ABSTRACT

Noble single-atom catalysts have rapidly been attracting attention due to their unique catalytic properties and maximized utilization. Atomic layer deposition (ALD) is an emerging powerful technique for large-scale synthesis of stable single atom. In this review, we summarize recent developments of single atom synthesized by ALD as well as explore future research direction and trends.

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1. Introduction

Noble metal catalysts play a very important role in a wide range of industrial applications. Noble catalysts, such as Pt, Pd, Ru, Rh, and Ir have been widely used in chemical transformation, energy conversion, and environmental protection. However, owing to the high price and low natural abundance of such noble metals, the increasing need for these elements cannot be met. One strategy toward maximizing the catalytic use of nobel metals is to reduce the catalyst size in order to increase the active surface area. Downsizing noble metal catalyst particle size to nanometers, clusters or even single atoms, is an effective strategy to significantly increase catalytic activity and enhance efficiency. Recently, noble single-atom catalysts (SAC) have attracted rapidly increasing attention due to their unique catalytic properties and maximized utilization leading to reduced cost.

Single-atom catalysts have shown unexpectedly high specific activity, with a significant reduction in usage for CO oxidation [1–3], water-gas shift reaction [4–6], fuel cells [7,8] and hydrogenation reactions [9–11]. For examples, single-atom Pt supported on FeO_x substrates demonstrated a 2–3 times higher activity than its cluster counterpart. Furthermore, this unique combination displayed excellent stability toward CO oxidation and preferential oxidation of CO in H_2 [1]. The remarkable performance of single atom Pt supported on FeO_x stems from the unique electronic structure of partially vacant 5*d* orbitals of the positively charged and high-valent Pt atoms, as confirmed by X-ray absorption near edge structure (XANES) and density functional theory (DFT) analysis. Single Pd atom catalysts were also achieved by the anchoring of Pd atoms into the cavities of mesoporous polymeric graphitic carbon nitride [10]. Single Pd atoms showed high activity and product selectivity for the flow hydrogenation of alkynes and nitroarenes compared with supported Pd nanoparticles. The Pd single atoms surpassed the activity of conventional heterogeneous nanoparticle catalysts and maintained an outstanding degree of product selectivity (> 90%). Single atom catalysts are a promising new generation of water gas shift (WGS) catalysts for maximizing their activity and catalytic efficiency [12–14] An isolated Au species an-

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chored through -O ligands to different supports such as ceria [15,16] and titania [17] have been successfully prepared for WGS reaction. The atomically dispersed gold species, with surrounding extra surface-OH groups, (Au-$(OH)_x$) have been identified as the active sites for the WGS reaction.

Single atom catalysts were also designed for oxygen reduction reaction (ORR). The inherently sluggish kinetics of the ORR and instability of platinum at the cathode are the foremost challenges for widespread commercialization of polymer electrolyte fuel cells (PEMFCs) [18,19]. Pt is the high cost and scarcity. It is extremely desirable to develop highly active, stable and inexpensive ORR electrocatalysts. When Pt nanoparticle downsized to single atoms, the Pt single atoms does not show good ORR activity because the ORR need platinum ensemble sites in acid media [8]. The similar results were also obtained on the single Pt atoms anchored in sulfur-doped ZTC (HSC). Single Pt atom catalysts do not follow a conventional four electron pathway producing H_2O, but selectively produces H_2O_2 without significant degradation of the activity. However, the single-atom catalyst of single niobium atoms trapped within the graphitic layers showed a good ORR activity in alkaline solution [20]. The advanced structure of trapped single atom not only enhance the overall conductivity for accelerating the exchange of ions and electrons, but also suppress the chemical/thermal coarsening of the active particles. Experimental and theoretical studies revealed that the single niobium atoms produced a redistribution of *d*-band electrons, thus becoming extremely active for O_2 adsorption and dissociation, and exhibiting high stability. Recently, Sun et al. [21] reported a cost-effective, high performance and durable carbon-supported Pt SAC for highly efficient 4e ORR in acid media. DFT calculations indicate that the single-pyridinic-nitrogen(P-N) -atom-anchored single Pt atom centers are the main active sites, which are highly active for ORR.

However, upon downsizing noble metal catalysts, to clusters or single-metal atoms, structural stability is compromised, resulting in a natural tendency for metal atoms to diffuse and agglomerate, causing larger particles to form. In practical applications, it is required that the single atom and cluster catalysts have an activity on the scale of (if not higher than) conventional Pt nanoparticles, while also maintaining their stability with cycling in order to prevent particle growth with time. This suggests that not only must single atoms be successfully prepared, but they must also exhibit high activity and high stability. In order to solve the challenges facing single atom catalysts, we first need to explore fabrication methods employed for the preparation of stable single atom catalyst with high loading. Many methods such as co-precipitation method [22–24], impregnation method [2,8,25,26], pyrolysis synthesis [27,28], mass-selected soft-landing method [29,30] and atomic layer deposition (ALD) [31,32] have been developed to fabricate single atom catalysts. In this review, we will focus on how to design highly stable and active single atom catalysts by atomic layer deposition (ALD). We will introduce the mechanism of ALD for synthesis of single atom catalysts. We also summarize state-of-the-art progresses on single atom catalysts. This will provide a useful platform upon which to design industrial catalyst.

2. The mechanism of ALD for single atom

ALD is gaining increasing attention as a technique for deposition of noble metals and metal oxides due to its ability in preparing uniform and conformal thin films, as well as the deposition of uniformly distributed particles ranging from single atoms, to sub-nanometer clusters, to NPs in high-aspect-ratio structures and porous materials [33–37]. Generally, the ALD process includes four steps, as shown in Fig. 1 [38,39]: (1) Exposure to first precursor, (2) purge of the reaction chamber, (3) exposure to second reactant precursor, and (4) a further purge of the reaction chamber. In ALD process, the key character is self-limiting reactions, which makes it possible to precisely control over size or thickness of the deposited materials at the atomic level. In the first half reaction (steps (1) and (2)), the first precursor reacts with all available active sites (functional groups or defect) on the substrate, in which a fraction of ligands of the precursor are partially removed. Then residue of the first precursor and reaction byproducts are purged with an inert gas. In the second half reaction (step (3) and (4)), the reactant precursor reacts with the adsorbed precursor on the substrate to get the target material by removing the remaining ligands of the first precursor. In this reaction, it is very important to regenerate active sites on the surface of deposited materials for the next cycle deposition. The residuals of the second precursor and byproducts are purged with an inert gas and complete the reaction cycle. The desired thickness or size can be achieved by the controlled number of cycles. Based on sequential and self-limiting reactions, ALD is capable of producing a variety of thin films with precise control at the atomic level. However, some deviations from ideal growth, such as nucleation delay or island growth during the initial film growth stage of noble metals ALD, are often observed. The following reasons are responsible for the formation of nanoparticle instead of Pt film: (1) Limited functional groups on the substrate surface. During the initial of ALD process, the precursor first reacts with functional groups on the surface of the substrate

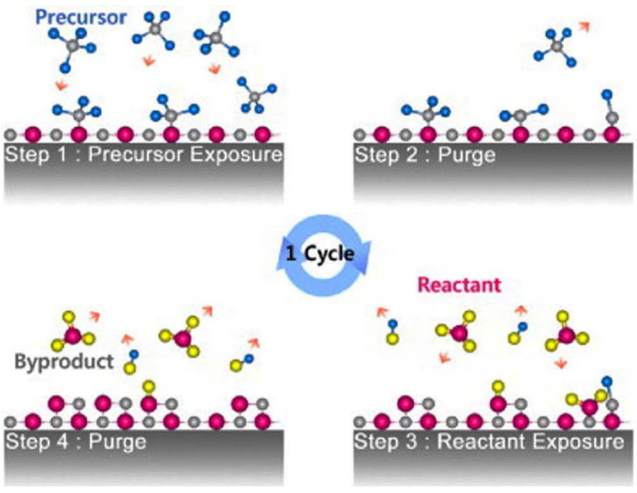

Fig. 1. Schematics showing the growth process of ALD. Reproduced with permission from Ref. [39].

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