

Review

Surface Modification of Catalysts via Atomic Layer Deposition for Pollutants Elimination

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Abstract: In recent years, atomic layer deposition (ALD) is widely used for surface modification of materials to improve the catalytic performance for removing pollutants, e.g., CO, hydrocarbons, heavy metal ions, and organic pollutants, and much progress has been achieved. In this review, we summarize the recent development of ALD applications in environmental remediation from the perspective of surface modification approaches, including conformal coating, uniform particle deposition, and area-selective deposition. Through the ALD conformal coating, the activity of photocatalysts improved. Uniform particle deposition is used to prepare nanostructured catalysts via ALD for removal of air pollutions and dyes. Area-selective deposition is adopted to cover the specific defects on the surface of materials and synthesize bimetallic catalysts to remove CO and other contaminations. In addition, the design strategy of catalysts and shortcomings of current studies are discussed in each section. At last, this review points out some potential research trends and comes up with a few routes to further improve the performance of catalysts via ALD surface modification and deeper investigate the ALD reaction mechanisms.

Keywords: atomic layer deposition (ALD); conformal coating; uniform particle deposition; area-selective deposition; pollutants removal

1. Introduction

Currently, environmental pollution attracts increasing attention, and the removal of poisonous gases (e.g., CO and NO_x), heavy metal ions, and organic pollutants, in an efficient and fast way, has become an important issue [1,2]. Thus, synthesis and surface modification of novel materials, including catalysts, adsorbents, and membranes, have been widely investigated to improve the performance of contamination elimination via catalysis, adsorption, and a separation process [3–5]. There are several methods to functionalize and decorate the surface of materials, e.g., impregnation [6], sol-gel [7], sputter deposition [8], and chemical vapor deposition (CVD) [9]. Impregnation and sol-gel are the two conventional methods with the advantage of simple operation, which are used widely in preparation and surface decoration of photocatalysts. Sputter deposition is a physical vapor deposition (PVD) method, and the sputtering gas is often an inert gas such as Ar. During the process, the sputtered ions can fly from the target to the substrates, e.g., Si wafers, and the films will grow gradually. CVD is applied for thin films' deposition on substrates through chemical reactions, and the film thickness can be controlled at a nanometer scale. During the CVD process, all precursors enter the chamber simultaneously and react on the substrates to form a thin film. These methods are developed for decades, and a number of achievements on the synthesis and surface modification of catalysts have been achieved. However, it is a challenge to control the coated film thickness precisely at the sub



nanometer scale through these methods. It is well known that the film thickness and deposited particle size on the substrates affect the property and performance of materials enormously. Thus, it is crucial to precisely adjust the film thickness and particle size at an atomic level, and the goal can be achieved by atomic layer deposition (ALD).

ALD is a surface-controlled layer-by-layer gas phase coating process based on self-limiting sequential surface reactions [10,11]. In a typical ALD process, two precursors are controlled to enter the reactor and react with the functional groups on the substrates alternately, and are separated by inert gas purging to remove the unreacted precursors and any byproducts during the reaction, which is different from the CVD process. Here, Al₂O₃ ALD is taken as an example, and as shown in Figure 1, a typical coating cycle includes the following steps: Precursor trimethylaluminum (TMA) dose, inert gas (e.g., N₂) purge, precursor H₂O dose, and inert gas (e.g., N₂) purge. For one Al₂O₃ ALD cycle, first, the TMA reacted with the –OH group on the substrates, and then, after the purge, the second precursor, H₂O, was introduced and reacted with the -CH₃ group to form a layer of Al₂O₃. In general, during the ALD process, the products, such as metal and metal oxides, grow on the substrates with a film growth or island growth model. By adjusting the number of ALD cycles, the thickness of film can be precisely controlled at an atomic level. In addition, since the precursors are gas, they can enter inside the pores of materials and react to form a conformal coating on the inside walls of nano-channels or micro-channels, and, thereby, ALD can be used for complex 3D topography structures coating. Moreover, for the metal ALD, such as Pt, Co, and Fe ALD, the particle size and loading can be tailored by adjusting the number of ALD cycles and the dose time of precursors. Therefore, ALD is widely used in semiconductors, catalysis, energy, and some other areas due to these unique characterizations and advantages.



Figure 1. Schematic representation of Al₂O₃ ALD using precursors TMA and H₂O.

In recent years, a number of studies reported the applications of ALD in the environmental remediation, including CO or soot oxidation, selective catalytic reduction (SCR) of NO_{x} , and photocatalytic degradation of dyes, through surface modification/preparation of catalysts. Much progress has been achieved [12–16]. In addition, some reviews on ALD were published, which discussed the ALD reaction mechanisms [17,18] and the surface functionalization by ALD [19,20], and summarized the recent advances in catalysis [21–25], solar cells [26], and batteries [27]. However, there is a lack of review that focuses on the recent advances of ALD in environmental remediation. In this review, we summarize the state-of-the-art progress of ALD in removing pollutants via surface modification in recent years, and we classify these methods into conformal coating, uniform particle deposition, and area-selective deposition, as shown in Figure 2. Conformal coating via ALD is used to tailor the surface properties of catalysts, including the redox and hydrophilic/hydrophobic property, to enhance the activity of removing contamination. In addition, the film coating works as a protective layer to enhance the thermal stability and photostability in some studies. The particle deposition with a uniform particle size, e.g., single atoms, clusters, and NPs, by ALD is adopted to design and synthesize rational metal-based catalysts for removing CO, soot, and organic pollutants via catalytic oxidation,

combustion, and photodegradation, respectively. The high dispersion improves the utilization efficiency of metal atoms and the catalytic activity, especially for noble metals. Area-selective deposition utilizes the growth characteristics of films and particles by ALD to deposit metals or metal oxides on the surface of certain species to form desired structures, such as bimetallic NPs, protective layer on active sites, and overcoating on defects of materials. We also discuss the mechanisms and shortcomings of current studies in each section, and, lastly, we point out some potential research trends and come up with a few approaches to further improve the performance of catalysts via ALD surface modification and investigate the ALD reaction mechanisms. We hope that this review can not only help researchers better understand the development of ALD applications in environmental remediation but also offer some new ideas for catalysts design.



Figure 2. Surface modification by ALD for pollutants removal.

2. Conformal Coating

2.1. Applications in Photocatalytic Degradation of Organic Pollutants

Conformal coating is a major category to functionalize materials by ALD with uniform and precise film thickness control at a sub-nanometer scale. A main application of this complete encapsulation is surface modification of photocatalysts, such as TiO_2 [28], and g-C₃N₄ [29], to enhance the photoactivity for degradation of organic pollutants under UV light or visible light, as shown in Table 1. It is well known that only a narrow light wavelength range can be utilized, which is a shortcoming, and a high recombination rate of photo-generated electrons (e⁻) and holes (h⁺) is the main factor limiting the degradation rate [30]. Through metal oxide coating, the band gap of catalysts and the recombination rate of electron/hole pairs can be reduced. However, if the film is too thick, it will prevent the utilization of light by catalysts. Thus, it is critical to coat an ultrathin film with a controllable thickness, which can be realized by adjusting the number of ALD cycles.

Entry	ALD	Number of Cycles	Catalyst	Pollutant	Light	k _{app} (min ⁻¹) ¹	Reference
1	Al ₂ O ₃	10	TiO ₂ /V ₂ O ₅ /Al ₂ O ₃	RhB	UV light	-	[31]
2	Al_2O_3	(-8 nm)	Al-rich Al ₂ O ₃ ultra-thin film	RB5	UV light	0.163	[32]
3	TiO ₂	5	g-C ₃ N ₄ @TiO ₂	RhB	Visible light	0.00324	[33]
4	TiO ₂	30	30TiO ₂ @P25	2,4-D	λ >320 nm	5.0	[34]
5	SnO ₂ , TiO ₂	1000, 200	SnO ₂ @TiO ₂ nanopillar-array	MB	UV light	-	[35]
6	TiO ₂	1000	C-TiO ₂ -390	MB	Visible light	0.0917	[36]
7	TiO ₂	250	TiO ₂ inverse opals	MB	UV light	0.00415	[37]
8	TiO ₂	10	SnO ₂ /TiO ₂ core shell nanowires	МО	UV light	0.00147	[38]
9	TiO ₂	80	Au-80@TiO2	MB	UV light	-	[39]
10	TiO ₂	400	CNT/TiO ₂	MB	UV light	0.0101	[40]
11	TiO ₂	1125	TiO ₂ /Graphene	Methyl red	UV-vis light	0.0064	[41]
12	TiO ₂ , Ga ₂ O ₃	–(6.5 nm, 8.0 nm)	TiO ₂ -Ga ₂ O ₃	MO	UV light	-	[42]
13	TiN	100	TiO ₂ @100TiN	MO	Visible light	0.027	[43]
14	TiN	(-10 nm)	3D N-doped TiO ₂	MB	Solar light	-	[44]
15	ZnO	100	g-C ₃ N ₄ @ZnO	cephalexin	Solar light	0.0735	[14]
16	ZnO	300	ZnO/ZFO-2 JHNFs	MB	Visible light	0.0187	[45]
17	ZnO	5	g-C ₃ N ₄ @ZnO	MB	Visible light	0.0263	[29]
18	ZnO	400	PAN@PANI@ZnO nanofibers	MB	UV light	0.040	[46]
19	ZnO	400	ZnO/glass	MB	UV light	0.0037	[47]
20	ZnO	300	Pt@ZnO NRs/CFs	MO	UV light	-	[48]
21	ZnO	120	CNT-ZnO	MO	UV light	0.0026	[49]
22	ZnO, TiO ₂	30, 30	ZnO-TiO ₂ /CNT membrane	MB	UV light	0.0203	[50]
23	CeO ₂	40	CeO ₂ /TiO ₂	MB	UV light	0.079	[51]
24	ZrO_2	45	ZrO ₂ /TiO ₂	MB	UV light	0.127	[52]
25	SnO	236	SnO/TiO ₂	MB	UV-vis light	0.010	[53]
26	SnO	(-3 nm)	Sn (O,S)/TiO ₂	MB	Visible light	0.114	[54]
27	Fe, Pt	30, 30	g-C ₃ N ₄ /FePt-2	RhB	Visible light	0.0891	[55]
28	Pd	10	BaZrO ₃ /Au-Pd	RhB	UV light	0.0408	[56]
29	Fe	2	Fe/TiO ₂	MB	UV light	0.155	[13]
30	MgO	5	5_MgO@Ag_TiO2	phenol	Solar light	-	[57]
31	Pd	50	Pd-TiO ₂	2,4-D	UV-vis light	-	[58]

Table 1. Photocatalytic degradation of pollutants over catalysts prepared by ALD.

 1 k_{app} is an apparent kinetic constant.

As shown in Table 1, some studies adopted Al_2O_3 , TiO₂, or ZnO ALD to prepare photocatalysts, and degradation of organic chemicals, including rhodamine B (RhB) [31,33], methylene blue (MB) [35–37], methyl orange (MO) [38,42,48], phenol [57], and cephalexin [14], are used as the probe reactions to evaluate the photoactivity of catalysts. Generally, Al₂O₃ is photo-catalytically inactive, but it can play a role as a protective layer to prevent soluble catalysts from dissolving into water. For example, Kwon et al. reported that an ultrathin Al₂O₃ film (less than 1 nm) was coated on a TiO_2/V_2O_5 catalyst via 10 cycles of Al_2O_3 ALD in order to ensure the stability of soluble V_2O_5 in the water, and the results showed that the photo activity of TiO₂/V₂O₅/Al₂O₃ was high in the degradation of RhB [31]. In addition, Azizpour et al. found that the Al₂O₃ coating would affect the photoactivity of TiO₂, and it decreased with the increase of Al₂O₃ film thickness because the coating blocked the light [28], which is consistent with a previous study [59]. In contrast, a recent study reported that the Al_2O_3 ultra-thin films with an amorphous structure prepared by ALD showed the photoactivity in the degradation of textile dyes under UV light, such as Remazol Black 5 (RB5), owing to the relatively low energy gap and short bond length [32]. Since the temperature of the Al_2O_3 ALD is not high (less than 200 °C), the Al₂O₃ was amorphous in most studies, but no similar phenomena were reported before what could be ascribed to the fact that Al_2O_3 was usually decorated on photocatalysts instead of being used as a photocatalyst in previous studies. The Al_2O_3 ALD reaction mechanism using TMA and H_2O_3

is clear and mentioned above, while the degradation mechanism over amorphous Al₂O₃ film needs to be further investigated, and the intermediate species during the process need to be identified.

TiO₂ is one kind of effective photocatalysts for degradation of organic pollutants. Thus, TiO₂ ALD is widely adopted to synthesize novel photocatalysts [33–42]. The widely used Ti precursors are titanium tetrachloride (TiCl₄) and tetrakis (dimethylamino) titanium (TDMAT), and another precursor is H₂O. When the TiCl₄ and H₂O are used as precursors, the byproducts contain HCl, which could corrode the ALD reactor and pump. Instead, no acid is produced when the TDMAT was used [60], even though the exact ALD reaction mechanism needs to be further investigated.

Generally, the TiO₂ film is amorphous through the ALD coating, and the photoactivity is low. After heat treatment, the amorphous TiO_2 changes to anatase and rutile and the photoactivity will be improved. It is noted that, since the crystal size of anatase and rutile is relatively large, the TiO_2 film will aggregate and become NPs if the film is ultrathin after heat treatment [61]. For example, as shown in Figure 3a, 1000 cycles of TiO₂ ALD were applied for carbon fiber fabrics at 150 °C, and the two precursors were titanium (IV) isopropoxide (TIP) and H₂O. After calcination, the TiO₂ aggregated and closely contacted with nano-graphite sheets, which formed Ti-O-C bonds. The photoactivity of C-TiO₂ boosted, which was more than two times that of P25 (a commercial TiO_2) under visible light, and the stability was good (Figure 3) [36]. In contrast, the TiO_2 film still remained unchanged on carbon nanotubes even after annealing at 800 °C when it was thick (>10 nm) [40]. The improvement of the photocatalytic activity of carbon materials supported TiO₂ films and NPs, which was reported to be due to the reduction of the recombination rate of electron/hole pairs [41,62]. The TiO₂ films were also coated on g-C₃N₄ [33], P25 [34], and Au [39], by ALD to form a core-shell nanostructure to photodegrade RhB, 2,4-D (a persistent pesticide pollutant), and MB, respectively, and the rate constant (k_{app}) of 2,4-D reached as high as 5 min⁻¹ over 30 cycles of TiO₂ ALD coated P25 (30TiO₂@P25). In addition, an ultrathin TiO₂ film was deposited on ceramic membranes by ALD to improve the removal efficiency of MB through photocatalytic degradation besides the separation process [63]. The TiO₂ ALD was also used in conjunction with other ALD films, including SnO_2 [35], Ga_2O_3 [42], and ZnO [49,50], and SnO₂@TiO₂ and TiO₂-Ga₂O₃ heterojunction accelerated the separation of electron/hole pairs and boosted the photoactivity [38].

In addition to TiO₂ ALD, ZnO ALD was also adopted to prepare ZnO-based photocatalysts or decorate other materials for degradation of organic pollutants [14,29,45–48,50,64–66], and, generally, diethyl zinc (DEZ) and H_2O are used as precursors [67,68]. Park et al. deposited ZnO ultrathin film on glass substrates with different film thicknesses, and found that at least 50 nm of the film thickness could ensure the high photoactivity in the degradation of MB [47]. ZnO ALD can be performed at a very low temperature (~40 °C). Therefore, it can be used in the materials without good thermostability, such as polymers. For instance, Zhu et al. [46] and Mauro et al. [66] reported the ZnO thin films were coated on polyaniline (PANI)@polyacrylonitrile (PAN) nanofibers (NFs) and polyethylene naphthalate (PEN) by ALD, and they showed relatively high activity in degradation of MB and phenol under UV light, respectively. In addition, as shown in Figure 4a,b, the ZnO nanorods (NRs) were synthesized through ALD and hydrothermal growth, and then Pt was coated on the ZnO NRs/carbon fibers (CFs) via sputtering to obtain a core-shell Pt@ZnO NRs/CFs photocatalyst. The activity of the Pt@ZnO NRs/CFs was higher than that of the ZnO NRs/CFs, which could be attributed to the fact that electrons could transfer at the Pt-ZnO interface and reduce the recombination rate of photogenerated electron/hole pairs (Figure 4c,d) [48]. ZnO was also used as a promoter to enhance the photoactivity of other materials. Li et al. designed a Z-scheme g-C₃N₄@ZnO catalyst with a heterostructure by ZnO ALD, and the apparent kinetic constant (k) of the g- C_3N_4 @ZnO was more than five times that of the g- C_3N_4 in the degradation of cephalexin under simulated sunlight irradiation [14]. Jang et al. reported the g-C₃N₄@ZnO heterojunction photocatalysts via ALD and the k_{app} was as high as 0.0263 min⁻¹ in the degradation of MB under visible light for five cycles of ZnO ALD-coated g-C₃N₄ [29].



Figure 3. (a) Schematic illustration of the fabrication procedure of CFFs-TiO₂ using the ALD method, and followed by calcining, (b) pseudo-first-order fitted degradation of methylene blue (MB) by CFFs-TiO₂-1000, P25, and C-TiO₂-t, and (c) repeated recycling of photocatalytic degradation of MB by C-TiO₂-390 min under visible light irradiation. Reproduced with permission [36]. Copyright 2020, the Royal Society of Chemistry.

As shown in Table 1, some other metal oxides and nitrides ALD were reported to enhance the activity of photocatalyst by lowering the band gap energy and suppressing the recombination of electron/hole pairs [51,52,57]. Han et al. prepared a series of SnO-coated TiO₂ catalysts by ALD, and the Sn(O,S)/TiO2 showed a 16-fold enhancement of the degradation rate constant of MB under Xe lamp irradiation, as compared to that of the pure TiO_2 [53,54]. Wang et al. reported the CeO₂ and ZrO₂ ultrathin film deposited anatase TiO₂ NPs via ALD, and the k of optimal ZrO₂/TiO₂ catalyst exceeded that of TiO_2 by a factor of more than ten. It is noted that the ZrO_2 worked as an electron trap in the photocatalytic process, which could inhibit the recombination of the electron/hole pairs and, thereby, reduced the exciton recombination rate [51,52]. TiN would be converted to N-doped TiO₂ through thermal annealing. Thus, TiN ALD was adopted in the decomposition of organic pollutants. As presented in Figure 5, first, 20 nm of TiO_2 thin film was deposited on an epoxy template by TiO_2 ALD, and, after annealing, a 3D hollow TiO₂ was obtained. Then a 10 nm of TiN film was conformally coated on it by TiN ALD, so the N could be introduced to TiO_2 to form N-doped TiO_2 after annealing, and the photoactivity was higher than that of the undoped TiO_2 [44]. The TiN plasma enhanced ALD (PEALD) was also adopted to modify the anatase TiO₂ NPs by depositing an ultrathin TiO_xN_y film (~1 nm), which improved the activity of the catalyst in the degradation of MO under visible light [43].



Figure 4. (a) Scheme of synthesizing Pt@ZnO NRs/CFs composites, (b) SEM images of (1) original CFs, (2) CFs deposited with a ZnO seed layer, (3,4) hydrothermal growth of ZnO NRs on CFs with different magnifications and (5,6) magnetron sputtering Pt NPs on ZnO NRs/CFs with different magnifications, (c) photocatalytic degradation of MO over different catalysts, and (d) proposed an enhanced mechanism of Pt@ZnO NRs/CFs in the photocatalytic degradation. Reproduced with permission [45]. Copyright 2017, the Royal Society of Chemistry.



Figure 5. (a) Schematic illustration of the fabrication process, (b) digital image of a large area 3D N-doped TiO_2 film, (c,d) cross-sectional microscopic image of a 3D N-doped TiO_2 film. Reproduced with permission [41]. Copyright 2018, the Royal Society of Chemistry.

Overall, conformal coating with controllable film thickness by ALD is an effective approach to boost the activity and performance of photocatalysts in degradation of organic pollutants, and some results are very attractive. However, most of the studies chose degradation of dyes as probe reactions, and it will be more practical if antibiotics or persistent organic pollutants (POPs) are used as model pollutants in future studies.

2.2. Applications in Removal of Air Pollutants

Generally, CO and CH₄ can be removed by catalytic oxidation over metal or metal oxide-based catalysts [69–72]. Among various catalysts, supported Pd catalysts are attractive due to their high activity. However, the aggregation and deactivation during a high reaction temperature is a major problem for the Pd-based catalysts, which needs to be solved. Thus, some studies deposited ultrathin films on Pd NPs via ALD to stabilize them and prevent Pd NPs sintering. For example, as shown in Figure 6, Duan et al. reported that the porous Al₂O₃ overlayers stabilized Pd NPs on SiO₂ during catalytic combustion of CH₄ at 200–850 °C, which was ascribed to a strong interaction between Al³⁺ sites and adjacent surface PdO_x phases [15]. Onn et al. chose to deposit the uniform LaFeO₃ thin film on the Pd/MgAl₂O₄ via ALD, and the catalysts showed stable performance for CH₄ oxidation after heat treatment. They also found the high-surface area CeO₂-ZrO₂ films prepared by ALD, which maintained high activity at 1000 °C [73,74]. In addition, Chen et al. reported a Pd@Pt core-shell catalyst. The thickness of the Pt shell was controlled by the number of ALD cycles and the Pt shell improved the selectivity of CO in preferential oxidation of CO in hydrogen (PROX) due to the higher temperature for H₂ oxidation than that for CO oxidation over the core-shell NPs [75].



Figure 6. TEM, HAADF-STEM, and EDS elemental mapping images of (**a**,**b**) Al₂O₃/cubic-Pd/SiO₂ and (**c**,**d**) Al₂O₃/octahedral-Pd/SiO₂. Reproduced with permission [15]. Copyright 2019, Wiley.

Soot is a major pollutant from diesel combustion, and CeO₂ is a type of effective catalysts for catalytic combustion of soot due to its strong oxygen storage capacity [76,77]. Ivanova et al. deposited the CeO₂ film on Si (100) by ALD, and found that a higher deposition temperature was helpful to enhance the activity in the soot catalytic combustion [78]. The same group also combined Ag ALD and CeO₂ ALD, and fabricated the Ag doped CeO₂ thin films, which showed a high activity and stability [79]. In addition to catalytic combustion of soot, CeO₂ ALD was adopted in NH₃-SCR for

removal of NO. It has been reported that an outer ZrO_2/CeO_2 layer, which was coated on the ZSM-5 particles, had a positive effect on adsorption of NO_x [16].

Though there are few research studies on the applications of ALD conformal coating in removal of air pollutions, uniform thin films with sub-nanometer-sized control of film thickness is a potential and promising way to improve the activity and stability of catalysts by tailoring the surface properties of materials. Thus, further studies are needed to expand the applications of conformal coating except for photocatalysis and investigate the related mechanism deeply.

3. Uniform Particle Deposition

In recent years, ALD has been used to deposited highly dispersed metal or metal oxide particles on substrates with a uniform particle size, and it is helpful to improve the metal utilization and activity of catalysts in gas and liquid phase reactions [80-82]. In addition, it has been reported that the size of metal particles could be controlled precisely by adjusting the number of ALD cycles and precursors dose time. In addition, single atoms, clusters, and NPs with different particle sizes could be achieved [13,83]. Thus, some studies adopted ALD to prepare and optimize nanostructured catalysts for removal of pollutants. For example, Chen et al. deposited the Pd NPs on SrTiO₃ (STO) single crystal nanocuboids by ALD, and they found the TiO₂-(001)-STO supported small Pd NPs (~2 nm) showed a higher activity than the large Pd NPs (~3 nm) in CO oxidation due to an abundant edge and corner sites [84]. As shown in Figure 7a,b, Wang et al. synthesized the Fe single atom catalysts (SACs) supported on various substrates, including TiO₂ NPs, SiO₂ NPs, and multi-walled carbon nanotubes (MWCNTs) by adjusting the dose time of the Fe precursor. The structure of Fe SACs was further verified by extended X-ray absorption fine structure spectroscopy (EXAFS) of the Fe K-edge, and, as presented in Figure 7c, there was only one notable peak in the region of 1–2 A from the Fe-O contribution and no peak in the region of 2–3 Å from the Fe-Fe contribution, confirming the sole presence of dispersed Fe atoms on all substrates. However, the growth model of Fe atoms by ALD was not clear even though a possible reaction pathway was proposed. The Fe/SiO₂ SAC presented an outstanding efficiency for CO oxidation, which was more than two orders of magnitude higher than that of the reported iron oxide catalysts. Moreover, the activity of the SAC remained unchanged after 400 h of reaction at 550 °C (Figure 7d) [13]. It is noted that the ALD-prepared Fe/SiO₂ (Fe NPs) showed a good stability in CO oxidation at a high temperature as well [85], which could be due to the chemical bonding and strong interaction between Fe NPs and substrates [86], but the reason needs to be further studied and verified.

ALD-prepared Pt catalysts with high dispersion were also used to remove CO and hydrocarbons through catalytic oxidation [82,87–89]. Gao et al. reported several supported Pt NPs on cordierite honeycombs for efficient low-temperature diesel oxidation via ALD, and they exhibited a high catalytic oxidation activity over CO, individual hydrocarbons, e.g., propylene and propane, and total hydrocarbon (THC) at low reaction temperatures [88,89]. Ye et al. deposited the Pt single atoms on the CeO₂ nanorods with loadings up to 4 wt.%, and found that the Pt–O–Ce bond interactions played a vital role for the stability of Pt SAC in the water-mediated CO oxidation reaction [82]. So far, (methylcyclopentadienyl) trimethyl platinum ((MeCp) PtMe₃) is the main Pt precursor in the Pt ALD process, and the possible reaction mechanism was reported previously [90], but the growth model of Pt NPs is still unclear, which needs to be further studied. In addition to metal ALD, metal oxides can also be highly dispersed on substrates in the form of particles instead of films by ALD. For instance, Han et al. [91] and Jeong et al. [92] prepared the supported NiO NPs on the mesoporous Al₂O₃ and SiO₂ for catalytic oxidation of CO and toluene with a high stability.



Figure 7. HAADF-STEM images of (**a**) 10c-Fe/MWCNTs (10 cycles of Fe ALD, 0.36 wt.% Fe) and (**b**) 15c-Fe/TiO₂ (15 cycles of Fe ALD, 1.78 wt.% Fe) single atom catalysts, (**c**) Fourier transformed (FT) k^3 -weighted χ (k)-function of EXAFS spectra of 10c-Fe/MWCNTs, Fe/TiO₂, and Fe/SiO₂ samples in comparison to Fe foil, FeO, and Fe₂O₃, and (**d**) long-term stability test of 25c-Fe/SiO₂ SAC for CO oxidation. Reproduced with permission [23]. Copyright 2020, American Chemical Society.

Another application of uniform particle deposition is to fabricate and optimize photocatalysts with high activity for degradation of organic pollutants [58]. As mentioned above, after two cycles of Fe ALD, 2c-Fe/TiO₂ SAC prepared by Wang et al. showed the highest activity for the degradation of MB under UV light among the TiO₂ and Fe/TiO₂ catalysts due to the reduction of band gap energy, and the degradation kinetic constant of 2c-Fe/TiO₂ SAC was more than six times than that of the pure TiO₂ [13]. You and Guo combined Fe ALD and Pt ALD to deposit fcc-FePt NPs on g-C₃N₄ for the enhancement of photocatalytic degradation of RhB under visible light, and the catalyst could be separated from solutions by a magnet [55].

At present, uniform particle deposition is mainly applied to preparation of catalysts for removal of CO, hydrocarbons, and organic pollutants, and the high dispersion and uniform particle size of metal particles are helpful for the improvement of catalytic activity and metal utilization, but there is no report on the elimination of NO_x and SO_2 , which are two major emissions released in the flue gas. In addition, some studies found that the interaction between metal NPs deposited by ALD and various substrates was different, and it affected the stability of catalysts. It is essential to investigate what factor dominates it and how to optimize it. Moreover, the particle ALD can take full advantage

of the high surface area of substrates, and it is suitable to fabricate adsorbents with high capacity for adsorption of inorganic and organic pollutants. Thus, more efforts are needed to explore these two applications based on particle ALD in the future.

4. Area-Selective Deposition

The area-selective deposition is developed to construct a unique nanostructure by depositing metals or metal oxides on a specific type of sites or components, e.g., low-coordination sites [19,23]. Several papers have reported that certain metal or metal oxides ALD preferred to deposit on specific sites [93,94]. For example, Al_2O_3 and FeO_x preferred to selectively cover the low-coordination sites and high-coordination sites via ALD and blocked them, respectively [95]. Through area-selective ALD, the defects can be covered and the bimetallic catalysts can be synthesized precisely, including Pt-Co [96,97], Pd-Ni [98], and Pt-Ru catalysts [99], to improve the activity and selectivity to target products. Thus, area-selective deposition is an effective approach to eliminate pollutants via catalytic reactions.

Removal of CO through catalytic CO oxidation and PROX at a low temperature is a challenge, but it is vital in some fields, such as room air purification and protection of proton-exchange-membrane fuel cells (PEMFCs). As shown in Figure 8a,c–i, Cao et al. selectively deposited the atomically dispersed iron hydroxide on the silica-supported Pt NPs (Fe-Pt/SiO₂) by ALD, and the catalysts could completely remove CO through the PROX reaction with a 100% selectivity at a temperature range of -75 to 107 °C (Figure 8b). A theoretical calculation showed that Fe₁(OH)_{*x*}-Pt single interfacial sites played an important role in the catalytic CO oxidation, and facilitated oxygen activation [12]. Lu et al. also reported other attracting catalysts with good performance through selective decorated TiO₂ at the low-coordination sites of Au NPs by ALD, and verified that the low-coordination sites were not related to the size effect of Au NPs based on the catalytic performance of CO oxidation.

Area-selective deposition can be used to stabilize the metal NPs and keep the high activity of catalysts at the same time. As presented in Figure 9, Liu et al. first deposited the Pt NPs on the Al_2O_3 by ALD, and then 1-octadecanethiol (ODT) was introduced to protect Pt NPs to be covered by the Co_3O_4 film after the Co_3O_4 ALD and ODT was removed by calcination. The catalyst showed a high activity and excellent sintering resistance in CO oxidation at room temperature after 600 °C calcination due to the strong interaction between Pt and Co_3O_4 [103]. NH₃-SCR is an effective route to remove NO_x from automobiles and stationary sources, and the commercial catalyst, V_2O_5 , is easy to be deactivated due to steam or SO₂ poison. Thus, the poison resistance to steam and SO₂ is critical for the NH₃-SCR catalysts. In order to solve this problem, Sun et al., designed a MnO₂-Graphene-Oxide-Scroll-TiO₂ catalyst $(MnO_2$ -GOS-TiO₂), and TiO₂ was selectively deposited on the functional groups of graphene oxide (GO) by ALD to protect the carbon layer and enhance the resistance to steam and SO_2 . As shown in Figure 10, MnO₂-GOS-TiO₂ exhibited good low-temperature SCR activity (120–280 °C) and stability in comparison with the catalysts without a TiO_2 overcoat [104]. Selective decoration is also used to boost the photocatalytic activity of catalysts [56,105]. For example, TiO_2 NPs was site-selective deposited on $g-C_3N_4$, which acted as the electron transport channel in the structure and suppressed the recombination of electron/hole pairs to improve the photoactivity of the $TiO_2/g-C_3N_4$ hetero-structural catalyst.

(a)

P

SiO₂

FeO, ALD

Self-limiting and selective deposition

666666

0





Figure 8. (a) Schematic illustration of low-temperature selective FeOx ALD on a Pt/SiO₂ catalyst to form isolated FeOx on Pt nanoparticles. (b) CO conversion over $xcFe-Pt/SiO_2$, Pt/SiO₂, and Pt/Fe₂O₃ catalysts in the PROX reaction. Scanning transmission electron microscopy images of the 10cFe-Pt/SiO₂ catalyst at low (c) and high (d,e) magnifications. (f–i), Scanning transmission electron microscopy image (f) and the corresponding energy-dispersive X-ray spectroscopy elemental mapping images of Pt La1 (g), Fe Ka1 (h), and the reconstructed Pt + Fe composition (i). x represents the number of ALD cycles. Reproduced with permission [12]. Copyright 2019, *Nature*.

In recent years, area-selective deposition is mainly applied for preparation and surface modification of catalysts to contaminations elimination, especially for CO removal, and some excellent results has been achieved. In addition, there is a rare study on the adsorption and separation process now, and selective ALD could be a technique with strong potential to modify and functionalize the surface of materials for enhancement of adsorption capacity and separation efficiency of contaminations.



Figure 9. (a) Preparation of Co₃O₄ nano-trap-anchored Pt NPs on Al₂O₃ supports, and TEM images of (b,c) Pt/Al₂O₃, (d,e) Co₃O₄/Pt/Al₂O₃, and (f,g) Co₃O₄@Pt/Al₂O₃. Reproduced with permission [98]. Copyright 2017, Wiley.



Figure 10. (**a**–**d**) TEM, and (**e**–**j**) STEM images of MnO₂-GOS-TiO₂, and (**k**) activity and (**l**) anti-SO₂ poisoning time of MnO₂, MnO₂-TiO₂, MnO₂-GOS, and MnO₂-GOS-TiO₂. Reproduced with permission [104]. Copyright 2019, the Royal Society of Chemistry.

5. Summary and Outlook

In this review, we summarize representative publications on pollutants elimination by the ALD technique in recent years from the perspective of surface modification approaches, including conformal coating, uniform particle deposition, and area-selective deposition. Conformal coating is widely used in photocatalytic degradation of dyes, antibiotics, and other organic pollutants as well as an adsorption and separation process, and can offer a protection layer or adjust the surface properties of catalysts to enhance the performance for removal of pollutants. Uniform particle deposition and area-selective deposition are mainly adopted to fabricate and decorate nanostructured catalysts, and much progress has been achieved for efficient elimination of toxic gases, especially CO. Though some excellent results were obtained, some challenges and barriers of ALD applications in pollutants' elimination need to be overcome in the future. So far, the ALD reaction mechanisms and products' growth models are not clear for some metal and metal oxide ALD. In addition, more attempts are needed to focus on elimination of POPs, NO_x, and hydrocarbons instead of dyes and CO. Moreover, the incomplete deposition is a critical problem when low-temperature ALD is applied, which needs to be overcome in the future. These challenges are discussed in detail as follows.

First, although many metal and metal oxide ALD have been achieved using various precursors, the exact reaction mechanisms are still unclear for most of ALD processes now, e.g., Pt ALD and Fe ALD. Though adopting advanced in-situ characterizations, the intermediate products and final products during the reaction can be identified and the reaction process can be revealed. It is crucial to explore and further understand the ALD reaction mechanisms, so the surface of materials can be decorated and optimized precisely based on the mechanisms in order to boost the specific property and performance of catalysts.

Secondly, most of the studies focused on photocatalytic degradation of dyes, and some excellent results were obtained. However, it is noted that the dyes are easy to photodegrade in comparison with cephalexin, phenol, and POPs. Thus, more efforts are needed to design photocatalysts with high activity via ALD and solve the pollutions of POPs and cephalexin, which is more difficult to degrade under UV or solar light. In addition, during the degradation of POPs and cephalexin, some toxic intermediates may be produced, which needs to be identified and more attention needs to be paid. Moreover, CO oxidation can be achieved at room temperature over the ALD prepared catalysts, but it needs much higher temperature for removal of hydrocarbons, e.g., CH₄, in the oxidation reactions. Thus, more attempts are deserved to lower the catalytic oxidation temperature for removal of hydrocarbons through synthesis of more efficient catalysts via ALD.

Last, but not least, some materials are temperature sensitive, e.g., polymers, and only low-temperature ALD can be performed to modify the surface and protect the materials. However, low-temperature ALD may lead to the incomplete deposition. Some organic ligands exist in the film, which affect the activity of the catalysts for removal of pollutants. In addition, in certain conditions, ultrathin films prepared by ALD would decompose or aggregate to NPs after heat treatment, and result in the failure of protecting the core materials and influence the performance of the catalysts. In order to solve this issue, more efforts are needed to improve the low temperature completion and high temperature stability of films prepared by ALD by introducing a protection layer and enhancing the interaction between films and substrates.

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