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Recent Development of VUV-Based Processes for Air Pollutant Degradation

Haibao Huang [1,2]*, Haoxian Lu [1], Huiling Huang [1], Lei Wang [1], Jieni Zhang [1] and Dennis Y. C. Leung [3]*

[1] Department of Environmental Engineering, School of Environmental Science and Engineering, Sun Yat-Sen University, Guangzhou, China, [2] Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, Sun Yat-sen University, Guangzhou, China, [3] Department of Mechanical Engineering, The University of Hong Kong, Hong Kong, Hong Kong

As air pollution poses a great challenge around the globe, it is essential to fashion out a way of efficiently degrading the air pollutants. Vacuum Ultraviolet (VUV)-based processes are an emerging and promising technology for environmental remediation such as air cleaning, wastewater treatment, and air/water disinfection. When VUV irradiation, photolysis, photocatalysis, and ozone-assisted oxidation are involved at the same time, it results in the fast degradation of air pollutants because of their strong oxidizing capacity. The mechanisms of how the oxidants are produced and how they react are discussed in this review. This paper focuses mainly on the three VUV-based oxidation processes including VUV photolysis, VUV combined with ozone-assisted oxidation, and VUV-PCO with emphasis on their mechanisms and applications. Also, the outlook of these processes are proposed in this paper.

Keywords: VUV-PCO, photolysis, ozone-assisted oxidation, photocatalysis, air pollutants

INTRODUCTION

Common Air Pollutions

With the rapid development of industry and increasing population, air pollutions presently poses a more serious challenge. Solving the problem of air pollution is one of the most difficult challenges faced by a number of governments around the world (Spigno et al., 2003). Air pollutants, including biological and gaseous substances exist in ambient as well as in indoor environments and require simultaneous removal for better air quality (Yu et al., 2009). Gaseous pollutants can be classified into organic and inorganic, and among them organic compounds take a majority of the emission category. Inorganic pollutants mainly refer to sulfur dioxide, nitric oxide, hydrogen sulfide, and so on, while organic pollutants mainly consist of Volatile Organic Compounds (VOCs) with boiling points between room temperature and 260°C (Huang et al., 2015b) including alkanes, aromatic hydrocarbons, aromatics, olefins, alcohols, aldehydes, ketones, halogenated hydrocarbon, and so on. Among the list of 25 toxic gaseous pollutants listed by U.S. EPA, 18 of them are organic compounds (Lee, 1991). The generation, transportation and storage processes of the raw chemicals and industries, such as pharmaceutical chemicals, printing, and petrochemical industries produce most of the VOCs (Li et al., 2009; Brito et al., 2015). VOCs cause great harm to the human health. Long time exposure to VOCs may cause health problems, such as Sick Building Syndromes (SBS) (Järnström et al., 2006), cancer, genetic mutation, and so on. It can also cause air pollution like PM2.5, photochemical smog, ozone, and global warming (McGwin et al., 2010; Wu et al., 2012).

In the past, most of the studies focused on the degradation of single pollutant but not on multiple air pollutants (Thiruvenkatachari et al., 2008). VUV-based processes are advanced oxidation processes (AOPs) without selectivity, which is of a great advantage for the degradation of multiple air pollutants.

Common Air Purification Methods

Air purification process can be generally divided into physical, chemical, and biological methods.

Physical Methods

In physical methods, pollutants can be separated from waste gas due to the different physical properties like boiling point and solubility. It can be divided into absorption, adsorption, membrane separation, and condensation. Moretti et al. (Moretti, 2002) tried to absorb the organic gas by Nonpolar mineral oil such as light diesel and engine oil with a removal efficiency of 90%. Noll (Standeker et al., 2009), Moura (Moura et al., 2011), Daifullah (Daifullah and Girgis, 2003), and Kwong (Kwong and Chao, 2010) adopted the silica aerosol, alumina, activated carbon, and fly-ash in order to adsorb VOCs. High removal rate of VOCs can be achieved under membrane separation (Xing et al., 2000). Baker et al. (1994) recycled VOCS from waste gas by compression, condensation, and membrane separation.

However, there are some disadvantages that tend to limit the application of physical methods. For example, most of the VOCs are insoluble in water which reduces the absorption efficiency. In addition, the solution after absorption needs further disposal. Although the adsorption process is simple and it can also recycle the useful compounds of the waste gas, secondary pollution will occur during the desorption process which may increase the cost. The high cost also greatly restricts the application of membrane separation.

Biological Methods

In biological treatment, pollutants are generally decomposed into carbon dioxide, water, and cytoplasm by microbial metabolism (Deshusses and Johnson, 2000). Biological degradation has many operational and cost advantages over the conventional physico-chemical methods (Aizpuru et al., 2001). Niu et al. (2014) discovered that a bio-tricking filter can be used to remove inorganic pollutants such as NO from air stream using bacteria extracted from waste water sludge. Lu et al. (2000) used bio-trickling to destruct BTEX vapor and they found that more than 90% BTEX could be achieved. Rene et al. (2009) discovered that removal efficiencies of benzene is higher than 90% in a laboratory scale bio-filtration. However, this system needs a large area and long start-up time (Wang et al., 2008).

Chemical Methods

Chemical methods can remove pollutants by a series of reactions like neutralization and redox reactions. The processes include incineration and catalytic combustion (Barbero et al., 2008), plasma treatment (Daniels, 2002), and acid-base spray (Dulin and Rosar, 1975). Harmful substances can be degraded completely into non-toxic substances by chemical methods. However, the cost is higher than physical and biological methods as special chemicals are needed in the processes, thus, it is highly necessary to reduce their cost. The required temperature of VOCs catalytic combustion can be greatly decreased by developing efficient catalysts, thereby reducing the energy consumption. Wang et al. (Wang, 2004) adopted γ-Al_2O_3 supported transition-metal oxide catalysts in order to oxidize methylbenzene which can be degraded completely under a temperature of 360℃. Wang et al. (2006) also used CuO/CeO_2 for catalytic oxidation of toluene which can be completely degraded at temperature lower than 240°C.

As shown above, the application of traditional technology is limited by some disadvantages such as byproducts, cost, and degradation capacity. Therefore, it is essential to develop a cost-effective and environmental-friendly treatment method under increasingly complicated air pollution problems and stringent air quality standards. As such AOPs have been studied for air pollution control because of its high efficiency and mild reaction condition (Zhu et al., 2015). Among them, VUV-based processes are emerging processes for the degradation of air pollutants that can provide an efficient solution for air pollution control.

Introduction of UV and VUV Irradiation

UV irradiation refers to the electromagnetic radiation with wavelength from 1 to 380 nm. It can be categorized into UV-A (380–315 nm), UV-B (315–280 nm), UV-C (280–200 nm), vacuum-UV (VUV, 200–100 nm), and extreme UV (100–1 nm) (Oppenländer, 2003). The main method used to produce UV radiation is through the discharge from low pressure mercury lamp. Medium pressure mercury lamp can also be used to produce UV-A, UV-B, and UV-C. However, UV-B and UV-C can be absorbed by the glass tube and it needs special material like quartz to avoid loss of UV light (Thiruvenkatachari et al., 2008). As for the VUV lamp, it required a quartz with high purity in order to prevent the absorption of the shorter wavelength's UV irradiation. Therefore, barrier discharge (Masschelein and Rice, 2002) and Xe-excimer radiators (Wang et al., 2010) are generally used to produce VUV irradiation.

Recently, among the different AOPs, VUV-based processes have attracted much attention in the degradation of air pollutants. Yang (Yang et al., 2007), Huang (Huang et al., 2011), and Jiang (Jiang et al., 2015) have tried to eliminate the air pollutants with VUV photolysis. Compared with UV, VUV can degrade air pollutants more efficiently due to the following reasons: (1) VUV can directly destruct the compounds due to its energetic photons; (2) With certain humidity, VUV irradiation can interact with water vapor and produce hydroxyl radicals that can degrade compounds; (3) Oxygen species like $O(^1D)$, $O(^3P)$, and O_3 can be formed from the reaction between VUV irradiation and oxygen (Bergonzo and Boyd, 1993; Hashem et al., 1997; Fu et al., 2011). When degradation capacity and cost are put into consideration, the application of VUV becomes more attractive. However, it also has some disadvantages such as the formation of residual ozone that will cause secondary pollution.
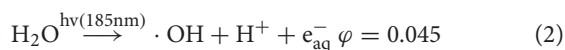
GENERATION OF THE OXIDANTS

General VUV-based processes include the VUV photolysis (Alapi and Dombi, 2007a), VUV–PCO (Huang et al., 2011), VUV combined with Ozone-assisted Catalytic Oxidation (VUV–OZCO) (Huang, 2015). The sections below will focus on the oxidants generated from these three processes.

Hydroxyl Radicals Formation

Photolysis
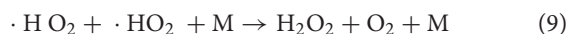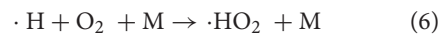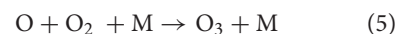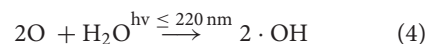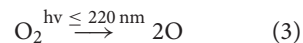
As the wavelength of VUV spectral domain (100–200 nm, mainly at 185 nm) is shorter than that of normal UV (Gonzalez et al., 2004), it can produce photons with higher energy level. Therefore, many studies have been carried out to achieve photo-degradation of pollutants by VUV photolysis alone (Ye et al., 2014). Energetic photons play an important role in the degradation process because they can result in direct degradation of the pollutants and in the formation of oxidizing species like hydroxyl radical and ozone that can oxidize pollutants (Bergonzo and Boyd, 1993; Kutschera et al., 2009; Zoschke et al., 2014). Hydroxyl radical is highly reactive for the oxidation of the pollutants in gaseous or aqueous phase with no selectivity.

In the VUV photolysis of aqueous reaction systems, photolysis of water is the main pathway to produce hydroxyl radical (Gonzalez et al., 2004; Zoschke et al., 2014). Water absorbs light strongly at wavelengths lower than 190 nm. However, due to the high absorption rate, the VUV irradiation is absorbed within a narrow layer around the lamp (approx. 300 mm at 185 nm) (Kutschera et al., 2009). The ionization of water occur via the homolysis (Equation 1) and photochemical (Equation 2; Zoschke et al., 2014) reactions. The oxidants formed are mainly hydroxyl radicals, hydrogen atoms, and solvated electrons all of which initiate manifolds of reduction and oxidation reactions (Oppenländer, 2003). The quantum yields (φ) of the hydroxyl radical and the solvated electrons are 0.33 and 0.045, respectively (Lopez et al., 2000; Kutschera et al., 2009).

$$H_2O \xrightarrow{hv(185\,nm)} \cdot OH + \cdot H \quad \varphi = 0.33 \tag{1}$$

$$H_2O \xrightarrow{hv(185nm)} \cdot OH + H^+ + e_{aq}^- \; \varphi = 0.045 \tag{2}$$

In the same way, the photolysis of moisture gas takes place in gaseous phase and hydroxyl radicals are generated with the VUV irradiation. In addition, another way to form $\cdot OH$ is in a humidified O_2 stream which can open up another pathway for the decomposition of pollutants. With wavelengths under 220 nm, oxygen can be dissociated into two O atoms (Equation 3; Atkinson et al., 1996). The O atom does not only interact with water to produce hydroxyl radicals (Equation 4), it also reacts with oxygen to produce ozone (Equation 5; Alapi and Dombi, 2007b). Therefore, there is a competition between the generation of hydroxyl radicals and ozone. It was reported that humidity inhibits O_3 formation in an O_2 stream and ·OH will be formed due to the reaction of O atom and water (Atkinson et al., 1996). Further reactions in the system will lead to the formation of hydrogen peroxide (Ye et al., 2013; Equations 7–9). Also, the generated H_2O_2 will also be decomposed into hydroxyl radicals (Equation 10) under the irradiation of 185 and 254 nm UV light (Atkinson et al., 2004).

$$O_2 \xrightarrow{hv\,\leq\,220\,nm} 2O \tag{3}$$

$$2O + H_2O \xrightarrow{hv\,\leq\,220\,nm} 2 \cdot OH \tag{4}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{5}$$

$$\cdot H + O_2 + M \rightarrow \cdot HO_2 + M \tag{6}$$

$$\cdot OH + \cdot OH + M \rightarrow H_2O_2 + M \tag{7}$$

$$\cdot HO_2 + \cdot HO_2 \rightarrow H_2O_2 + O_2 \tag{8}$$

$$\cdot HO_2 + \cdot HO_2 + M \rightarrow H_2O_2 + O_2 + M \tag{9}$$

$$H_2O_2 \xrightarrow{hv(185\,nm\;and\;254\,nm)} 2 \cdot OH \tag{10}$$

Overall, hydroxyl radicals are generated in gaseous phase via four pathways: (1) homolysis of water, (2) photochemical ionization of water, (3) reactions between O atom and water, and (4) photolysis of hydrogen peroxide.

Photocatalysis of Semiconductor

Hydroxyl radicals produced by photolysis are mainly attributed to the 185 nm UV irradiation. However, VUV lamp can only emit <10% 185 nm irradiation while the majority 254 nm UV irradiation has not been fully utilized in photolysis (Alapi and Dombi, 2007a). Therefore, semiconductor like TiO_2 was used to produce more hydroxyl radicals via photocatalysis. The mechanism of photocatalytic oxidation (PCO) is similar to that of UV/TiO_2, which is shown in **Figure 1**.

As one of the semiconductor catalysts, TiO_2 photocatalytic material has special electronic structure. Unlike metals which have a continuum of electronic states, semiconductors possess a void energy region where low energy levels are available to promote recombination of electrons and holes produced by photo-activation within the material. The void region which extends from the top of the filled valence band to the bottom of the vacant conduction band is called the band gap (Linsebigler et al., 1995). With the irradiation of UV light, TiO_2 absorbs the energy of photon. When the energy of photon is higher than the width of the semiconductor's void band, the electron of valence band will transfer to the conduction band. Therefore,
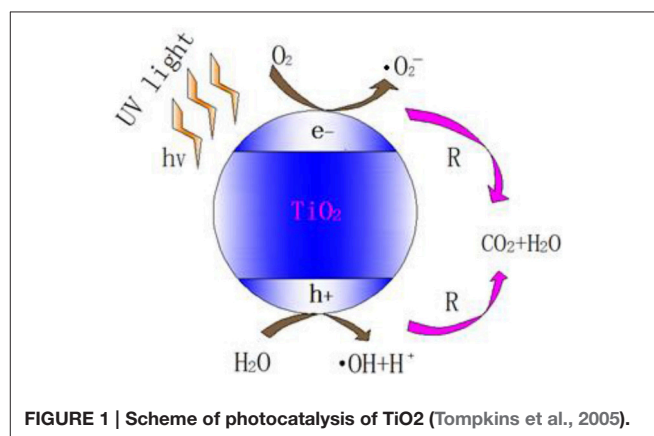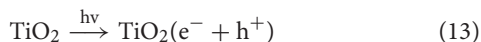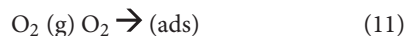

FIGURE 1 | Scheme of photocatalysis of TiO2 (Tompkins et al., 2005).

the pairs of electron-holes are created in the semiconductor, and the charge will be transferred between electron-hole pairs and adsorbed species (reactants) on the semiconductor surface, photo-oxidation will then occur (Zhao and Yang, 2003).

The photo-generated electron (e^-) has strong redox potential and is able to reduce the electron acceptor of the semiconductor's surface. The photo-generated hole (h^+) generated by activation is a strong oxidant. It reacts with absorbed water (H_2O) or surface hydroxyl ion chemically (OH^-) and produces hydroxyl radical with strong oxidizing property (Schwitzgebel et al., 1995).
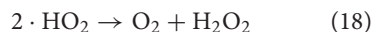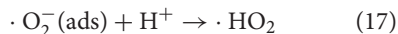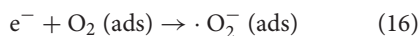
O_2 and H_2O will interact with the electrons and photo-generated holes in humid air. The overall reaction is as follows (Konstantinou and Albanis, 2004): First, O_2 and H_2O are absorbed on the surface of the TiO_2 and then form adsorbed oxygen and adsorbed water, respectively (Equations 11, 12). Subsequently, the surface of the TiO_2 produces photo-generated electron (e^-) and photo-generated hole (h^+) under UV irradiation (Equation 13).

$$O_2 \text{ (g)} \rightarrow O_2 \text{ (ads)} \tag{11}$$

$$H_2O \text{ (g)} \rightarrow H_2O \text{ (ads)} \tag{12}$$

$$TiO_2 \xrightarrow{h\nu} TiO_2(e^- + h^+) \tag{13}$$

Afterwards, the photo-generated hole is captured by the surface of adsorbed water and hydroxyl ion, producing hydroxyl radicals (Equations 14, 15).

$$h^+ + H_2O \rightarrow \cdot OH + H^+ \tag{14}$$

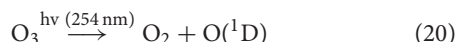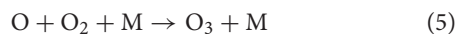$$h^+ + OH^- \rightarrow \cdot OH \tag{15}$$

Furthermore, the addition of O_2 leads to an increase in the upward band bending, and therefore, suppresses the electron-hole recombination process, leading to a more efficient photo-activity (Linsebigler et al., 1995). Meanwhile, further reaction will continuously produce hydroxyl radical (Equations 16–19).

$$e^- + O_2 \text{ (ads)} \rightarrow \cdot O_2^- \text{ (ads)} \tag{16}$$

$$\cdot O_2^- \text{ (ads)} + H^+ \rightarrow \cdot HO_2 \tag{17}$$

$$2 \cdot HO_2 \rightarrow O_2 + H_2O_2 \tag{18}$$

$$H_2O_2 + \cdot O_2^- \text{ (ads)} \rightarrow \cdot OH + O_2 + OH^- \tag{19}$$

Generation of Ozone

The VUV irradiation at 185 nm can be used for the generation of ozone using oxygen. As shown in Equations (3) and (5), O atom will be generated by the photolysis of oxygen when absorbing VUV irradiation and then reacted with an oxygen molecule, forming ozone. This reaction takes place in the presence of a molecule M which absorbs the excessive kinetic energy (Bolton and Denkewicz, 2008). Meanwhile, ozone can be decomposed by 254 nm UV irradiation, forming an O atom and an oxygen molecule, as shown in Equation 20.

$$O_2 \xrightarrow{h\nu \leq 220nm} 2O \tag{3}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{5}$$

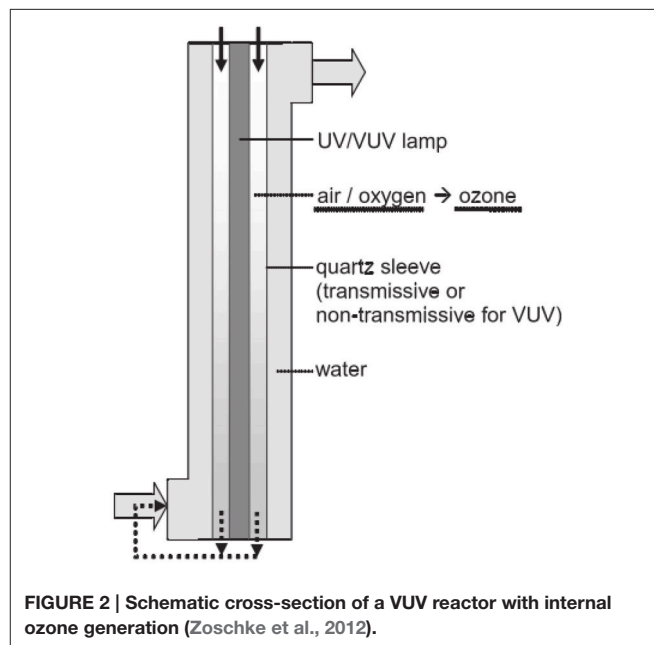$$O_3 \xrightarrow{h\nu \text{ (254 nm)}} O_2 + O(^1D) \tag{20}$$

The yield of ozone from VUV irradiation is very low. About 9 g/kWh and 7.2 g/kWh of ozone can be produced from oxygen and air, respectively (Hashem et al., 1997). Two reasons might be responsible for the low ozone generation. First, the emission intensity at 185 nm constitutes only 8% of all UV irradiation. Also, partial ozone could be decomposed by 254 nm UV light. In addition, VUV irradiation can be easily absorbed by the water vapor. The generated O_3 increases with the decreasing water content. Ye et al. (2013) studied the effect of the operating parameters on ozone formation. It was found that H_2O and O_2 contents, as well as flow rate, could significantly affect O_3 production. The increased H_2O content led to the decreased O_3 production, whereas O_2 content had an opposite effect.

Despite the low ozone yields of low-pressure mercury vapor lamps, ozone generation and photolysis of pollutants can be simultaneously achieved by a single irradiation source (Hashem et al., 1997). The VUV systems with internal ozone generation has been used for the disinfection of micro-pollutants (Bolton and Denkewicz, 2008; Zoschke et al., 2012), as shown in **Figure 2**. The air or oxygen go through the annular space between the UV lamp and the quartz sleeve which can absorb the VUV radiation at 185 nm to generate ozone. The gas containing ozone is injected into the water on the other side of the quartz sleeve. In addition, the UV/VUV radiation passes directly through the quartz sleeve into water to achieve the photolysis of an aqueous phase.

Ozone is a strong oxidant and has a great potential to be utilized for the degradation of pollutants. It was reported that high efficiency of degradation of benzene (Einaga and Futamura, 2004a; Einaga et al., 2009), ethanol (Shayan and Vahedpour, 2013), and acetone (Reed et al., 2006) can be achieved by ozone catalytic oxidation treatment.

The key of ozone catalytic oxidation technology is the preparation of catalysts with high CO_2 selectivity, stability, and removal efficiency. Ozone decomposition catalysts consist
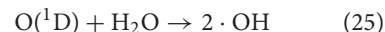

FIGURE 2 | Schematic cross-section of a VUV reactor with internal ozone generation (Zoschke et al., 2012).
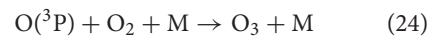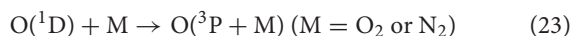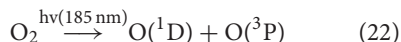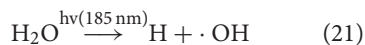
of precious metals (such as palladium, silver) and transition metal oxides, and so on. The application of precious metals is greatly limited by its high cost and the difficulty of regeneration. In recent years, transition metal oxides have attracted much attention. Among the transition metal oxides, the supported catalysts are more attractive because of its lower cost and better catalytic stability. The supports include Al_2O_3 (Einaga and Futamura, 2004b, 2005; Konova et al., 2006), TiO_2 (Radhakrishnan and Oyama, 2001), SiO_2, and molecular sieve (Einaga et al., 2013). Einaga (Einaga and Ogata, 2009) investigated the performance of ozone catalytic oxidation of benzene over Mn catalysts with different carriers such as SiO_2, Al_2O_3, TiO_2, and ZrO_2. The results showed that the increased specific surface area of the support can enhance benzene degradation. The high specific surface area does not only facilitate the absorption of pollutants but also prolongs the reaction time between ozone and pollutants.

Transition metals including Mn, Fe, Co, Cu, Ni, and Ag were generally used as active components. Among different Al_2O_3 supported transition metals, Mn has excellent catalytic activity toward both ozone decomposition and benzene degradation (Einaga and Ogata, 2010). Ebrahim et al. (Rezaeia et al., 2013) studied the effect of Mn loading on ozone catalytic degradation of toluene and found that high Mn loading is detrimental for ozone decomposition and benzene degradation. Despite its potential for efficient pollutant degradation, ozone catalytic oxidation technology is still faced with some problems like the deactivation of catalyst, emission of residual ozone, and generation of byproducts.

VUV-BASED PROCESSES FOR AIR POLLUTANTS DEGRADATION

Direct VUV Photolysis

Direct photolysis by Ultraviolet (UV) and Vacuum Ultraviolet (VUV) have been intensively studied for removing both organic and inorganic compounds from water or air. VUV lamp has its main emission at 254 nm with a small (around 6%) intensity of irradiation at 185 nm, while UV lamp has its output only at 254 nm (Alapi and Dombi, 2007a). VUV photolysis is known for better performance on the removal of pollutants based on the following reasons: (1) the high-energy photons generated by 185 nm irradiation can degrade organic compounds; (2) in the presence of water, 185 nm irradiation can produce strong oxidants such as hydroxyl radical (●OH); (3) 185 nm irradiation can generate ozone in the presence of O_2 (Yang et al., 2007). Oxygen species [for example, $O(^1D)$, $O(^3P)$, and O_3] and hydroxyl radicals (●OH) are generated by the dissociation of oxygen and water molecules under VUV with high-energy photon according to the following reactions (Bergonzo and Boyd, 1993; Hashem et al., 1997; Fu, 2011; Equations 21–25):

$$H_2O \xrightarrow{hv(185\,nm)} H + \cdot OH \qquad (21)$$

$$O_2 \xrightarrow{hv(185\,nm)} O(^1D) + O(^3P) \qquad (22)$$

$$O(^1D) + M \rightarrow O(^3P + M)\ (M = O_2\ or\ N_2) \qquad (23)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (24)$$

$$O(^1D) + H_2O \rightarrow 2 \cdot OH \qquad (25)$$

These energetic oxidants can be utilized to improve removal efficiencies of the pollutants. It has been proven that VUV photolysis is a more efficient and economical process than the UV photolysis (Huang et al., 2013).

VUV photolysis has also been used in the treatment of wastewater. It has proven to be effective for the treatment of certain types of wastewater pollutants such as fluorescence of phenol, nitrobenzene, SDBS surfactants, Methylene Blue (MB), and other pollutants (Imoberdorf and Mohseni, 2011a,b; Zoschke et al., 2014). Alapi et al. (Alapi and Dombi, 2007a) compared the UV and VUV photolysis of phenol and revealed that the rate of degradation of phenol in the VUV process is about 2 times faster than that in the UV-irradiated process, as shown in **Figure 3**. Phenol decomposition is initiated by direct photolysis via a biphotonic process in the UV-irradiated solutions, while it can also take place by ·OH-based reactions in VUV-irradiated solutions (Alapi and Dombi, 2007a).

Recently, much attempt was made using VUV to degrade air pollutants, such as benzene (Huang H. B. et al., 2014), methylbenzene (Jeong et al., 2006), chlorinated methanes (Alapi and Dombi, 2007b), gaseous α-pinene (Chen et al., 2010). Cheng (Cheng, 2011) investigated the photo-degradation of
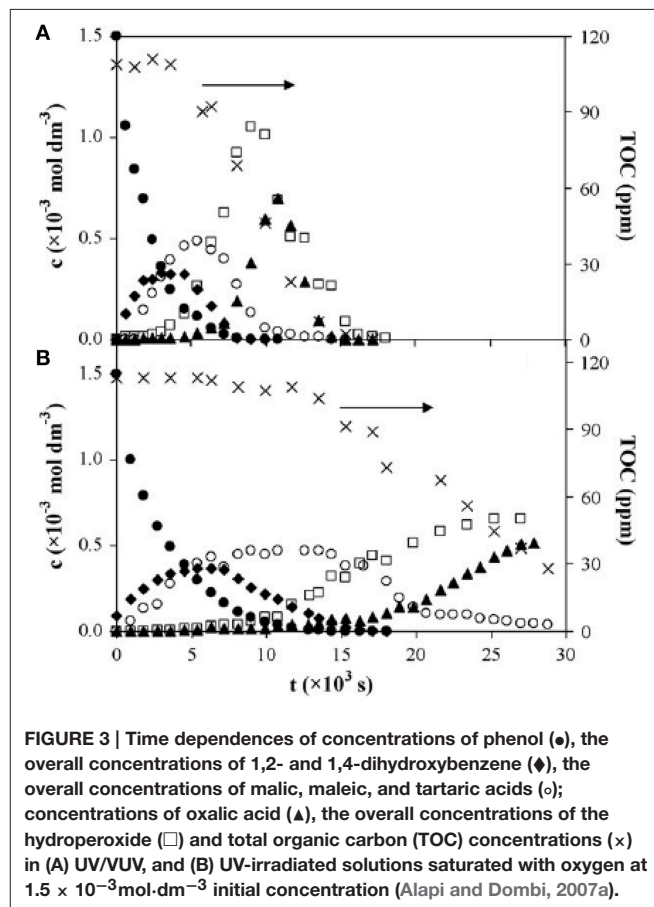
FIGURE 3 | Time dependences of concentrations of phenol (●), the overall concentrations of 1,2- and 1,4-dihydroxybenzene (♦), the overall concentrations of malic, maleic, and tartaric acids (○); concentrations of oxalic acid (▲), the overall concentrations of the hydroperoxide (□) and total organic carbon (TOC) concentrations (×) in (A) UV/VUV, and (B) UV-irradiated solutions saturated with oxygen at 1.5×10^{-3} mol·dm^{-3} initial concentration (Alapi and Dombi, 2007a).
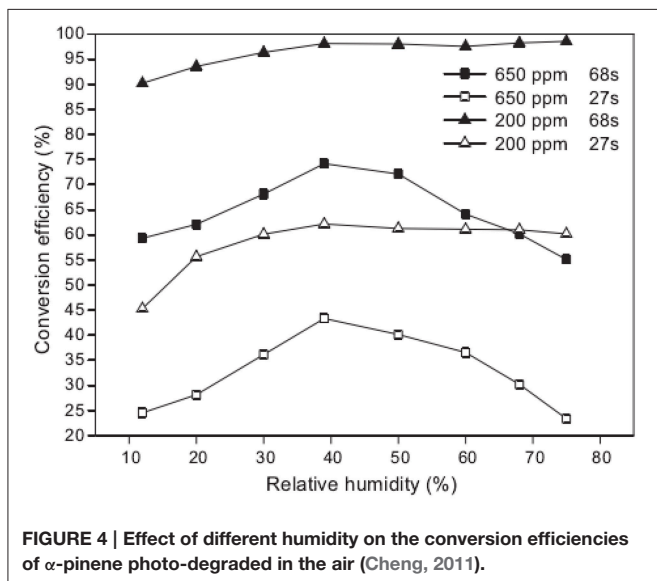
gaseous α-pinene by a VUV light. It was discoveredthat most efficient conversion was obtained under the moderate humidity condition. As shown in **Figure 4**, nearly 100% conversion efficiency of α-pinene was achieved in about 70 s under moderate humidity condition.

Meanwhile, Alapi et al. (Alapi and Dombi, 2007b) investigated the effect of relative humidity and pollutant concentration on the degradation of chlorinated methanes and their mixtures in an oxygen stream under direct VUV photolysis. Chen et al. (2010) used VUV photo-degradation to improve the removal capacity of gaseous α-pinene which is hydrophobic and poorly biodegradable. ? investigated the effect of relative humidity, residence time, initial benzene concentration, and reaction temperature on photo-oxidation of gaseous benzene by 185 nm VUV irradiation. It was discovered that benzene removal efficiency can be greatly improved in the presence of vapor and the formation of hydroxyl radicals is mainly responsible for the degradation. The abovementioned experiments indicated that VUV photolysis is a promising approach to degrade air pollutants.

However, VUV photolysis alone is not effective enough for the total oxidation of organic compounds because of the limited efficiencies that may lead to the formation of organic intermediates (Zhao and Yang, 2003; Alapi and Dombi, 2007a). More importantly, VUV photolysis will generate much toxic O_3 (Alapi and Dombi, 2007b; Yang et al., 2007), which is harmful to human health as it causes headaches, throat dryness and damage to mucus membranes at levels as low as 0.1–1 ppm (Huang et al., 2011). Thus, the residual O_3 will cause secondary pollution if not removed before emission.

VUV Photolysis-Ozone Catalytic Oxidation (VUV-OZCO)

Apart from the VUV photolysis, there is another process in the VUV-based processes which has great potential to deal with air pollution. Ozone used for ozone-assisted catalytic oxidation was

FIGURE 4 | Effect of different humidity on the conversion efficiencies of α-pinene photo-degraded in the air (Cheng, 2011).
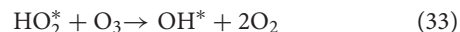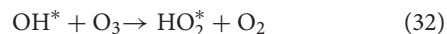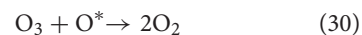
generally generated from high voltage discharge. The cost of this is high and the system is relatively complex. In addition, the degradation efficiency of VUV photolysis alone is low and the residual ozone brings new pollution (Bergonzo and Boyd, 1993; Hashem et al., 1997; Fu, 2011). To avoid the above problems, VUV photolysis can be combined with ozone-assisted catalytic oxidation to make use of the residual ozone and eliminate it. Such a novel process is called VUV-OZCO, in which VOCs would be initially destructed by the VUV photolysis and then be further oxidized by the OZCO using the residual O_3 from the VUV photolysis. VUV-OZCO would not only save the cost but also improve the pollutants removal efficiency and eliminate the problem of residual ozone. A possible system of the abovementioned process is shown in **Figure 5**.

As mentioned above, VUV-OZCO degrades pollutant via two path ways: (1) VUV photolysis; (2) Ozone-assisted catalytic oxidation. The mechanism of VUV photolysis has been described above. The mechanism of catalytic oxidation of ozone varies under different reaction conditions. Under low temperature and low humidity condition, catalytic decomposition of ozone involves two irreversible reactions, that is, the adsorption of ozone and desorption of oxygen atom on the surface of catalyst. The specific processes are as follow (Dhandapani and Oyama, 1997; Li and Oyama, 1998; Equations 26–28):

$$O_3 + * \rightarrow O_2 + O^* \tag{26}$$
$$O_3 + O^* \rightarrow O_2 + O_2^* \tag{27}$$
$$O_2^* \rightarrow O_2 + * \tag{28}$$
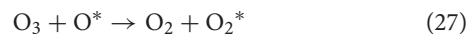
where * is the symbol of the catalyst surface active site.

Under high humidity, the catalyst surface will form a layer of liquid membrane and generate active site by the interaction between metal ions and adsorption liquid membrane. Besides, the liquid film will react with intermediate O^* to generate hydroxyl radicals, which can be used to degrade ozone and pollutants. Some studies have shown that the increased humidity is beneficial to improve the removal efficiency of ozone decomposition and air pollutants. Specific processes are shown in Equations (29–34) (Dhandapani and Oyama, 1997; Einaga and Futamura, 2004b):

$$O_3 + * \rightarrow O_2 + O^* \tag{29}$$
$$O_3 + O^* \rightarrow 2O_2 \tag{30}$$
$$H_2O + O^* \rightarrow 2OH^* \tag{31}$$
$$OH^* + O_3 \rightarrow HO_2^* + O_2 \tag{32}$$
$$HO_2^* + O_3 \rightarrow OH^* + 2O_2 \tag{33}$$
$$HO_2^* + OH^* \rightarrow H_2O + O_2 + * \tag{34}$$

Under certain humidity, ozone catalytic oxidation uses highly reactive intermediates O^*, O_2^*, and ·OH to degrade organic pollutants (Equations 35–37).

$$R + * \rightarrow R^* \tag{35}$$
$$R^* + O^* \rightarrow CO + CO_2 \tag{36}$$
$$R^* + OH^* \rightarrow H_2O + CO_2 \tag{37}$$

where R represents the pollutant to be degraded.

Huang et al. (Huang, 2015) firstly developed this system to degrade VOCs and studied its performance and mechanism. The results show that both benzene and O_3 are completely removed by VUV-OZCO with Mn/ZSM-5 catalysts. As a new technology, few studies have been carried out using VUV-OZCO for air pollution control. However, it provides an efficient and promising process for the degradation of VOCs. This VUV-OZCO process would not only improve the degradation and the mineralization rate, but it will also remove residual ozone.

Photocatalytic Oxidation under VUV Irradiation (VUV-PCO)
VUV-PCO without Ozone Oxidation
Besides the emission of by-products such as ozone, VUV photolysis alone will cause wastage of the UV energy since only 185 nm VUV irradiation can be directly used to destruct the air pollutants while the 254 nm UV irradiation, which is the main emission of the VUV lamps, is not utilized. To fully make use of the UV irradiation, photocatalysts were introduced into the VUV photolysis process. Such process is called VUV-PCO

process. A possible installation of the VUV-PCO system is shown in **Figure 6**.

It is well known that conventional PCO has some disadvantages, such as catalyst deactivation (Peral and Ollis, 1997; Cao et al., 2000), low degradation rate (Mo et al., 2009), formation of toxic byproducts (Huang and Li, 2011), recombination of electron-hole pair, and low efficiency (Mo et al., 2009; Huang and Li, 2011). It has proven that VUV-PCO can obviously improve the efficiency and stability performance of PCO of pollutants and reduce the generation of intermediates (Zhang and Liu, 2004; Yu and Lee, 2007; Huang et al., 2009; Huang and Li, 2011). Huang et al. (2011) compared the VUV, VUV-PCO, UV-PCO processes for toluene destruction. Results showed that the toluene removal efficiency in the VUV-PCO process was 7 times more than that in the UV-PCO process, and no obvious deactivation was observed in the former, as shown in **Figure 7**.

Compared with VUV photolysis, toluene removal was greatly improved. Meanwhile, both the organic compounds and ozone were significantly reduced. In contrast with the UV-PCO, the VUV-PCO can destruct pollutants with more pathways, besides UV-PCO and UV photolysis (Huang et al.,
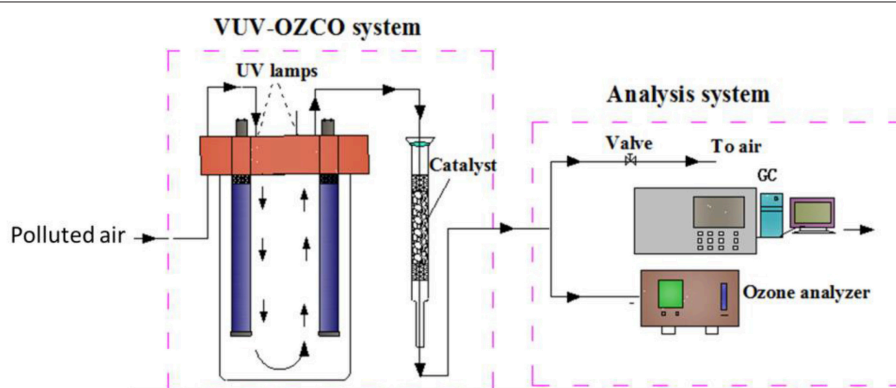

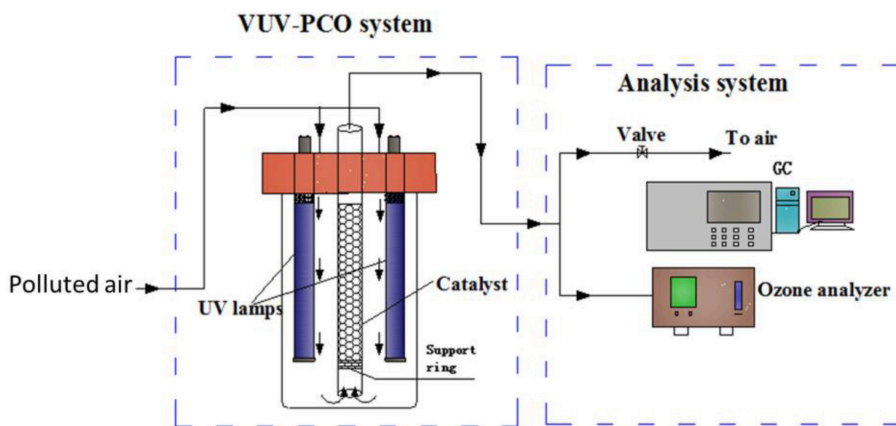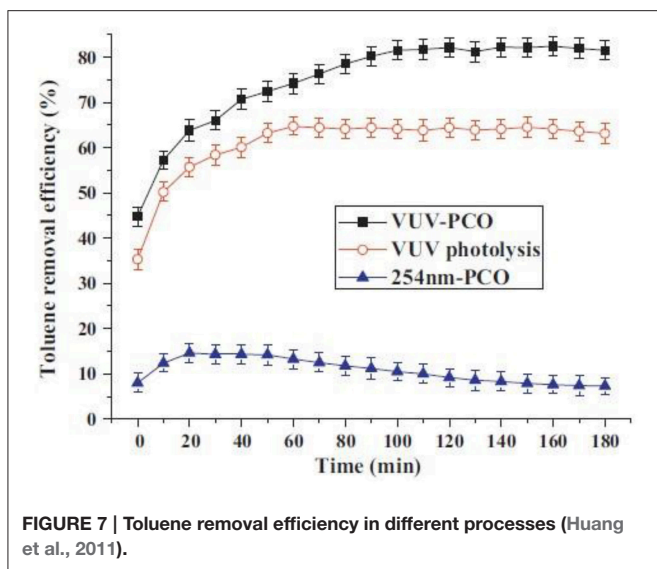**FIGURE 5 | The schematic diagram of VUV-OZCO system (Huang, 2015).**

FIGURE 6 | Schematic diagram of a VUV-PCO system (Huang et al., 2015a).

FIGURE 7 | Toluene removal efficiency in different processes (Huang et al., 2011).

FIGURE 8 | Ultra high-resolution FESEM image of TiO$_2$ film modified with Pt nanoparticles (Fu, 2014).

2011, 2015a). Ozone has a strong electro-negativity, which improves the ability to capture the photon-generated electrons to produce hydroxyl radicals (Huang et al., 2009; Huang and Li, 2011). Meanwhile, ozone can inhibit the combination between electronics and electronic acupuncture point to improve the photoluminescence efficiency (Huang et al., 2009; Huang and Li, 2011). O$_3$ is a byproduct from the VUV lamp, which is also a strong oxidizing agent. Although ozone alone cannot directly oxidize refractory VOCs such as benzene and toluene, it can be decomposed into highly active oxygen through catalytic decomposition for VOCs oxidation (Huang et al., 2015a).

VUV-PCO with Ozone Oxidation

Despite the fact that ozone can help to decompose the VOCs, it can only be partially decomposed and utilized since most of the photocatalysts developed have limited activity toward ozone decomposition (Jeong et al., 2004). The residual ozone still posesa great challenge to achieve a good solution of free secondary pollution. Recently, modified photocatalysts were studied to further eliminate O$_3$ efficiently while enhancing the removal performance of VOCs.

In the study of Fu (2014), Pt modified TiO$_2$ was used to degrade gaseous formaldehyde and O$_3$ byproduct under the UV, UV+O$_3$, and VUV-PCO processes. The FE-SEM image of TiO$_2$ film modified with Pt nanoparticles is shown in **Figure 8**. It was discovered that ∼4–8 Pt nanoparticles (NPs) were deposited onto each TiO$_2$ particle and this uniform dispersion of Pt(NPs) was beneficial for increasing the amount of reactive sites and metal-TiO$_2$ contact area, which result in better performance of HCHO degradation. The above experiments showed that the degradation rate of HCHO decreases in the order of VUV>O$_3$+UV254 nm>UV254 nm for both photocatalysts studied, as indicated in **Figure 9**. In addition, in the VUV-PCO process, O$_3$ is utilized to strengthen the efficiency of PCO of VOCs.
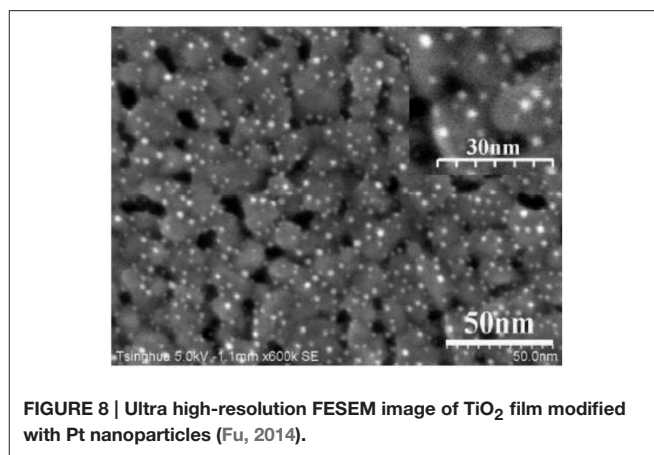
Meanwhile, Kim (Kim et al., 2014) deposited palladium nanoparticles onto TiO$_2$ film for simultaneous removal of toluene and ozone byproduct. Compared with the direct VUV photolysis and the TiO$_2$/VUV photocatalytic processes, Pd–TiO$_2$/VUV process exhibited a better performance toward toluene degradation and 90% of the ozone generated by the 185 nm VUV photolysis was simultaneously degraded, as shown in **Figure 10**. Immersion time reflects to the time that he immersed the TiO$_2$ film into a palladium colloid solution in order to deposit palladium nanoparticles onto the TiO2 film.

Huang et al. (2015a) prepared TiO$_2$ modified by transition metals (Mn, Co, Cu, Ni, and Fe) for studying the PCO of gaseous benzene under VUV irradiation. They found that the PCO efficiency of benzene under VUV irradiation reached 58%, which is over 20 times higher than that under 254 nm UV irradiation, as shown in **Table 1**. In addition, ozone can be completely eliminated by MnO$_2$/TiO$_2$.

Compared to UV-PCO and VUV, VUV-PCO showed higher performance, less byproducts and better stability during VOCs oxidation. Among the multiple pathways in VUV-PCO, photolysis, and catalytic ozonation played a dominant role in VOCs destruction while the contribution of UV-PCO is relatively low, as shown in **Table 1** (Huang et al., 2015a). More efforts should be made to develop efficient materials with excellent photocatalytic activity and superior capacity for ozone decomposition. Although the stability of VUV-PCO was greatly increased compared to UV-PCO, VUV-PCO still faces the challenge of catalytic deactivation due to the accumulation of organic intermediates and water vapor on the surface (Quici et al., 2010). Thus, how to inhibit catalyst deactivation and increase the stability poses another challenge in the VUV-PCO process.

The porous support may be a way to solve the deactivation problem and increase the efficiency of degradation. Yuan et al. (2013) have used H-ZSM-5 as the photocatalyst support to generate the TiO$_2$/M-ZSM-5 catalyst (M = Zn, Cu, Mn). The prepared samples were used as catalyst for degradation of gaseous acetaldehyde in the presence of UV light irradiation, O$_3$ or UV–O$_3$. TiO$_2$/Mn-ZSM-5 presents the highest activity with acetaldehyde degradation rate of 78.9%, as shown in **Figure 11**.
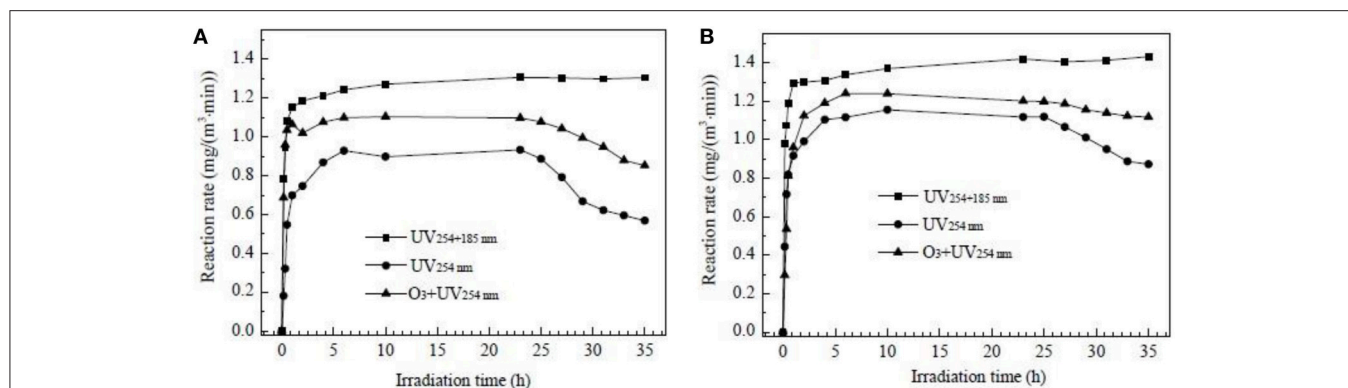
FIGURE 9 | Degradation rate of formaldehyde as a function of irradiation time under UV254, O$_3$+UV254, and UV254+185 nm irradiation over pure TiO$_2$ (A) and Pt-TiO$_2$ films (B) (Fu, 2014).
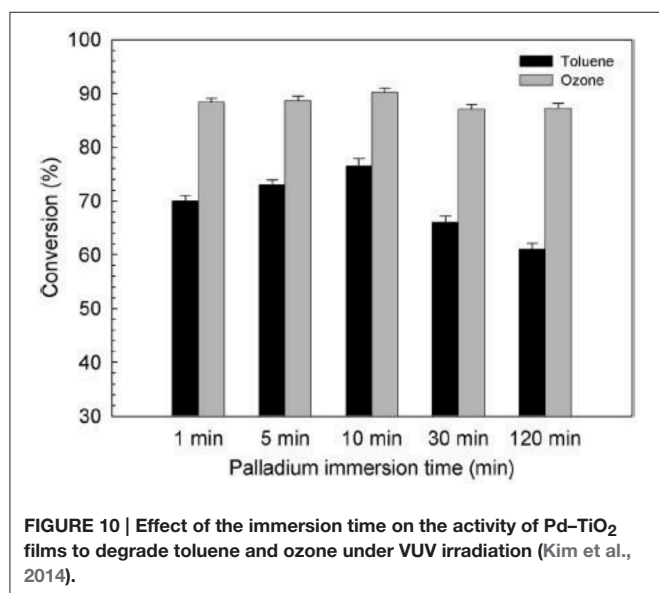

FIGURE 10 | Effect of the immersion time on the activity of Pd–TiO$_2$ films to degrade toluene and ozone under VUV irradiation (Kim et al., 2014).

FIGURE 11 | Degradation of acetaldehyde on M-ZSM-5 and TiO$_2$/M-ZSM-5 under UV–ozone (UV main wavelength, 254 nm; inlet concentration of CH3CHO, 269 ppm; space velocity, 67,000 h^{-1}; inlet concentration of ozone, 131 ppm) (Yuan et al., 2013).

TABLE 1 | Contribution of various sub-processes to benzene removal (Huang et al., 2015a).

	Mn/TiO$_2$	Cu/TiO$_2$	Co/TiO$_2$	Ni/TiO$_2$	P25	Fe/TiO$_2$	TiO$_2$
VUV-PCO, %	58	50.9	51.5	50.3	50.2	45.3	45.7
VUV, %	38	38	38	38	38	38	38
UV-PCO, %	2.4	1.2	2.1	1.5	2	0.8	1.6
Catalytic ozonation, %	17.6	11.7	11.4	10.8	10.2	6.5	6.1

The superior performance results from the coupling effect of photocatalytic and ozone oxidation.

Porous material like ZSM-5 can adsorb the pollutants so that it can prolong the reaction time of photocatalysis and ozone catalytic oxidation thereby improving the efficiency of degradation of pollutants. With its intensive oxidation performance, it will accumulate less intermediates thereby solving the problem of deactivation. Therefore, further research
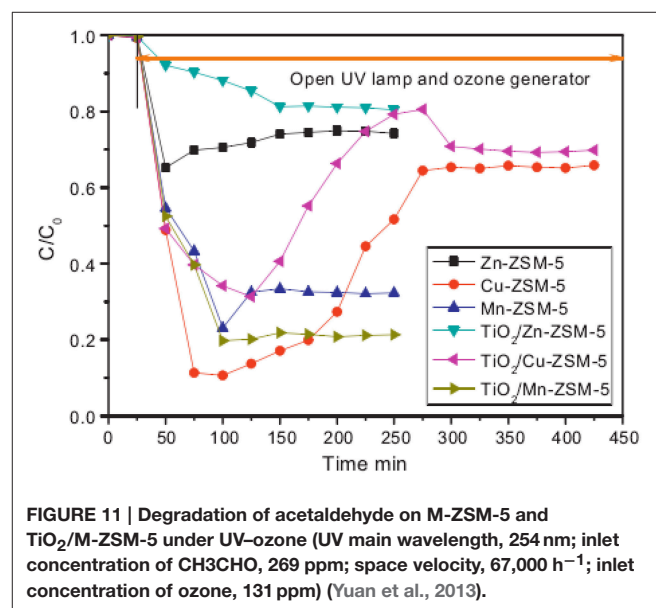
on VUV-based process in the future should adopt this catalyst and find out its potential.

OUTLOOKS IN VUV-BASED PROCESSES FOR AIR POLLUTANTS DEGRADATION

To increase the utilization of VUV irradiation and the residual ozone, VUV-OZCO, and VUV-PCO with ozone oxidation should be focused on, in further study. More attention should be paid on:

(1) Catalytic deactivation. Catalyst deactivation is mainly caused by water deposition and the accumulation of intermediates on the surface of catalysts (Gandhi et al., 2012). It may be solved by hydrophobic catalysts (Zhao and Lu, 1998; Kuwahara et al., 2009) and by metal doping on the catalysts to improve the rate of mineralization and oxidation ability (Qi and Yang, 2004; Wang et al., 2012; Yang et al., 2014).

(2) Mechanism study. VUV-PCO is an emerging process for VOCs degradation and few works were carried out. The mechanism of it is still unclear, which prevent making the best use of it for air pollution control. Therefore, further study should be continued to find out the relationship between VUV photolysis, photocatalysis, and ozone oxidation.

(3) Immobilization of the catalysts (Lei et al., 2009). Most of the catalysts developed are powder or particle catalysts. They cannot be widely used in the industry since it is hard to be reused and regenerated. It is necessary to develop supported catalysts such as honeycomb.

SUMMARY

VUV-based process is an emerging technology. It is very efficient for pollutants degradation as compared with conventional process. The development of VUV-based processes has provided new direction for the generation of reactive hydroxyl radicals for pollution degradation (Chih-Ming et al., 2011).

The technology mainly involves three processes that can efficiently degrade organic compounds: direct photolysis, photocatalysis, and ozone oxidation produced by the by-product ozone. In this paper, the generation of the active groups and the effect of active group are reviewed. By producing hydroxyl radicals, these three kinds of effects can all result in fast degradation of organic matter, despite they act alone or together. The combination of the three processes enhances the oxidation and offers many opportunities in the air pollution treatment.

Although, only a few practical applications of VUV-based processes have so far been carried out this technology has great potential for air pollution control. Unlike water treatment, there is no need to worry about the low penetration of the VUV light, which is the main technical limitation on waste-water treatment. VUV irradiation will not be strongly limited by the pollutant molecules and the particles compared with the wastewater treatment. Therefore, it can improve the efficiency of the VUV lamp. In addition, existing problems of the VUV-based processes include the catalyst deactivation and the unclear degradation mechanism and the immobilization of catalyst. It is anticipated that these problems can be solved in future for efficient utilization of the process in the industry.

AUTHOR CONTRIBUTIONS

Haibao Huang was in the charge of writing the review paper. HL and LW were in the charge of VUV-based processes for air pollutants degradation. Huiling Huang and JZ were in the charge of introduction and generation of the oxidants. DL was in the charge of outlooks and summary.

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