CVD synthesis of Cu$_2$O films for catalytic combustion of VOCs

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Abstract
Catalytically active thin films of Cu$_2$O were synthesized by a home-made pulsed-spray evaporation chemical vapor deposition for the deep oxidation of C$_2$H$_2$ and C$_3$H$_6$. The obtained films were comprehensively characterized with X-ray diffraction (XRD), Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The results indicate that the prepared films at 270 °C are pure Cu$_2$O and none of the impurities could be detected. The catalytic tests reveal that the synthesized Cu$_2$O leads the complete oxidation decreased by 250 °C for C$_2$H$_6$ and 175 °C for C$_2$H$_2$ relative to the non-coated mesh with good reusability and reproducibility.

1. Introduction
Volatile organic compounds (VOCs) are the main air pollutants emitted from the combustion of fossil fuels in many industry processes and transportation activities. VOCs are associated with various health-related problems. Catalytic combustion was commonly used for the abatement of VOCs in the past decades. The involved catalysts are mainly composed of noble metals such as Au, Pt and Rh [1-3] and transition metal oxides (TMOs). Noble metals generally exhibit good catalytic performance, but they are expensive and easy to be poisoning. For these reasons, catalytic oxidation of VOCs over TMOs has captured increasing attention, and considerable efforts have been devoted to the synthesis and application of TMOs for such purposes [4-7]. Specifically, CuO, Co$_3$O$_4$, Mn$_3$O$_4$ and Fe$_2$O$_3$ exhibited good performance as active catalysts for VOCs treatment [8-12].

Compared to other TMOs, Cu$_2$O owns attractive stability and has excellent catalytic applications for VOCs [13]. Rostami and Jafari used Cu$_2$O nanoparticles as catalysts to remove aromatic compounds. They reported that Cu$_2$O was an efficient catalyst at 350 °C [6]. Barreca et al. used Cu$_2$O films on Al$_2$O$_3$ substrates as gas sensor in the detection of VOCs. Kim and Shim investigated the catalytic characteristic of Cu$_2$O and concluded that Cu$_2$O was active for the removal of VOCs [13].

Several methods were involved in the production of Cu$_2$O, such as sol-gel [14], top-down approach with nanosecond and picosecond lasers [15], honey aided solution synthesis [16], electrochemical synthesis [17] and photonic crystal template-assisted electrodeposition [18]. In recent years, pulsed-spray evaporation chemical vapor deposition (PSE-CVD) has been successfully used to prepare a series of TMOs, e.g., Co$_3$O$_4$ and Mn$_3$O$_4$. Compared to the above-mentioned techniques, PSE-CVD is easy to control the thickness and quality of the films and relatively cheap. Thus, PSE-CVD exhibits potential to prepare Cu$_2$O thin films.

In the current work, the Cu$_2$O thin films were synthesized by a home-made PSE-CVD system for the deep oxidation of VOCs with C$_2$H$_2$ and C$_3$H$_6$ existed in the exhaust emissions as representatives. The prepared Cu$_2$O samples were characterized in terms of structure, morphology and composition.

2. Material and methods
2.1 Preparation of Cu$_2$O thin films
The Cu$_2$O thin films were synthesized in a PSE-CVD system combined with cold-wall stagnation point-flow CVD reactor and waste collector, as presented in Fig. 1. The preparation process consists of four steps. Firstly, copper acetylacetonate (Cu(acac)$_2$) was dissolved in ethanol at a concentration of 2.5 mM, which was delivered as liquid feedstock by a PSE unit. The PSE delivery frequency was set at 4 Hz and the opening time of PSE was 2.5 ms. The feeding rate was 1.03 mL/min. The evaporation chamber is 30 cm long and kept at 3000 Pa and 180 °C. Secondly, the resulting vapor was transported into the deposition chamber with O$_2$ and N$_2$ with flow rates of 1.0 and 0.5 standard liter per minute (SLM), respectively. Thirdly, the Cu$_2$O thin films were formed on different substrates (planar glass, silicon, stainless steel and mesh grid) kept at 270 °C. Finally, the waste vapor was collected by a liquid nitrogen trap.

Fig. 1 Schematic diagram of the PSE-CVD system.

2.2 Characterization
The obtained Cu$_2$O films were characterized in terms of structure, morphology and chemical composition with X-ray diffraction (XRD), Scanning
electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), respectively. XRD analysis was performed on Bruker D8 Focus with Cu Kα radiation, scan angle of 5-90° and scanning step of 0.02°. The microstructure was examined using SEM (S-4800 Hitachi) with the resolution of 1.5 nm (15 KV). The chemical composition was identified by the XPS (ESCALAB 250Xi) with pass energy of 20 eV and energy step size of 0.050 eV. The XPS results were analyzed by Avantage. The elemental content in the film samples was quantitative analyzed by non-linear least square fitting method and the form of oxygen was analyzed by Unimodal fitting method [19].

2.3 Catalytic test

The performances of the Cu₂O films for C₃H₈ and C₂H₆ conversion were investigated by a fixed bed quartz reactor, as shown in Fig. 2. A 60 cm long alundum tube (8.0 mm inner diameter) was fixed in a digital electrical furnace. 20 mg of the Cu₂O supported on grid mesh of stainless steel was put in the same temperature area. A K-thermocouple was used to measure the temperature of Cu₂O film. A gas mixture consisted of 1 % fuel gas (C₃H₈ or C₂H₆), 10 % O₂ and 89 % Ar was introduced into the alundum tube with a total flow rate of 15 ml/min. The temperature of this furnace rised with a ramp of 2 °C/min from 150 to 1000 °C. Finally, the exhausting gas was measured by a gas chromatograph (NETZSCH, GC3000) for a quantitative analysis.

3. Results and discussion

3.1 Growth

By measuring the weight difference of the substrates before and after deposition, the growth of the prepared films can be estimated. Five experiments at different total deposition time were carried out on the mesh grid of stainless steel and the result is displayed in Fig. 3. A linear behavior is observed and the growth rate of Cu₂O is calculated to be 1.6 nm/min. The results indicate that the synthesis of Cu₂O with PSE-CVD system can be tailored with respect to thickness.

3.2 Phase identification

The X-ray diffraction pattern of the obtained thin film is shown in Fig. 4. The well-defined diffraction peaks are observed at 29.73°, 36.41°, 42.24°, 61.88° and 73.81°, which can be well attributed to (110), (111), (200), (220) and (311) orientations of Cu₂O in the literature (JCPDS no. 05-0667). No characteristic peaks of any other impurities were observed in the XRD patterns, indicating the formation of monoclinic Cu₂O phase [20,21]. The sharp and strong reflection peaks suggest that the as-prepared samples are well crystallized. The crystallite size and the micro-strain of Cu₂O thin films were calculated to be 29 nm and 0.0583 by applying Scherrer’s formula: D = 0.9λ/β cosθ; and the equation ε = β/2cosθ to the most intense diffraction peak, where λ = 0.154056 nm and where β and θ represent the full width at half maximum and diffraction angle of the observed peak, respectively [22].

3.3 Microstructural studies

SEM inspection was carried out to reveal the morphology of the as-obtained Cu₂O samples. The representative SEM images with different magnifications are shown in Fig. 5. The SEM images reveal that the film is homogenous and is composed of a large quantity of small ball-like particles. The particle size is estimated to be 30 nm, which agrees well with the crystallite size calculated by XRD results. Besides the ball-like shapes, a number of hollows are also observed. These hollows could adsorb more oxygen than the smooth surface, which would benefit for the catalytic oxidation of VOCs.

3.4 Surface composition

In order to explore the chemical composition of the Cu₂O films, ex situ XPS analysis was performed on both bare and etched surfaces. By comparing the numerical contents of C 1s, O 1s and Cu 2p shown in Table 1, it can be easily found that the content of Cu raises and O decreases as the depth deepens from surface (non-etched) to 95 nm etched. Based on the XPS results, the Cu/O atomic ratio of 95 nm etched layer was estimated to be about 2, which is consistent with the form of Cu2O obtained with XRD analysis.

As indicated in Fig. 6, the components of the as-synthesized thin films are mainly consist of Cu and O from the entire XPS spectrum (Fig. 6a). As exhibited in Fig. 6b, the Cu 2p 1/2 peak is centered at 952.25 eV and
Fig. 5 SEM images of thin Cu$_2$O films at different magnifications.

Table 1 Chemical composition of Cu$_2$O thin films

<table>
<thead>
<tr>
<th></th>
<th>Non-etched</th>
<th>5.7 nm-etched</th>
<th>95 nm-etched</th>
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<tr>
<td></td>
<td>Peak BE</td>
<td>Proportion (%)</td>
<td>Peak BE</td>
</tr>
<tr>
<td>C 1s</td>
<td>284.78</td>
<td>17.11</td>
<td>284.80</td>
</tr>
<tr>
<td>O 1s</td>
<td>529.87</td>
<td>43.73</td>
<td>529.61</td>
</tr>
<tr>
<td>Cu 2p</td>
<td>933.62</td>
<td>39.16</td>
<td>932.35</td>
</tr>
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were observed to be 529.65 and 531.45 eV (see Fig. 7b), corresponding to the lattice oxygen (O$_{\text{L}}$) and adsorbed oxygen (O$_{\text{ads}}$), respectively. The fitted profiles agree well with the measured profiles, as shown in Fig. 7.

3.5 Catalytic performance

The catalytic performance of the Cu$_2$O grown on mesh of stainless steel was tested for the complete oxidation of C$_2$H$_2$ and C$_3$H$_6$ at atmospheric pressure. The background effect of the stainless steel element on the oxidation was examined by carrying out the experiments on non-coated mesh (NCM) under the same conditions. Figure 8 compares the temperature-dependent conversion ratio of C$_2$H$_2$ and C$_3$H$_6$ with Cu$_2$O coated mesh and non-coated mesh. Compared to the non-coated mesh condition, the complete oxidation of C$_2$H$_2$ decreased from 450 °C to 300 °C and for C$_3$H$_6$ decreased from 675 °C to 425 °C with Cu$_2$O. The catalytic tests were carried out three times for the same sample and the results are quite close, demonstrating that the prepared Cu$_2$O has good reusability with reproduced results.

Figure 9 presents the releases of CO$_2$ and CO in the oxidation processes on both Cu$_2$O-coated mesh and
The maximum temperatures of CO₂ release in the oxidation processes of C₂H₄ and C₆H₆ agree well with the complete oxidation of C₂H₂ and C₆H₆. During the oxidation of C₂H₂ and C₆H₆ over Cu₂O-coated mesh, CO was not detected. However, a number of CO was measured over non-coated mesh, which could come from the partial oxidation. Based on the XPS results, both the lattice and adsorbed oxygen in the Cu₂O films could lower down the energy barrier for the complete oxidation and prevent from the formation of CO. Moreover, the hollow ball-like revealed by the microstructure analysis could expose more surface area and adsorbe more oxygen, which would make the oxidation occur at relatively low temperatures.

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**References**