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Preparing two-dimensional nano-catalytic combustion patterns using direct inkjet printing

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HIGHLIGHTS

- We demonstrate direct fabricating of two-dimensional catalytic combustion patterns.
- IJP method realized ultra low loading and high utilizing of Pt catalysts.
- Spontaneous combustion is achieved at room temperature and small scale (~800 μm).
- Accurate temperature control makes the catalyst an adjustable power source.

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ABSTRACT

Two-dimensional catalytic combustion patterns, which can be used as heat source in micro-nano scale MEMS devices such as gas sensor and micro-generator, are fabricated by inkjet printing (IJP). The performances of the catalytic patterns are evaluated by both traditional catalytic activity measurement and infrared thermography (IR) camera. Results show that ultra-low (0.014 mg cm^{-2}) loading and high utilizing (34,710 mW mg^{-1}) of Pt catalysts can be achieved by inkjet printing method. Spontaneous combustion is also observed for the printed Pt/Al_2O_3 powder membrane at rather low initiation temperature and small scale. The IR camera analysis indicates the uniform temperature distribution and rapid temperature response of the micro-patterned catalyst surface. With the advantages of the inkjet printing, this new direct-write method would, in principle, open up possibilities of these special catalyst patterns serving as micro energy sources for MEMS applications.

1. Introduction

Micro heater fabricated by MEMS technology, possessing advantages of small size, fast thermal response, high temperature at low power consumption, has gained specific attention as they are key constituent parts in micro-sensors such as wind sensors [1], humidity sensors [2] and gas sensor [3]. Another kind of heat source at small scale is catalytic combustor, normally used in micro-machined thermoelectric hydrogen sensors (micro-THS) [4–6]. Unlike the MEMS-based micro heater converting electric energy into stable heat energy, the catalytic combustor turn chemical energy into heat at low combustion temperature with extraordinary high energy density [7]. Furthermore, lower combustion temperature of catalytic combustion makes thermal stresses and heat losses less problematic [8]. Still, catalytic combustion acting as power supply for MEMS devices remains difficult, owing to the obstacles of reducing catalyst size below 1 mm^2, shape controlling, uniform temperature distribution on catalyst surface and self-ignition of catalyst at room temperature.

Traditional ways like screen printing have been investigated for catalyst deposition. Although screen printing is a simple, cost-

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effective coating technique, this method do have disadvantages like uniformity, direct-contact of printing surface which may bring damage to the fragile device structure when applying in MEMS. Furthermore, screen printing is not qualified for ultra low (<0.5 mg cm^{-2}) condition. Inkjet printing (IJP) is a technology for micro scale patterning, jetting solutions or turbid liquid with small particle size onto addressable sites on a specific substrate, flexible or inelastic. It has been considered as an alternative of lift-off process, since inkjet printing can achieve direct patterning without any masks at small scale [9]. It also has promising prospects in fields such as organic field-effect transistors (OFETs) [10], conductive features [11,12], sensor [13], polymer light-emitting diode (PLED) [14,15], radio frequency identification (RFID) tags [16], and fuel cell [17,18], etc. In general, it's more controllable, material saving and compatible with MEMS devices.

In this paper, we develop a rapid prototyping technique to fabricate Pt nano-catalytic patterns for use as a micro heater in MEMS devices. Chloroplatinic acid solution was chosen as the catalyst precursor ink to produce catalyst patterns at predefined position with different shapes. Catalysts characteristics including catalytic activity, catalytic combustion performance, temperature distribution and temperature response rate were investigated.

2. Experimental

2.1. Catalyst preparation and patterning

Platinum catalysts for low temperature methanol catalytic combustion were synthesized in situ on substrates via inkjet printing. An inkjet printable solution containing platinum ions was prepared by dissolving the commercially available chloroplatinic acid powder in water. Concentration of the printing ink was 0.01 mol L^{-1}. The chloroplatinic solution was then filtered three times by filter (pore size 0.45 μm) after stood for 48 h to prevent nozzle clogging. Catalyst precursor solution was then printed on the heated substrates with special shape and defined loading.

The inkjet printer used as micropatterning tool in this experiment was a commercial Autodrop micro dispensing system (Microdrop Technologies GmbH, Germany), which is for non-contact dispensing of liquids in single droplets of volume ranges from 20 pl to 380 pl. The picture of microdrop jetting system and schematic of ink jetting is shown in Fig. 1. The inner diameter of nozzles is 70 μm. Applied voltage and pulse width are two key factors to determine the printability and dimensions of the droplets [19]. Low voltage can't provide enough energy for droplets to be jetted. Conversely, higher applied voltage will results in the formation of satellite droplets, which are detrimental to the precisely control of catalyst amount and shape. A similar behavior can also be observed when changing the applied pulse width. Substrates are placed on the *x*-*y*-*z* table, which has a positioning accuracy of 5 μm. A stroboscopic camera was used to study the behavior of droplets between the nozzle and substrate.

Different amount and shape of the catalyst can be obtained by controlling the ink jetting process and the movement of the *x*-*y*-*z* table, thus different patterns were fabricated (Fig. 2). Optimum conditions of the voltage and pulse width were adopted here, which were 50 V and 24 μs respectively. The droplets were jetted from nozzle without satellite droplets with a flight speed of 1 m s^{-1} and diameter of 70 μm. Then printed arrays were reduced in methanol flow at 400 °C for 1 h to obtain platinum catalyst patterns, after which the color of printed arrays changed from yellow to black (in web version), indicating the formation of Pt.

2.2. Measurements of methanol catalytic combustion

The morphology of printed catalytic was evaluated by 3D microscope (VHX-600E, Keyence) to determine the size and uniformity of platinum catalyst.

Catalytic activity measurements were carried out to determine catalytic performance of prepared platinum catalyst. Samples were placed in center of a reactor ($8 \times 3.5 \times 0.5$ cm^3) under flowing 10 vol. % of methanol in air at different temperature to elucidated the conversion rate of methanol. The flow rate of air was 3 ml min^{-1}. The gas before and after reaction were analyzed on line by gas chromatograph (GC2060, Ramiin) with a flame ionization detection (FID) detector.

Methanol catalytic combustion performance of printed platinum catalysts was tested in a stainless reactor. Sealed chamber reactor with infrared transparent CaF_2 was designed to observe the oxidation reaction of methanol on catalytic surface, as shown in Fig. 3(a). The gas flow rates were regulated by a flow controller. An IRM-320 infrared thermographic camera (Shanghai Infrared Optoelectronics Technology, China) was used to observe the temperature profiles of inkjet printed catalyst patterns. This infrared thermographic camera has been demarcated by a certificated blackbody source (HFY-300A, Shanghai Institute of Technical Physics), and the temperature resolution is 2 °C. Fig. 3(b) shows the 2-D and 3-D infrared pictures of printed catalyst.

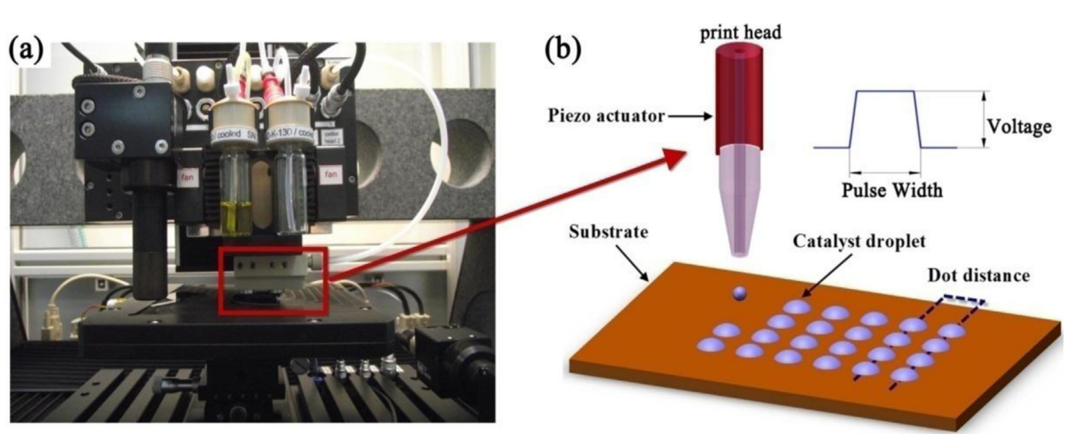

Fig. 1. Picture of microdrop jetting system (left) and schematic of ink jetting (right).