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Sonochemical Synthesis of HKUST-1 Based CuO Decorated with Pt Nanoparticles for Formaldehyde Gas Sensors

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Abstract

In this study, a facile and simple method to synthesize composites of copper(II) oxide (CuO) and Pt nanoparticles has been developed without altering the original morphology of CuO. CuO decorated with Pt nanoparticles was obtained by a sonochemical synthetic route and the gas sensing properties of CuO/Pt composites were investigated. Compared to CuO based gas sensors, CuO/Pt composites based gas sensors showed better performances in detecting formaldehyde gas from 100 ppb to 1500 ppb. Here, although only Pt nanoparticles were decorated to CuO, sonochemical synthesis can be expandable to decoration of other noble metals, such as Pd and Au, to various metal oxide materials for establishing a sensing material database useful for a principal component analysis or machine learning.

Key words: sonochemistry, gas sensor, formaldehyde, HKUST-1, CuO

Introduction

Formaldehyde is one of the well-known detrimental air pollutants, which lead to sick house syndrome, and it is required to monitor the concentration of formaldehyde. There have been substantial efforts to improve sensing properties such as response/recovery time, sensitivity and stability. In this respect, metal oxide is an attractive candidate for formaldehyde sensors owing to high sensitivity, portability and low cost. There have been many studies about CuO but there are still many parts to be improved in the CuO gas sensors. These problems such as power consumption reduction, fast recovery and long-term stability [1] can be solved by decoration of noble metals. In this study, we describe a sonochemical synthesis method for producing CuO from HKUST-1 with Pt nanoparticles and investigate their formaldehyde gas sensing properties. Sonochemical synthesis is one of the promising methods to synthesize nanomaterials without any strong reductant, such as $NaBH_4$. When liquids are irradiated with ultrasound, the expansive and compressive acoustic waves create bubbles and make the bubbles oscillate. The oscillating bubbles can overgrow and collapse, resulting in cavitational implosion with very localized and transient energy with a temperature of ~5000 K and a pressure of ~1000 bar [2]. In this paper, one of noble metals, Pt was decorated to metal oxide materials but other kinds of noble metals also can be applied to form composites by sonochemical synthesis and it is possible to be used for principle component analysis (PCA) or pattern recognitions.

Experimental Details

Synthetic processes of CuO/Pt composites are schematically described in Fig. 1. CuO powder was synthesized by the thermal decomposition of HKUST-1 at 500 °C for 2 h. To decorate Pt nanoparticels to CuO, $H_2PtCl_6{\cdot}6H_2O$, which acts as a Pt precursor, was added to CuO powder. The mixed solution was sonicated at 20 kHz and 150 W for 20 min with few amounts of deionized water. After sonication, the solution was washed and centrifuged several times and dried at 80 °C until the solvent was entirely evaporated.

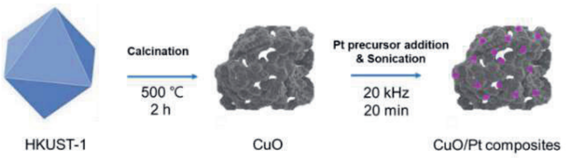

Fig.1. Synthetic scheme of HKUST-1 based on CuO/Pt composites

Results and Discussion

As shown in Fig. 2(a) and (b), octahedral structure of HKUST-1 was changed to CuO containing micropores as well as mesopores after the thermal decomposition at 500 °C for 2 h. Fig. 2(c) shows the XRD pattern of synthesized CuO/Pt composites after the Pt nanoparticles decoration to CuO. From the results, there was no notable change to XRD pattern of CuO (JCPDS card No. 00-045-0937) even after the Pt decorations.

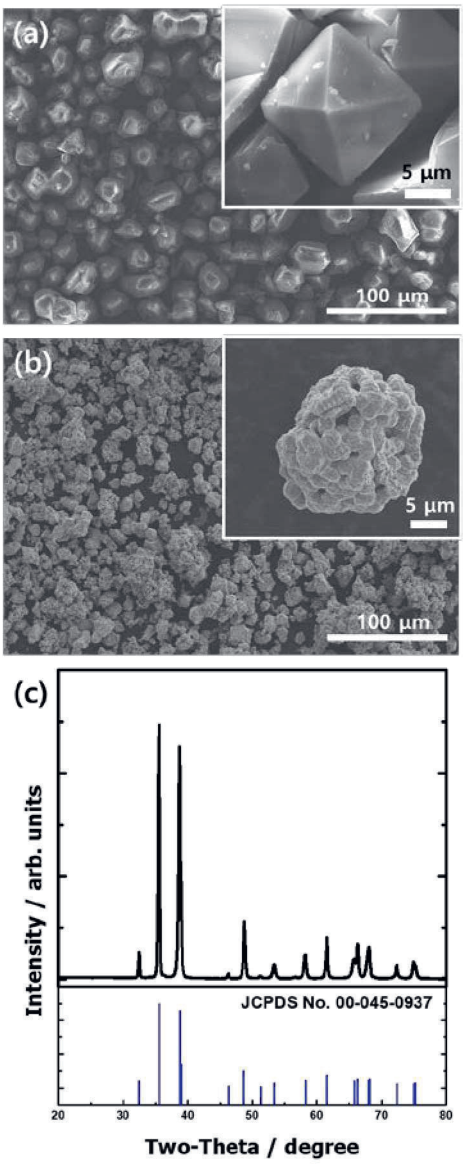

Fig. 2. SEM images of (a) HKUST-1 and (b) CuO after calcination of HKUST-1 at 500 °C for 2 h. (c) XRD pattern of CuO decorated with Pt nanoparticles.

Formaldehyde-sensing properties of CuO with and without Pt nanoparticles were studied at 225 °C under a dry condition as shown in Fig. 3. The sensor response is defined as eq. (1)

$$\text{Response} = R_{gas}/R_{air} \quad (1)$$

The surface of p-type material is known to be covered with negatively charged chemisorbed oxygen ions, which generate hole accumulation layers on the surface of metal oxide. CuO is one of p-type materials and when it is exposed to formaldehyde gas, the electrical conduction is decreased because formaldehyde molecules are oxidized by the surface oxygen anions and the consumption of hole accumulation layers occurs. The response values increased with increasing formaldehyde concentration. The absolute response value of CuO/Pt composite sensors was estimated to 1.891 while that of CuO without Pt nanoparticles sensors was estimated to 1.353 at the operating temperature of 225 °C and the concentration of 100 ppb.

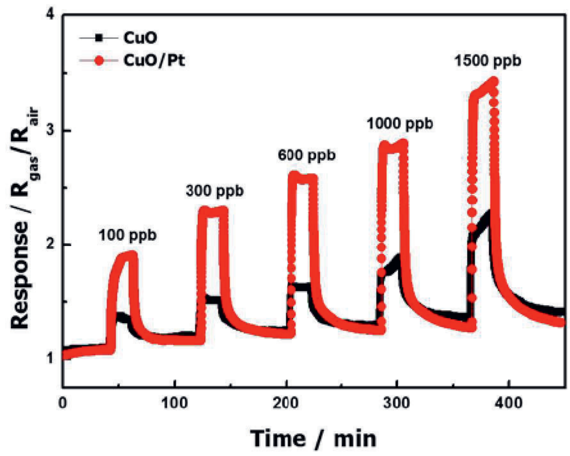

Fig. 3. Comparison of HCHO-sensing performance of CuO gas sensors with and without Pt decoration exposed to formaldehyde gas at 225 °C under a dry condition.

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