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# $Bi_2O_2CO_3$/CuO Micro-flowers with Abundant Oxygen Vacancies for Enhanced VOC Detection

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**Summary:**
This study introduces a cutting-edge sensor for nonanal, using a bismuth subcarbonate/copper oxide ($Bi_2O_2CO_3$/CuO) heterojunction. The sensor exhibits exceptional responsiveness to nonanal concentrations from 10-90 ppm, characterized by high sensitivity and excellent linearity. The enhanced sensing performance is attributed to the presence of oxygen vacancies and improved charge separation mechanisms within the heterojunction. Furthermore, we demonstrate the sensor's practical application in evaluating the quality of cooked rice through the detection of volatile organic compounds (VOCs). This research highlights the potential of this sensor as a valuable tool for agricultural product quality evaluation and food safety monitoring.

**Keywords:** gas sensor, room temperature, hetorojunction, high sensitivity, nonanal

## Background

$Bi_2O_2CO_3$ (BOC), an n-type semiconductor with a characteristic Aurivillius structure, comprises alternating $Bi_2O_2^{2+}$ and $CO_3^{2-}$ layers [1] and has been extensively used in gas sensors [2]. However, BOC-based sensors often struggle to achieve high sensitivity, stability, and selective detection simultaneously. Recent advancements in the fabrication of p-n heterostructures within ternary metal oxides offers significant potential for enhancing gas sensing performance [3]. By strategically combining different metal oxides, their electronic properties can be tailored, leading to enhanced charge carrier mobility [4]. This results in a more sensitive and selective response to target gases. Such innovations hold promises for advancing gas sensors in various applications, including environmental monitoring and industrial safety, leading to more reliable and efficient detection systems.

Nonanal is a volatile organic compound (VOC) produced during the deterioration of cooked rice quality [5]. The amount of nonanal increases with the duration of cooked rice storage, providing a valuable reference for assessing the freshness and quality of agricultural products.

## Description of the New Method or System

Here, a facile one-step hydrothermal approach was used to synthesize $Bi_2O_2CO_3$/CuO hetorojunction with varying CuO loading amounts, designated as BOC, BOC@10Cu, BOC@20Cu, BOC@30Cu, and BOC@40Cu, respectively, where the mass ratios of $CuCl_2$ to $Bi(NO_3)_3 \cdot 5H_2O$ were adjusted to around 0%, 10%, 20%, 30%, and 40%. Gas-sensing tests were conducted using a four-channel gas sensing testing instrument, which measures electrical resistance signals in highly pure air and target gas.

## Results

Due to limited space, we will focus our discussion on the sensor that yielded the best sensing results i.e., the BOC@20Cu (see Fig. 3). The structure of the samples was analyzed using electron microscopy. As shown in Fig. 1a-1c, BOC@20Cu exhibits a micro-flower structure with semi-hollow characteristics. The selected area electron diffraction pattern (Fig. 1d) confirms the single crystalline nature of BOC@20Cu. The energy-dispersive X-ray spectroscopy elemental mapping in Fig. 2e-2i reveals a uniform distribution of Bi, C, O, and Cu elements throughout the BOC@20Cu micro-flower.

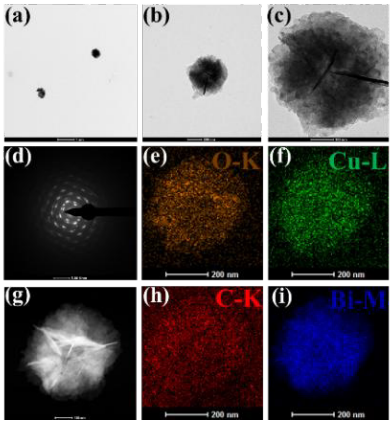

*Fig. 1. (a-c) TEM images of BOC@20Cu, (d) SAED pattern of BOC@20Cu, (e-f, h-i) EDS elemental mapping images of O, Cu, C and Bi of BOC@20Cu, (g) HAADF-STEM image of BOC@20Cu.*

The XPS O 1s spectra recorded in the different samples can be deconvolved into three components: lattice oxygen, oxygen vacancies ($O_V$), and surface-chemisorbed oxygen. Comparing the pristine BOC and the BOC@20Cu and samples, it becomes clear that the BOC@20Cu sample has a higher relative amount of quantity of $O_V$ (53.8%) than in the pristine (42.3%) (Fig. 2). This increase in $O_V$ suggests that lattice mismatch induces changes in the positions of electrons or ions within BOC@20Cu, leading to the formation of excess $O_V$.

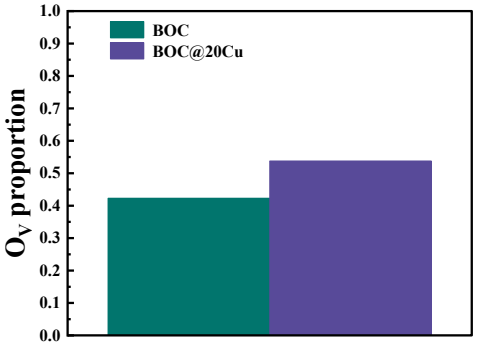


*Fig. 2. The percentage of $O_V$ in XPS results.*

Fig. 3 shows that BOC@20Cu exhibits the highest response to nonanal molecules compared to the other three sensors at room temperature. The order of response values is: BOC@20Cu > BOC@30Cu > BOC@10Cu > BOC@40Cu. The enhanced gas-sensing performance of BOC@20Cu can be attributed to the creation of a p-n heterojunction, which increases the number of $O_V$ in the material. This heterojunction alters the energy band structure and electric field distribution, leading to improved surface reactivity and facilitating the formation of additional $O_V$. Moreover, the defect energy levels associated with these $O_V$ was reported to enhance electron capture, resulting in heightened sensitivity [1].

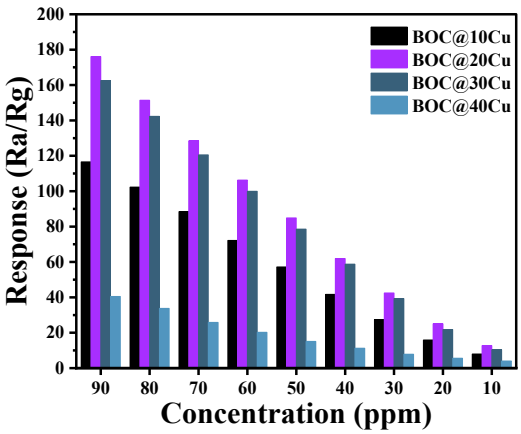


*Fig. 3. The response values of BOC@xCu (x = 10, 20, 30, and 40) film to nonanal (10-90 ppm) at room temperature.*

As shown in Tab. 1, the good linear correlation between the sensor response and the concentration of the detected gas has also been obtained, demonstrating its potential for practical application.

*Tab. 1: Concentration (X)-dependent response curves (Y) of the fabricated sensors for nonanal.*

| Sensor | Relationship | $R^2$ |
|---|---|---|
| BOC@10Cu | Y=1.41X-11.48 | 0.9954 |
| BOC@20Cu | Y=2.09X-17.06 | 0.9947 |
| BOC@30Cu | Y=1.97X-16.03 | 0.9950 |
| BOC@40Cu | Y=0.47X-5.19 | 0.9600 |

This study successfully synthesized $Bi_2O_2CO_3$/CuO hetorojunctions using a controlled hydrothermal reaction. The obtained micro-flowers exhibit abundant $O_V$ from CuO loading. The BOC@20Cu sensor shows a strong response to 10-90 ppm nonanal at room temperature, providing valuable insights for Bi-based semiconductor applications.

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