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Tuning ZnO Sensors Reactivity toward Volatile Organic Compounds via Ag Doping and Nanoparticle Functionalization

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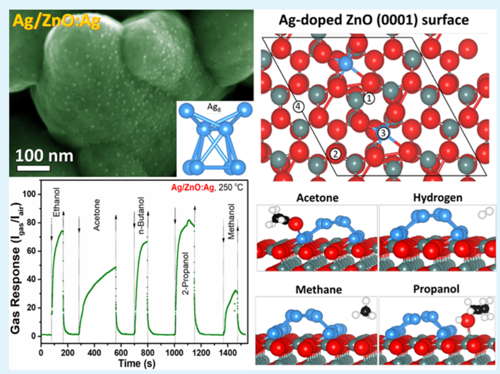
S *Supporting Information*

ABSTRACT: Nanomaterials for highly selective and sensitive sensors toward specific gas molecules of volatile organic compounds (VOCs) are most important in developing new-generation of detector devices, for example, for biomarkers of diseases as well as for continuous air quality monitoring. Here, we present an innovative preparation approach for engineering sensors, which allow for full control of the dopant concentrations and the nanoparticles functionalization of columnar material surfaces. The main outcome of this powerful design concept lies in fine-tuning the reactivity of the sensor surfaces toward the VOCs of interest. First, nanocolumnar and well-distributed Ag-doped zinc oxide (ZnO:Ag) thin films are synthesized from chemical solution, and, at a second stage, noble nanoparticles of the required size are deposited using a gas aggregation source, ensuring that no percolating paths are formed between them. Typical samples that were investigated are Ag-doped and Ag nanoparticle-functionalized ZnO:Ag nanocolumnar films. The highest responses to VOCs, in particular to $(CH_3)_2CHOH$, were obtained at a low operating temperature (250 °C) for the samples synergistically enhanced with dopants and nanoparticles simultaneously. In addition, the response times, particularly the recovery times, are greatly reduced for the fully modified nanocolumnar thin films for a wide range of operating temperatures. The adsorption of propanol, acetone, methane, and hydrogen at various surface sites of the Ag-doped Ag_8/ZnO(0001) surface has been examined with the density functional theory (DFT) calculations to understand the preference for organic compounds and to confirm experimental results. The response of the synergistically enhanced sensors to gas molecules containing certain functional groups is in excellent agreement with density functional theory calculations performed in this work too. This new fabrication strategy can underpin the next generation of advanced materials for gas sensing applications and prevent VOC levels that are hazardous to human health and can cause environmental damages.



KEYWORDS: *columnar films, VOC sensors, DFT, surface functionalization, Ag nanoparticles*

1. INTRODUCTION

Advanced nanomaterials for gas sensing applications that have been traditionally used to detect volatile organic compound (VOC) levels, which are hazardous to human health and can cause environmental damages, are of high demand. However, a renewed and important interest in sensing nanomaterials has been driven by future applications in the identification of VOCs as biomarkers at early stage diseases. It is known that VOCs detected in exhaled breath at the ppb level can be related to several diseases.[1] Conventional metal oxide sensors seldom offer reliable detection at such low levels and mostly cannot distinguish one VOC within a complex sample. Thus, an alternative strategy is required to fabricate new semiconducting oxide nanomaterials that are cost-effective, highly sensitive, and selective at the same time, allowing integration into a small portable device.

Zinc oxide (ZnO) has a great potential for a wide range of applications, such as short-wavelength optoelectronics, photo-

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