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Research Article

Surface Conversion of ZnO Tetrapods Produces Pinhole-Free ZIF-8 Layers for Selective and Sensitive H_2 Sensing Even in Pure Methane

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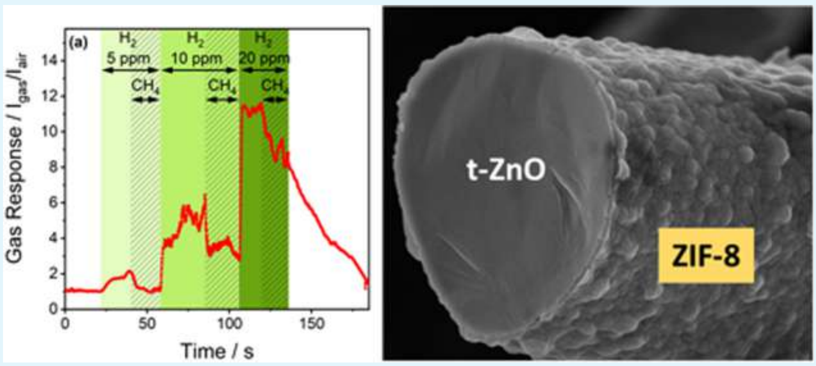

ABSTRACT: As the necessary transition to a supply of renewable energy moves forward rapidly, hydrogen (H_2) becomes increasingly important as a green chemical energy carrier. The manifold applications associated with the use of hydrogen in the energy sector require sensor materials that can efficiently detect H_2 in small quantities and in gas mixtures. As a possible candidate, we here present a metal–organic framework (MOF, namely ZIF-8) functionalized metal-oxide gas sensor (MOS, namely ZnO). The gas sensor is based on single-crystalline tetrapodal ZnO (t-ZnO) microparticles, which are coated with a thin layer of ZIF-8 ($[Zn(C_4H_5N_2)_2]$) by a ZnO conversion reaction to obtain t-ZnO@ZIF-8 (core@shell) composites. The vapor-phase synthesis enables ZIF-8 thickness control as shown by powder X-ray diffraction, thermogravimetric analysis, and N_2 sorption measurements. Gas-sensing measurements of a single microrod of t-ZnO@ZIF-8 composite demonstrate the synergistic benefits of both MOS sensors and MOFs, resulting in an outstanding high selectivity, sensitivity ($S \cong 546$), and response times (1−2 s) to 100 ppm H_2 in the air at a low operation temperature of 100 °C. Under these conditions, no response to acetone, *n*-butanol, methane, ethanol, ammonia, 2-propanol, and carbon dioxide was observed. Thereby, the sensor is able to reliably detect H_2 in mixtures with air and even methane, with the latter being highly important for determining the H_2 dilution level in natural gas pipelines, which is of great importance to the energy sector.

KEYWORDS: *zinc oxide tetrapods, metal–organic framework, ZIF-8, H_2 sensing, methane*

INTRODUCTION

In view of the ongoing transition from fossil-based to renewable energy, zero-carbon energy sources, especially green H_2 are of particular interest as a replacement for natural gas. Therefore, in the near future, it is envisioned to use the already existing infrastructure and feed up to 20% H_2 into natural gas pipelines, as transport in tanks will not be profitable. In return, safety concerns must be considered, for example, leaks that require precise measurements as well as detection of small amounts of hydrogen along these pipelines. Thus, tiny and selective solid-state devices are required to be deployed along existing infrastructure. Several H_2 sensor technologies are known,[1,2] and ongoing research focuses on higher selectivity and sensitivity,[3−5] faster response, lower power consumption, and on meeting the demands of technical applications.[6,7] Around 20% of gas-sensing materials are based on metal-oxide materials, which operate in the presence of oxygen.[8] One promising candidate is ZnO because of its good sensing response, easy fabrication, low cost, and chemical and thermal stability.[3] ZnO can be made in many morphologies ranging from nanowires, nanorods, nanoparticles, and tetrapods (t-ZnO).[9] The latter exhibits high crystallinity with low-defect density[10] and provides high textural porosity for gases

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ABBREVIATIONS

ALD, atomic layer deposition
DMF, *N,N*-dimethylformamide
HMeIM, 2-methylimidazole
MOF, metal−organic framework
MOS, metal-oxide semiconductor
TGA, thermogravimetric analysis
VOC, volatile organic compound
(P)XRD, powder X-ray diffraction
FIP, focused ion beam

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