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Functionalization of Black Phosphorus for Enhanced Hydrogen Detection

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Summary:

This study is dedicated to advancing phosphorene-based sensors for hydrogen detection. Through the strategic functionalization of phosphorene with urea, the sensor exhibits enhanced performance and exceptional stability in ambient air, making it well-suited for various applications. Extensive characterization techniques confirmed material stability and demonstrated the sensor's high sensitivity (up to 700 ppm) and selectivity for hydrogen at room temperature. The use of *operando* diffuse reflectance infrared Fourier transform provided real-time insights into the gas sensing mechanism, contributing to a deeper understanding of its operational principles.

Keywords: hydrogen detection, phosphorene, functionalization, 2D material, chemoresistive gas sensor

Introduction

Nowadays, hydrogen (H_2) stands as the definitive energy source of the twenty-first century, poised to replace conventional fossil fuels in the global power system. H_2, an odorless, flammable, and explosive gas, remains undetectable to the human senses even at concentrations of 4-75% in air [1]. This poses significant risks, necessitating sensors with high sensitivity and selectivity at low temperatures for detection during production, storage, and transportation. Commercially available H_2 gas sensors, including electrochemical and semiconductor devices, are promising, but face drawbacks such as lack of selectivity and high operating temperatures (200-600 °C) [2-3]. Two-dimensional materials (2D), such as graphene and transition metal dichalcogenides, have garnered significant interest for their distinctive properties, aimed at overcoming certain limitations. Their remarkable high-surface-to-volume ratio has been a focal point of attention. This characteristic results in a substantial active surface area, facilitating robust interactions with the target gas molecules. However, enhancing their performance remains a challenge. Recently, black Phosphorus (bP) has emerged as a potential solution due to its semiconductor properties, but its susceptibility to oxidation limits its practical use [4]. Surface functionalization strategies, such as incorporating nanoparticles or organic compounds, aim to improve stability and performance for gas sensing applications [5]. In this work, we proposed a new bP-functionalization with urea synthesis. This material can be used as a functional material for the fabrication of a chemoresistive gas sensor for H_2 detection, as suggested by catalytic properties featured in previous work [6-7]. Through a comprehensive morphological, chemical, and electrical characterization, we investigated environmental stability in dry air and sensing capabilities of amino-functionalized bP (bP-NH_2) films for H_2 detection at room temperature (RT). Finally, to evaluate the chemical interactions on the surface of the sensing film before and after the exposure of the target gas, we exploited a

dedicated test chamber for an *operando* diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy.

Materials & Method

The bP-NH_2 nanosheets were characterized by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), Raman, UV-Visible (UV-vis), and X-ray photoelectron (XPS) spectroscopies. Then, the sensing film was electrically characterized by providing "3S" rules (sensitivity, selectivity, and stability).

Results

The functionalization was accomplished via wet chemical reaction between exfoliated bP and urea (see Fig. 1). The material stability in air and the integrated surface was confirmed by PXRD and Raman spectroscopy. XPS confirmed the presence of -NH_2 groups (about 3%) on the surface. Concerning UV-vis and impedance measurements, these highlighted a significant increase of the band gap value and downward shift of the conduction band level respect to pristine bP.

The sensing performance of bP-NH_2 device was evaluated in a wide range of concentration, starting from 50 to 700 ppm of H_2 at RT (Fig. 2). The sensor demonstrated long-term stability over a period of three months, exhibiting the ability to maintain its structural integrity and sensing capabilities even when continuously exposed to dry air conditions. The gas sensing mechanism was investigated thought an advanced technique, i.e. DRIFT spectroscopy, providing information about the chemical interaction between the oxygen preabsorbed species and the target gas.

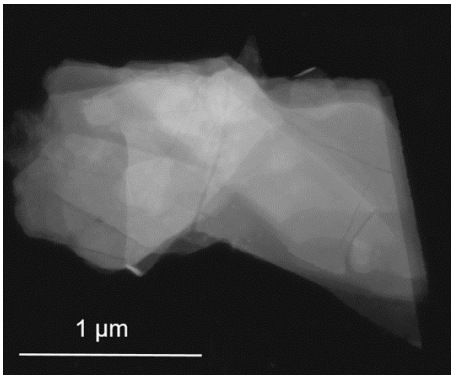

Fig. 1. STEM image of bP-NH_2 nanosheets.

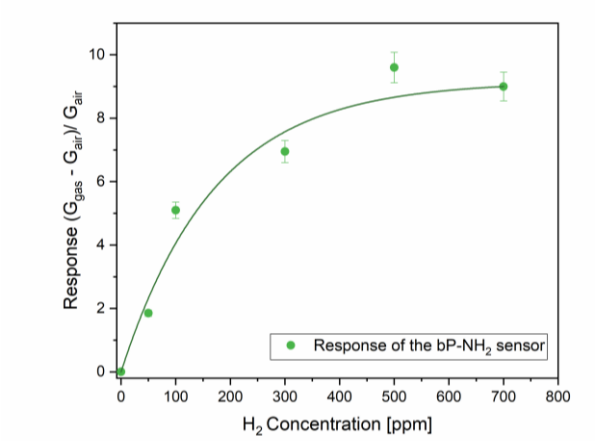

Fig. 2. Calibration curve of bP-NH_2 sensor at RT in dry conditions.

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