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Ultrasensitive and bifunctional ZnO nanoplates for an oxidative electrochemical and chemical sensor of NO_2: implications towards environmental monitoring of the nitrite reaction†

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Herein, we focused on the one pot synthesis of ZnO nanoplates (NP edge thickness of ~100 nm) using a chemical emulsion approach for chemical (direct) and electrochemical (indirect) determination of NO_2. The structural and morphological elucidation of the as-synthesized ZnO NPs was carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive analysis of X-ray (EDAX), thermogravimetric analysis (TGA) and BET-surface area measurements. The XRD studies of the as-synthesised NPs reveal that ZnO NPs have a Wurtzite type crystal structure with a crystallite size of ~100 nm. Such ZnO NPs were found to be highly sensitive to NO_2 gas at an operating temperature of 200 °C. Electrocatalytic abilities of these ZnO NPs towards NO_2/NO_2^- were verified through cyclic voltammetry (CV) and linear sweep voltammetry (LSV) using aqueous 1 mM NO_2^- (nitrite) in phosphate buffer (pH 7) solution. The results revealed enhanced activity at an onset potential of 0.60 V *vs.* RCE, achieved at a current density of 0.14 mA cm^{-2}. These ZnO NPs show selective NO_2 detection in the presence of other reactive species including CO, SO_2, CH_3OH and Cl_2. These obtained results show that this chemical route is a low cost and promising method for ZnO NPs synthesis and recommend further exploration into its applicability towards tunable electrochemical as well as solid state gas sensing of other toxic gases.

1 Introduction

Nitrogen dioxide (NO_2) gas is well known to be one of the irritant gases, and is a prominent intermediate product of the industrial synthesis of nitric acid. Moreover, other common and considerable contributors to NO_2 gas production are combustion engines, the burning of fossil fuels, fertiliser industries, cigarette smoke, and butane and kerosene heaters and stoves.[1] Unfortunately, NO_2 can cause respiratory infections, photochemical smog and acid rain[2] and it is injurious to human health. Exposure to unsafe and elevated levels in the body can cause severe underlying diseases such as chronic obstructive pulmonary disease or asthma. For example, NO_2 reacts with water droplets in the trachea and lungs forming droplets of nitric acid and these tiny droplets penetrate deep into the lungs causing various respiratory diseases.[3] Moreover, NO_2 exposure has also been associated with sudden infant death syndrome.[4] Thus, it is imperative to develop a sensor for detecting NO_2 gas. Significantly, many solid state gas sensors have been recently explored for NO_2 gas sensing such as WO_3,[5] VO_2,[6] NiO,[7] SnO_2 (ref. 8) and ZnO.[9] Among these, ZnO is a cheap, stable and nontoxic material and it is possible to further improve its chemical and physical properties by controlling its dimensions in a micro/nano-regime. This motivated us to develop a new, cost effective, safer synthetic method for the synthesis of its nanostructures by a chemical approach, taking into consideration energy and environmental factors. The past literature reflects that the properties and performances of ZnO based devices are significantly influenced by its structural features.[10,11] Recent studies in the literature have demonstrated that the crystal structure and its morphology have a significant influence on its surface sensitive reactions, especially gas-sensing, electronic, electrochemical and many more.[12,13] For example, one-dimensional (1D) nanostructures of ZnO, such as nanowires,[14] nanorods,[15] and nanobelts[16] and their hierarchical structures were widely used in gas sensor applications,[18] also, recently, two-dimensional (2D) structures, such as NPs, have been another common structure of ZnO.[17,18] Thus, the need for simple and cost effective ZnO based gas sensors further encourages us to design and develop a method for the synthesis

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