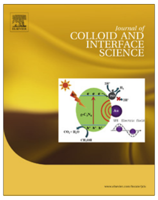
Journal of Colloid and Interface Science 494 (2017) 153–158

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis



Regular Article

Highly stable hydrazine chemical sensor based on vertically-aligned ZnO nanorods grown on electrode

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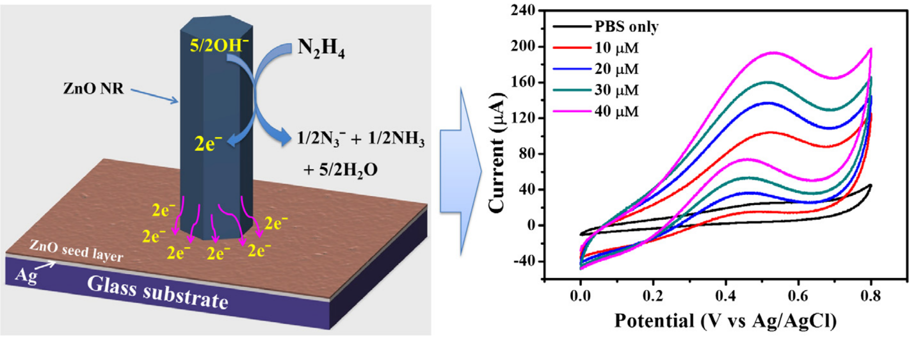
HIGHLIGHTS

- Development of high-performance hydrazine chemical sensor electrodes.
- ZnO NRs on Ag electrode provided high surface and easy substrate penetration structures.
- Sensor showed an excellent sensitivity, long-term stability, and good reproducibility.
- The sensor has potential for detection of hydrazine in water.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 December 2016
Revised 22 January 2017
Accepted 24 January 2017
Available online 25 January 2017

Keywords:
ZnO nanorods
Hydrazine
High sensitivity
Highly-stable
Chemical sensor

ABSTRACT

Herein, we report a binder-free, stable, and high-performance hydrazine chemical sensor based on vertically aligned zinc oxide nanorods (ZnO NRs), grown on silver (Ag) electrode via low-temperature solution route. The morphological characterizations showed that the NRs were grown vertically in high density and possess good crystallinity. The as-fabricated hydrazine chemical sensors showed an excellent sensitivity of 105.5 $\mu A\ \mu M^{-1}\ cm^{-2}$, a linear range up to 98.6 μM, and low detection limit of 0.005 μM. It also showed better long-term stability, good reproducibility and selectivity. Furthermore, the fabricated electrodes were evaluated for hydrazine detection in water samples. We found the approach of directly growing nanostructures as a key factor for enhanced sensing performance of our electrodes, which effectively transfers electron from ZnO NRs to conductive Ag electrode. Thus it holds future prospective applications as binder-free, cost-effective, and stable sensing devices fabrication.

1. Introduction

A number of comprehensive studies have been reported towards the development of highly sensitive and rapid detection of various toxic chemical analyte [1,2]. Among them, hydrazine is a volatile toxic compound which is widely used in industry as an emulsifier, antioxidant, corrosion inhibitor, photographic developer, explosives, dyes, pharmaceutical intermediate, pesticide and insecticide, chemical blowing agent, catalyst, rocket fuel, and plant growth regulator [3,4]. An exposure to hydrazine at even very low concentrations can be hazardous for living organism, mainly in human beings (i.e. skin irritation, dermatitis, and lethal damage to the central nervous system, kidney and liver) [5]. Many instrumental methods such as chromatography, electrochemical, chemilumi-

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http://dx.doi.org/10.1016/j.jcis.2017.01.094
0021-9797/

nescence, and various types of spectroscopy have been reported for the detection of organic pollutants, which are not only costly but also time-intensive with limitations in sampling and analytical techniques [6–8]. Among them, electroanalytical technique is one of the most efficient method for organic pollutants because of its high sensitivity, fast response, low cost and suitability for real-time detection [9–13].

For successfully fabricating electrochemical based hydrazine chemical sensors, various nanomaterials have been employed such as copper oxide (CuO), ZnO, iron oxide (Fe_2O_3), tin oxide (TiO_2), tungsten oxide (WO_3), and manganese dioxide (MnO_2) [14–18]. ZnO nanostructures, specifically have attracted much interest due to its simple and cost-effective synthesis, wide band gap (~3.37 eV), high exciton binding energy (60 meV), biocompatibility, high electron feature and good electrochemical properties, optical transparency, and so forth [19–21]. As well, fabrications of ZnO nanostructure based hydrazine chemical sensors have recently received interests from several research groups. A comparative study of previously reported ZnO nanostructure based hydrazine chemical sensors is listed in Table 1. In brief, Umar et al. have utilized ZnO NRs, nanonails, and nanowires for hydrazine chemical sensor fabrication, which showed improved sensitivities of 4.76, 8.56, and 12.76 $\mu A\ cm^{-2}\ \mu M^{-1}$, respectively [22–24]. Mehta et al. and Sultana et al. used ZnO nanoparticles for hydrazine chemical sensor fabrication and reported different sensitivities of ~97.133 and 1.6 $\mu A\ cm^{-2}\ \mu M^{-1}$, respectively [25,26]. Kumar et al. reported ultra-high sensitive hydrazine sensor, which had narrow linear range [27]. Zhao et al. utilized ZnO NWs for wide-linear range detection of hydrazine [28]. Ni et al. and Fang et al. used hierarchical ZnO micro/nanoarchitectures and carbon nanotube-wired ZnO nanoflowers, which showed poor sensitivity [29,30]. Liu et al. introduced utilization of alloy as electrode surface and used pristine ZnO NRs and carbon modified ZnO NRs for hydrazine detection [31]. Overall, these studies were associated with several shortcomings related to nanostructure synthesis, use of binders and expensive electrodes. Although, nanowires based sensor showed good sensing performance but they were synthesized at high temperatures, which is not applicable for low-cost fabrication. Furthermore, all of nanostructures were synthesized separately and then mixed with binder to fabricate sensing electrodes that is also not suitable for reproducibility and stability of electrodes. Importantly, most of them used expensive gold electrodes to fabricate hydrazine chemical sensors. Therefore, there is an urgent requirement of high-performance, cost-effective, stable, and reproducible hydrazine sensing devices to overcome these shortcomings.

In this study, we report fabrication of binder-free highly stable hydrazine chemical sensor based on vertically aligned ZnO NRs on Ag electrode. The as-fabricated hydrazine chemical sensors showed excellent sensitivity, wide linear range, low detection limit, better long-term stability, good reproducibility and selectivity. Furthermore, the practical applications of fabricated electrodes were investigated in water samples. We found the approach of directly growing nanostructures as a key factor for enhanced sensing performance of our electrodes, which effectively transfers electron from ZnO NRs to conductive Ag electrode.

2. Experimental details

2.1. Reagents

Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, 99%), hexamethylenetetramine (HMTA, 99%), hydrazine anhydrous (N_2H_4, 98%), glucose (D-(+)-99.5%), ascorbic acid (AA), uric acid (UA), dopamine (DA), potassium sulfate (K_2SO_4), potassium nitrate (KNO_3), sodium phosphate monobasic anhydrous (NaH_2PO_4), sodium phosphate dibasic dihydrate ($Na_2HPO_4{\cdot}2H_2O$), and sodium chloride (NaCl) were purchased from Sigma-Aldrich and used without further purification. Phosphate buffer saline solution (PBS, 10 mM, pH 7.0) was prepared by mixing solutions of NaH_2PO_4, $Na_2HPO_4{\cdot}2H_2O$, and NaCl (0.9%) in ultra-pure water purified by Millipore-Q system prior to the experiments.

2.2. Fabrication of hydrazine chemical sensor and characterization

To fabricate hydrazine chemical sensor electrodes, firstly, glass substrates (3 cm × 0.2 cm) were thoroughly cleaned by using detergent, deionized water, and acetone and ethanol. Then, a thin layer of Ag (~170 nm) was sputtered on cleaned substrate followed by deposition of ZnO seed layer (~60 nm) on sputtered on the selected area (0.04 cm^2) of Ag. In the next step, vertically aligned ZnO NR arrays were grown on the seeded region using our previous recipe [32]. In brief, an equal molar of $Zn(NO_3)_2{\cdot}6H_2O$ (0.03 M) and HMTA (0.05 M) were dissolved in 50 mL of deionized water and transferred into a Pyrex glass bottle, followed by heating in a laboratory oven for 8 h at 85 °C after suspending the pre-seeded substrates upside down. After completion of the reaction, the electrodes were rinsed with deionized water to remove impurities before characterization.

The morphologies of ZnO NRs on electrodes surface were examined by field-emission scanning electron microscopy (FESEM, Hitachi S4700, and SUPRA 40VP) equipped with energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM, JEOL-JEM-2010) and high-resolution TEM (HRTEM). The crystalline structure of the samples was analyzed by X-ray diffractometer (XRD) measured with Cu-Kα radiation (λ = 1.54178 Å) in the range of 30–55° with 8°/min scanning speed. All the electrochemical measurements including cyclic voltammetry and amperometry

Table 1
Comparison of the hydrazine chemical sensor based on ZnO nanostructures modified electrode.

Sensor electrode	Sensitivity ($\mu A\ \mu M^{-1}\ cm^{-2}$)	Linear range (μM)	Response time (s)	LOD (μM)	Ref.
ZnO NRs-Nafion/Au	4.76	0.2–2	<10	2.2	[22]
ZnO nanonail-Nafion/Au	8.56	0.1–1.2	<5	0.2	[23]
ZnO nanowires-Nafion/Au	12.76	0.5–1.2	<5	0.084	[24]
ZnO nanoparticles/Au	~97.133	0.1–1	<5	0.147	[25]
ZnO nanoparticles/Au	1.6	0.066–415	<3	0.066	[26]
ZnO nanocones-Nafion/Au	50×10^4	0.010–0.1	<2	0.01	[27]
Nafion/ZnO NWs/Au	3.8	3.0–562	3	0.0144	[28]
Hierarchical ZnO micro/nanoarchitectures-Nafion/Au	0.51	0.8–200	<3	0.25	[29]
Flower-like microstructure ZnO- Nafion/Au	0.095	3.0–120	<4	2.1	[29]
ZnO nanoflowers/MWCNTs/GCE	0.2469	0.6–250	3	0.18	[30]
Pristine ZnO NR array/alloy	4.48	0.1–3	<8	0.2	[31]
Carbon modified ZnO NR array/alloy	9.4	0.1–3.8	<4	0.1	[31]
ZnO NRs/Ag	105.5	0.01–98.6	~2	0.005	This work