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Reduced graphene oxide-based gas sensor array for pattern recognition of DMMP vapor

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ABSTRACT

In this work, a new sensor array was designed for the discrimination of dimethyl methylphosphonate (DMMP) vapor from some other vapors, capable of interfering with DMMP vapor in the reduced graphene oxide (RGO)-based chemiresistor sensor. The referred sensor array was constructed using different RGOs, obtained by the application of various reducing agents in synthesis of the RGO. Three kinds of reducing agents including hydrazine hydrate, ascorbic acid and sodium borohydride were utilized for the reduction of graphene oxide, synthesized by chemical oxidation of graphite. It was found that the kind of reducing agent, used in the reduction of graphene oxide (GO) had huge effect on the DMMP sensitivity of the related RGO. Sodium borohydride and ascorbic acid led to the RGOs which were much sensitive to DMMP vapor than that was reduced by hydrazine hydrate. The electrical resistance changes of three kinds of RGOs were recorded upon exposing of them to various vapors and the obtained data were analyzed by principal component analysis. The obtained results showed that the RGOs, prepared by hydrazine hydrate and sodium borohydride, were the best combinations of different RGOs to efficiently discriminate DMMP from other vapors.

1. Introduction

Nerve agents such as sarin and soman, are among the most toxic organophosphate-based chemical warfare agents [1,2]. Toxicity of nerve agents is mainly because of their interfering in operation of acetyl cholinesterase. They inhibit irreversibly the activity of enzyme acetyl cholinesterase, leading to accumulation of neurotransmitter acetylcholine. The accumulation of acetylcholine in body manifests itself by stopping the function of some vital organs like heart, brain, muscules and respiratory system which can finally leads to death [3]. Unfortunately, these highly killing agents have been used many times in human history during wars and also terrorist attacks [4–6]. Therefore, it is urgently required to access an early warning nerve agent sensing system to detect and monitor the presence of these hazardous agents in different environment for military and security applications.

Because of extremely high toxicity of nerve agents their handling in laboratory, when testing the related sensor, is very dangerous risk. Therefore, in place of the nerve agents an appropriate stimulant is usually utilized for the testing of sensing devices for nerve agents. Dimethyl methylphosphonate (DMMP), known as an appropriate simulant for the nerve agents of sarin or soman, has been generally used in developing various types of nerve agent sensors [2,7].

Various kinds of sensing devices including semiconducting metal oxides (SMO) [8–10], microcantilevers [11,12], quartz-crystal microbalance (QCM) [13] and surface acoustic wave (SAW) sensors [14,15] have been reported for the detection of DMMP. Carbon nanotube [16–18] and graphene [19–21] based materials have also been utilized as the new generation of chemiresistor gas sensor for DMMP detection, representing interesting sensing behavior. However, one major drawback of these sensors is the poor selectivity of them for DMMP recognition. In order to tackle with this disadvantage in most cases a sensor array, known as an electronic nose is applied in place of a single gas sensor [2,22,23].

Reduced graphene oxide (RGO) has shown to be high sensitive sensing material for various gases. In spite of the fact that the RGO material exhibits slight selectivity in sensing of some kinds of target vapors [20], however, it is not an ideally selective material for gas sensing. For instance, RGO has been applied as all-organic vapors sensitive material [24]. However, it has been shown that the selectivity of graphene can be managed by changing of the reducing agent used for the reduction of graphene oxide [19,25].

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In this work, we managed the gas sensing characteristics of the RGO via reducing of graphene oxide by various reducing agents. It was found that the kind of reducing agent had crucial effect on the sensitivity of the resulting RGO to DMMP vapor. Different RGOs with various DMMP vapor sensitivities were used to design a simple sensor array, capable to discriminate DMMP vapor from other vapors.

2. Experimental

2.1. Reagents

Hydrazine hydrate (HZ), ascorbic acid (A) and graphite powder were obtained from Merck (Germany). Dimethyl methylphosphonate and different solvents, applied as volatile organic vapors, were also from Merck (Germany). Sodium borohydride ($NaBH_4$) was purchased from Fluka (Buchs, Switzerland). All other chemicals were of analytical grade and purchased from Merck (Germany).

2.2. Synthesis of three kinds of graphene

Graphene oxide (GO) was synthesized by chemical oxidation and exfoliation of natural graphite according to a modified Hummers method [26]. The recipe, utilized for the preparation of GO can be found elsewhere [27].

In a typical synthesis procedure, 2 g of natural graphite and 1 g of $NaNO_3$ were mixed with H_2SO_4 (95%, 48 mL) in a flask. The mixture was stirred (for 30 min) in an ice bath. Then, 6 g of $KMnO_4$ was progressively added to the suspension under vigorous stirring. The mixture was removed from the ice bath and stirred further at

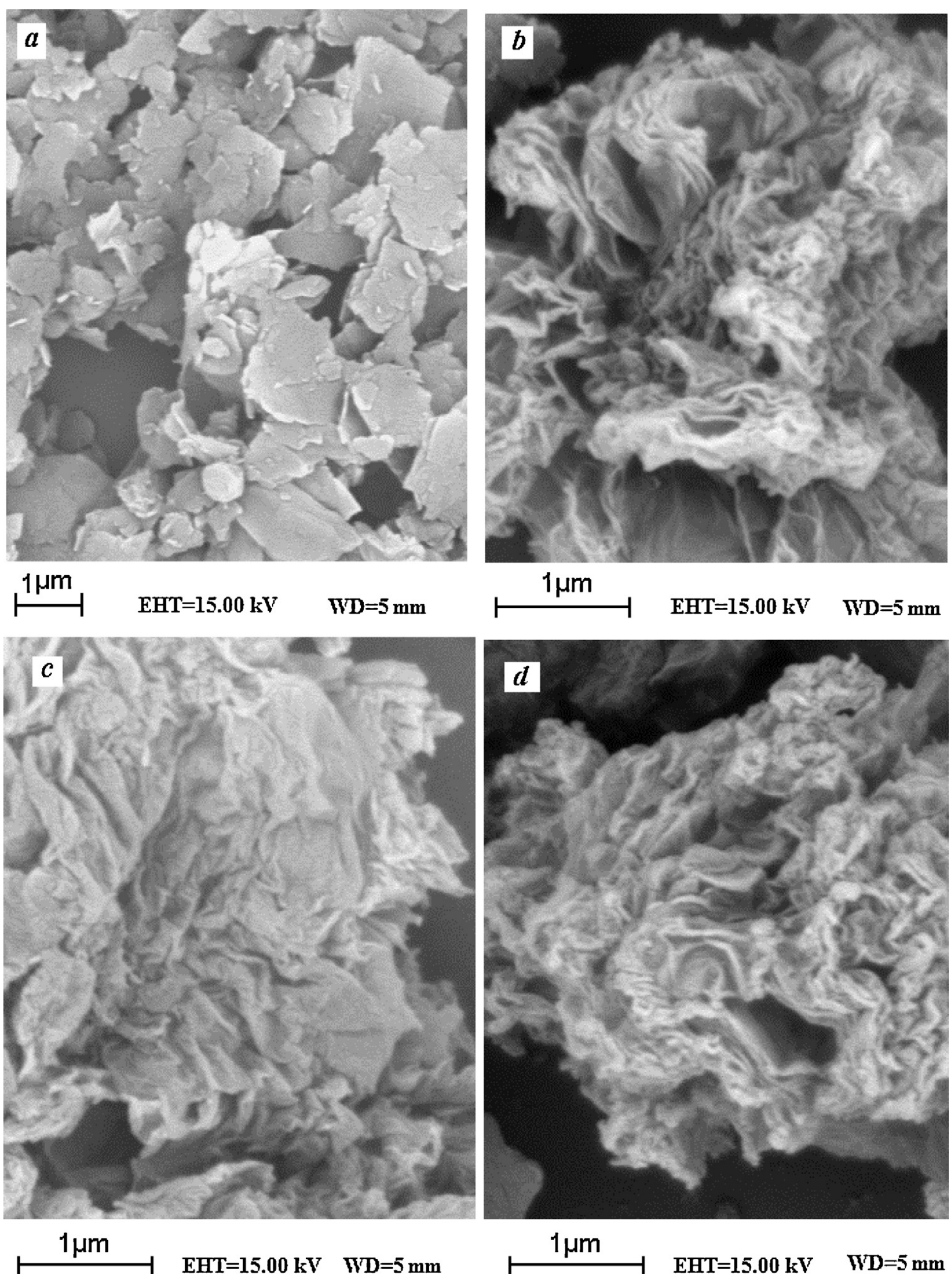

Fig. 1. scanning electron microscopy image of graphite sheets (a) and the graphene oxide materials reduced by hydrazine hydrate (b), sodium borohydride (c) and ascorbic acid (d).