Sensors and Actuators B 261 (2018) 83–90

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

A facile fabrication of colorimetric graphene oxide reflecting films for ultrasensitive optical gas sensing

Tingyuan Gong, Xiaoxiao Zhang, Yuchen Fu, Guowei Zhou, Hong Chi*, Tianduo Li*

Shandong Provincial Key Laboratory of Fine Chemicals, School of Chemistry and Pharmaceutical Engineering, Qilu University of Technology, Jinan 250353, People's Republic of China

ARTICLE INFO

Article history:
Received 7 June 2017
Received in revised form
12 December 2017
Accepted 15 January 2018

Keywords:
Graphene oxide
Colorimetric
Reflecting films
Ultrasensitive
EtOH sensor

ABSTRACT

A series of graphene oxide (GO) thin films for colorimetric sensing was fabricated by dip-coating technique. These films exhibited ultrafast response, good reversibility and obvious optical shifts within the visible range toward ethanol. Fourier transform infrared spectroscopy (FTIR) spectra confirmed that GO was successfully synthesized. Scanning electron microscope (SEM) and atomic force microscope (AFM) showed that the thickness of GO film can be modulated within 200 nm–275 nm. Ultraviolet-visible (UV–vis) spectrophotometer demonstrated that the spectra red shift with the increase of thickness of GO film. Dynamic study showed that absorption and desorption time was 120 ms and 80 ms, respectively. The selectivity of the GO sensor was studied by measuring the response time towards four kinds of vapor including EtOH, MeOH, H_2O and NH_3. The response time of EtOH was 120 ms and detection limit was 3.33 ppm. Colorimetric properties of GO film showed a promising application for fast and visualized sensing of ethanol with high performance.

1. Introduction

Continued development of industry and agriculture brings increased production and emission of irritant, toxic, and flammable volatile organic compounds (VOCs). Quick and precise detection of these harmful gases to human body is in highly demand to monitor environment and avoid personal injury [1–4]. So far, a variety of materials such as ceramics [5], polymers [6], and metal oxide [7] have been explored to fabricate gas sensors, but they are either dependent on electrochemical signal output or hardly to meet some requirements on fast response, long-term steady or easy fabrication which are desired for gas sensors.

Hence, developing a novel sensing material and method is highly desirable. Currently, major attentions have been paid to the synthesis of functional carbon materials such as carbon nanotubes [8,9], graphene and its derivatives [10] because of their peculiar structural characteristics, high surface activity, good electrical conductive and mechanical stiffness. Hatui et al. adopted a template free one pot hydrothermal route for the synthesis of CuO coated with SnS in presence of reduced graphene oxide (RGO) nanoflower for supercapacitor electrode material. RGO facilitated the in-situ electron transfer from Sn^{2+} to Cu^{2+} and improved the conductivity of the whole system [11]. Silva at al. used hot filament chemical vapor deposition (HFCVD) to synthesize electrowettable carbon nanowall (CNW)/diamond-based hybrid 3D materials, which can be applied for energy storage [12]. Mecklenburg et al. used ZnO as template to synthesize aerographite on the cm^{-3} scale by CVD process with the advantage of remarkable mechanical properties [13]. The graphene and its derivatives synthesized by CVD are uniform. Nevertheless, the process needs specific substrates and instruments, professional technicians, resulting in high cost. Novoselov and co-workers first reported that graphene based sensing devices could detect individual gas molecules by monitoring resistance [14]. This pioneering work made graphene materials been widely explored for the fabrication of gas sensors for its large specific surface area, excellent optical property, low electronic noise, and high carrier mobility [2,15–17]. Since then, various graphene based materials have been developed for gas sensing base on electrical signals. Yuan et al. fabricated reduced graphene oxide/polymer composite through assembling reduced graphene oxide (rGO) sheets onto the surfaces of electrospun polymer nanofibers. The formed ultrathin coating can be used for NO_2 sensing based on the conductance change [18]. Kodu et al. demonstrated single-layer CVD graphene with a few layers of laser deposited V_2O_5 for a highly sensitive NH_3 detection. NH_3 adsorption and desorption with the conductivity change of the V_2O_5–graphene system was measured

* Corresponding authors.
E-mail addresses: ch9161@gmail.com (H. Chi), litianduo@163.com (T. Li).

https://doi.org/10.1016/j.snb.2018.01.137
0925-4005/

[19]. Sun et al. prepared graphene membranes based sensing device by filtration to detect humidity by monitoring capacitance as well [20]. However, the uses of electrical gas sensors are either difficult or impossible in certain environments like remote places, potentially explosive atmospheres and certain environments [21]. Therefore, optical gas sensor is a promising candidate in terms of visualization. Due to the special energy gap, graphene can emit light only after doping or high-pressure treatments [22,23]. In 2007, Arsenault first highlighted the crucial role of structural color in the developing of dynamic digital plays [24]. Various inorganic and polymer opal structural materials have been widely explored [25–27]. Recently, thin film interference color has attracted considerable attention because of easy fabrication, stable color and energy-saving properties [28,29]. When a beam of sunlight irradiates a thin film, it will be reflected by both upper and lower boundaries of the film. The thin film which is usually formed by transparent medium induces an interference phenomenon of light waves. If the thickness of the film is thin enough (nanoscale), the interference of light will generate bright polychrome color displayed in the visible range [30,31]. Many natural phenomena can be explained by this mechanism, such as the dielectric film plating of camera lens, the oil films on water and colorful soap bubbles [32]. Many creatures display colors which are also associated with this mechanism, for example peacock and butterfly [33]. Even some animals, such as chameleons and squids, transform its thin layers' structure which affects the interference of light to change their colors [34]. Such structural color is stable, bright and independent of any external excitations. Therefore, high-performance gas sensors of graphene derivatives based on interference light response is promising in terms of high sensitivity, quick response, and long-term stability.

Herein, we report the fabrication of GO based thin film interference gas sensor with visualized colorimetric sensing properties. GO thin films with visualized colorimetric property were fabricated via simple dip-coating technique. The film on silicon wafer exhibited different colors by tuning the solution concentration (Scheme 1A). This color originates from the thin film interference of visible light reflected by the interfaces of air–coating and coating–substrate (Scheme 1B). Interestingly, the thin film coated can be regarded as the sensing layer, which exhibit ultrafast and reversible color changes when exposed to different gas atmosphere which is induced by thickness variation resulting from adsorption or desorption of the coating (Scheme 1C). The change can be simply distinguished by naked eyes without any equipment or power source. The composition of GO was verified by the FTIR spectra. The surface and cross-section of GO film was characterized by SEM and AFM images. A simple spectrophotometric method was efficiently applied for the adsorption and desorption properties of GO film gas sensing which were exposed to various gas atmospheres. The gas sensing mechanism was explored by UV–vis spectrometer also. The GO-based optical gas sensor reported here shows many interesting features for real on-site sensing with low cost fabrication, fast response, high reproducibility and suitability for large scale manufacturing.

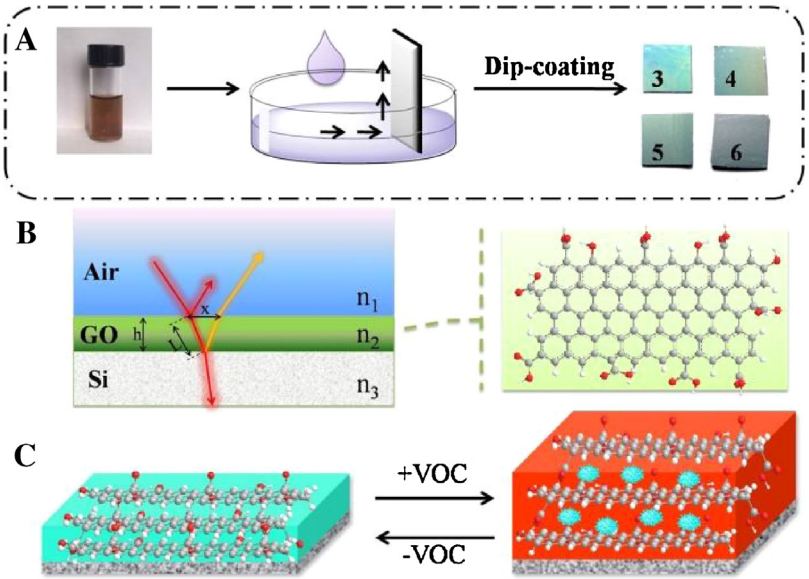
2. Experimental

2.1. Materials

Graphite (200 mesh) was purchased from Alfa Aesar. Concentrated sulfuric acid (95–98%), hydrogen peroxide (33%), phosphorus pentoxide (99%), potassium persulfate (99.99%), potassium permanganate (>99.5%) were purchased from Sinopharm chemical reagent. All reagents were analytical grade (AR). Ultrapure water (18.2 MΩ cm) was prepared with Milli-Q integral water purification system. All chemicals were obtained from the commercial sources and used directly without further purification, and all glassware were cleaned successively with detergent, ultrapure water, and then dried before use.

2.2. Instruments and methods

Infrared (IR) spectra were measured using an IRPrestige-21 FT-IR spectrometer (Shimadzu). The spectra were recorded for 32 scans, and signal averaged with a resolution of 1 cm^{-1}. JEOL FESEM JSM6700F was used to examine the surface and cross section of films. The accelerating voltage was set to 5 kV. The samples were first sputtered with gold for 20 s prior to SEM analysis. Atomic force microscope (AFM, Bruker) with mutimode 8 nanoscope V system was used to analyze the film thickness. Reflectance spectra were recorded by Shimadzu UV-3100PC UV-VIS-NIR spectrometer. An ISR-3100 integrating sphere attachment was used for reflectance



Scheme 1. (A) Schematic illustration of the fabrication of colorimetric GO reflecting films at different GO concentration ([c] = 3 mg/mL, 4 mg/mL, 5 mg/mL, 6 mg/mL) by dip-coating technique. (B) Schematic diagram of the interference of a beam light across the GO film (left) and the molecular structures of GO (right). (C) Sketch of the adsorption and desorption of VOCs in the GO film with obvious color change.