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Multilayer films of layered double hydroxide/polyaniline and their ammonia sensing behavior

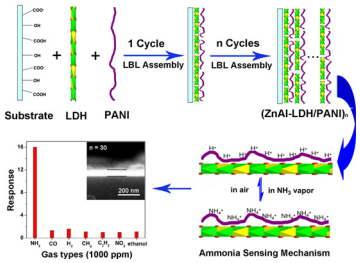
Dong-Mei Xu, Mei-Yu Guan, Qing-Hong Xu, Ying Guo*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, P.O. Box 98, Beijing 100029, PR China

HIGHLIGHTS

- $(ZnAl\text{-}LDH/PANI)_n$ multilayer films have been fabricated via a layer-by-layer assembly way.
- The multilayer films have relatively ordered morphology and controllable thickness.
- The multilayer films show extremely high selectivity to ammonia at room temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper reports the fabrication of layered double hydroxide (LDH)/conductive polymer multilayer films by alternate assembly of exfoliated ZnAl-LDH nanosheets and polyaniline (PANI) on silicon wafer substrates using the layer-by-layer (LBL) deposition technology. UV–vis absorption spectroscopy indicates a stepwise and regular growth of the $(LDH/PANI)_n$ multilayer films upon increasing deposition cycles. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) demonstrate that the surfaces of the films are microscopy smooth and uniform with a thickness of 2 nm per bilayer. Furthermore, the resulting $(LDH/PANI)_n$ multilayer films possess high selectively response to ammonia at room temperature. The presence of LDH nanosheets plays a critical role on the gas sensing for the pure PANI film has very low response to ammonia. The LBL assembly process based on LDH combines the conducting polymer and nano-inorganic material, which provides opportunities to develop new inorganic–organic films for gas sensing.

1. Introduction

It is well known that ammonia has been widely applied in food technology, chemical engineering, firepower plant, medical diagnosis, and refrigeration industrial processes, etc. [1–3]. However, ammonia is also a poisonous gas, which could bring a threat to the human health. For instance, even short-term exposure to 1000 ppm or above ammonia would lead to a fatal respiratory system and lung disorder [4–6]. Accordingly, a leak in the systems, including the chemical industry, fertilizer factories and refrigeration systems where make use of almost pure ammonia, would definitely result in a serious life-threatening situation [1]. For that reason, there is an increasing demand to fabricate ammonia gas sensors with good stability, considerable sensitivity as well as high selectivity. Nowadays, the most common ammonia gas sensors available on the market are semiconductor oxides sensors, but always with a high operation temperature. Compared with the semiconductor oxides, the advantages of conducting polymers are their diversity, easy synthesis and their gas responses particularly at room temperature [7,8]. Among the conducting polymers, polyaniline (PANI) has recently achieved widespread attentions for its high yield, good environmental stability, appreciable conductivity and interesting redox behavior controlled by simply doping/dedoping approach [9–12]. However, similar to other polymers, pure PANI used as gas sensor

* Corresponding author. Tel.: +86 10 64412115.
E-mail addresses: guoying@mail.buct.edu.cn, guoyingbuct@gmail.com (Y. Guo).

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is limited in application due to its poor processing performance [13]. For solving this problem, many kinds of hybrid films based on PANI have been prepared and fabricated for gas detection. Particularly, these hybrid films with PANI and inorganic materials have shown the extended application of PANI as well as its improved gas sensing behavior [14–16], which is partly attributed to its better process ability and enhanced heat resistance result from the addition of inorganic components [17].

Nevertheless, the fabrication and manufacture techniques are as important as the preparation of new materials themselves. Nowadays, a large number of gas sensing materials have been prepared as thin film which involves namely the physical or chemical techniques. The physical techniques include chemical vapor deposition, thermal vapor deposition, sputtering, laser ablation, etc., whereas the sol–gel, Langmuir–Blodgett, spin coating, layer by layer (LBL) assembly, etc. belong to chemical routes [18]. The advantage of gas sensing films achieved via chemical route is that, large quantity of processable nanostructures can be obtained at a cost-effective, highly-scalable and mild reaction condition. In particular, for inorganic–organic hybrid thin films, since the vapor pressure and decomposition temperature of the organic and inorganic individual compounds differ significantly, they cannot be prepared by the standard physical techniques [19]. As such, among the chemical methods that have been developed for preparing films, LBL assembly, based on sequential adsorptions of oppositely charged species in solution, is an advisable method for the deposition of inorganic–organic hybrid thin films owing to the merits of LBL assembly, such as low cost, room temperature process, high reproducibility, and especially the controllable thickness at a molecular scale [20,21].

Layered double hydroxide (LDH) is a class of anionic layered clay with a general formula of $[M^{2+}_{1-x}M^{3+}_{x}(OH)](A^{n-})_{x/n}\cdot yH_2O$, in which M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively, and A^{n-} is the intercalated guest anion [22]. LDH can be used as a host matrix for the orientation and dispersion of interlayer anions, in order to afford tailored catalytic [23], sensor [24], optical [25], thermal [26] and magnetic [27] functional materials, etc. Admitting that there are reports about electrochemistry films of LDH-supported polyaniline, those films have been applied in solution phase and couldn't be obtained with controlled morphology and structure [28]. It is worth noting that LDH can be exfoliated into positively charged nanosheets, which can be used to construct inorganic–organic multilayer films by layer-by-layer (LBL) assembly technique which involves the alternative deposition of LDH nanosheets and polymers by the driving force between them, such as electrostatic force, hydrogen bonding, covalent bonding and coordination bonding [29]. Moreover, to the best of our knowledge, there still lacks reports on gas sensing properties of LDH nanosheets and conductive polymer films obtained by LBL process till now. Therefore, in this paper ZnAl-LDH/PANI multilayer and ultrathin films have been fabricated with uniform morphology, ordered structure and controllable thickness by LBL assembly of PANI with exfoliated ZnAl-LDH nanosheets (Scheme 1) and their resistance change in different gas phase has been further observed. It turns out that the ZnAl-LDH/PANI multilayer films show higher ammonia response compared with the PANI film alone. Therefore, it can be concluded that the ZnAl-LDH nanosheets have provided a confined and stable microenvironment for the immobilization of PANI as well as increasing the reaction spaces between PANI and gas molecules. This assembly under the nanometer scale has resulted in a high dispersion of PANI with uniform orientation and avoidable aggregation, which brought out the high ammonia response of PANI.

2. Experimental

2.1. Preparation of ZnAl-LDH nanosheets

The starting materials were $Zn(NO_3)_2\cdot 6H_2O$ (99.0% purity from Xilong Chemical Co., Ltd.), $Al(NO_3)_3\cdot 9H_2O$ (99.0% purity from Xilong Chemical Co., Ltd.), urea (99.0% purity from Xilong Chemical Co., Ltd.), methanol (AR from Beijing Chemical Works) and HNO_3 (AR from Beijing Chemical Works).

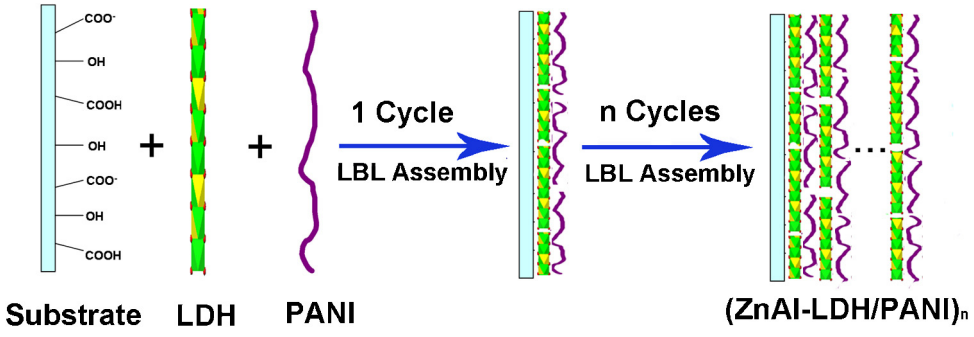
In this paper, CO_3^{2-} intercalated ZnAl-LDH (ZnAl-CO_3^{2-}-LDH) with a high degree of crystallization was synthesized using a similar procedure reported by Sasaki [30]: $Zn(NO_3)_2\cdot 6H_2O$ (10 mM), $Al(NO_3)_3\cdot 9H_2O$ (5 mM) and urea (35 mM) were dissolved and mixed in aqueous solution and the solution had been further heated at 97 °C under refluxing and continuous magnetic stirred for 2 days. The obtained product ZnAl-CO_3^{2-}-LDH was washed with water and ethanol for several times before being dried in air at 60 °C.

As NO_3^- interacted LDH is found to possess excellent delamination behavior, the sample of ZnAl-CO_3^{2-}-LDH was converted to NO_3^- intercalated (ZnAl-NO_3^--LDH) by ion exchange process using 6.6 mM HNO_3 with 90 mL methanol solution [31] while being purged by nitrogen gas for 3–5 h at ambient temperature. The resulting precipitate was separated through centrifugation before being washed with methanol and dried under vacuum.

At last, 0.5 g of ZnAl-NO_3^--LDH was shaken in a 500 mL formamide solution for 72 h to produce a colloidal suspension of exfoliated ZnAl-LDH nanosheets. To remove the unexfoliated particles, the resulting translucent colloidal suspension was further treated by centrifugation at 6000 rpm for 4 min. After that, the rest of colloidal suspension was transparent and stable, in which a clear Tyndall light was observed.

2.2. Fabricate of $(ZnAl\text{-}LDH/PANI)_n$ multilayer films

The $(ZnAl\text{-}LDH/PANI)_n$ multilayer films were fabricated through the LBL assembly technique. The quartz glass and silicon substrate were immerse and cleaned beforehand in concentrated methanol/HCl (v/v = 1/1) and concentrated H_2SO_4 for 20 min each,



Scheme 1. LBL assembly process for $(ZnAl\text{-}LDH/PANI)_n$ films.