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Effect of combined chemical and electrochemical reduction of graphene oxide on morphology and structure of electrodeposited ZnO

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Abstract

This study reports a novel method of tailoring the properties of ZnO nanostructures by electrodeposition in presence of chemically-reduced graphene oxide (rGO). The coupled electrochemical and chemical reduction of graphene oxide resulted in few-layer graphene-based material. The presence of rGO in the electrolytic bath showed a marked influence on the morphology and structure of the hybrid nanostructures. The results indicated the presence of 5 mg L^{-1} rGO results in a 42.9% decrease in resistivity of the hybrid material with respect to the pure ZnO. The proposed approach shows very promising for the fabrication of transparent conductive oxide electrodes.

Keywords: B. Nanocomposites; B. Spectroscopy; B. X-ray methods; C. Electrical properties; D. ZnO

1. Introduction

In the past years a lot of interest was shown for the development of novel composite nanomaterials for transparent conducting oxides applications. To this end, ZnO has been extensively investigated being a semiconducting and piezoelectric material with a direct wide band gap and large exciton binding energy at room temperature. Various methods were envisaged for tailoring either its optical or electronic properties due to its potential in electronics, optoelectronics, electrochemical and electromechanical micro-systems [1,2]. Un-doped ZnO exhibits a high electrical resistivity due to a low carrier concentration [3]; however, its conductivity can be significantly increased by substituting Zn with other metals such as Co, Al, Mn or Cu [4,5].

Triggered by the large freedom degree at tailoring ZnO final properties as a matter of interest from an industrial standpoint, the combination of ZnO and graphene at nano-scale is very appealing for scientists expecting intriguing novel properties based on the excellent capacitive and mechanical properties, superior chemical stability and high surface area of the present graphene-based materials. [6,7]. Although ZnO nanostructures attracted large research interest, fine tuning of their properties and the use of graphene to anchor the metal oxide material to form new nano-hybrid material with potential application in optoelectronics are still a challenge [8].

A wide range of techniques have been applied for the synthesis of ZnO nanostructures including physical and chemical vapor depositions, electro-spinning and wet-chemical methods [9–11]. Amongst all these techniques, the electrodeposition is considered to be a cost-effective and powerful method for manufacturing tailored ZnO nanostructures [12,13]. Moreover, known for large area and high throughput production, the electrochemical deposition approach is also considered to be suitable for industrial use [14–16].

Regarding the fabrication of graphene materials, various technologies have been reported under this aspect starting with the ‘scotch tape’ method. However, given the concerns raised

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along, graphene oxide (GO) has soon been preferred as the starting material for graphene fabrication due to the cheapness and large scalability of the method. Thus, chemical reduction became a widely used approach to reduce the GO material for many applications [17] and various agents have been explored to this end from hazardous hydroquinone and hydrazine [18,19] to environmentally free ones such as vitamin C [20,21], melatonin [22], sugar [23], glucose [24], bovine serum albumin [25], polyphenols [26] or bacteria [27]. Lately, electrochemical methods have also received considered attention towards the reduction of GO owing to the versatility of the modes offered to monitor and control the reduction process both in solids and solution [28] in comparison to other green reduction methods including flash photoreduction, hydrothermal dehydration and photocatalytic reduction [29–31].

In this paper, single-step co-electrodepositions of chemically-reduced graphene oxide (rGO) and ZnO are reported. Since the structure of the carbon plane can be induced differently as per the reduction process [20], this work proposes to study the effect of combined chemical and electrochemical reduction of GO on morphological and structural properties of electrodeposited ZnO. The chemical reduction of GO with ascorbic acid [20,21] is considered here as a non-toxic alternative to hydrazine and a cheap and an easily available way for scalable production of pre-reduced GO. Further, the negative potential applied for the deposition of ZnO was used for simultaneous electro-reduction of rGO, as an additional step in the removal of oxygen functionalities of GO. In addition, we investigated the influence of rGO content on the electrical properties of electrodeposited ZnO nanostructures by coupling the experimental results with statistical analysis.

2. Experimental

2.1. Synthesis of chemically-reduced GO

All materials were provided by Sigma-Aldrich and used as received. The synthesis of GO was carried out as described previously [21]. Basically, 1 g graphite powder was oxidized with 25 mL H_2SO_4 98% and 3 g $KMnO_4$ (Aldrich) at 35 °C for 3 h. Further, the mixture was diluted with deionized water while maintaining the temperature below 90 °C. Successively, 30% H_2O_2 was added to the mixture. The mixture was filtered, purified with HCl and washed with deionized water till neutral pH was reached and dried at 50 °C for 24 h.

A typical procedure for chemical conversion of GO into rGO requires the dispersion of graphite oxide (0.1 mg mL^{-1}) in water by sonication treatment for 1 h. Ascorbic acid (AA) was employed for the chemical pre-reduction of GO thanks to its non-toxicity and to the reducing results in terms of C/O ratio and conductivity comparable to the ones achieved by hydrazine in a parallel experiment [19,21]. The green reduction process took place by employing a reducing agent:GO ratio of 20:1 w/w for 24 h at room temperature, under mechanical stirring. The obtained rGO was isolated by filtration, washed with water and vacuum dried at 50 °C for 24 h.

2.2. Co-electrochemical deposition of rGO–ZnO nanostructures

The co-electrodeposition of graphene/ZnO hybrid material was carried out at −0.8 V (Autolab potentiostat) by a 0.1 M KCl supporting electrolyte containing $ZnCl_2$ and rGO under continuous flow of O_2. The electro-reduced rGO material is further denoted with e-rGO while the initial content introduced in the electrolytic bath is rGO. Thus, the hybrid is denoted by ZnO/e-rGO. The material growth was performed in a three-electrode cell and the deposition potentials referred to a Saturated Calomel Electrode (SCE); Pt and an ITO substrate were used as counterelectrode (CE) and working electrode (WE), respectively. The bath temperature was controlled at different values in the range 65–80 °C. After being grown, the material was annealed for 30 min in Ar atmosphere at 300 °C.

2.3. Characterization

Absorbance ultraviolet–visible (UV–vis) spectra were recorded with a Lambda 35 (Perkin-Elmer) spectrophotometer. A JEOL 6300 Scanning Electron Microscope (SEM), working at 15 kV, was employed to image the morphology of nanostructures. Raman spectroscopy (Renishaw, inVia) was performed using a 514.5 nm excitation source. Finally, the electrical conductivity of the rGO–ZnO composite materials fabricated was recorded by 4-point probe measurements.

2.4. Statistical study

For the two level factorial design [32] adopted as a first insight with the purpose of investigating the influence of rGO content on the electrical properties of electrodeposited ZnO nanostructures, the control parameters were chosen to be: $ZnCl_2$ concentration (A), rGO concentration (B), and the bath temperature (C) whereas the resistivity of the materials in question was used as an output variable. The combination of the three parameters at two different levels (1 and 5 mM, 2 and 5 mg L^{-1} and 65 and 80 °C, respectively), labeled as low (−) and high (+), respectively, provided 2^3 experiments/samples corresponding to any possible combination of these. The calculation was based on the design matrix.

Once the experiments were statistically ordered (STATGRAPHICS Plus), Yates algorithm [32] was employed to analyze the values of the output variable. It should be noted that the term significance or significant in statistics means probably true (not due to chance). The change in the output variable as a function of the level used for input variable is named here as the effect of the input variable. Combined effect of 2 input variables results in an interaction (noted for example as I_{AB}) if the effect of one variable changes with varying levels of the other input variable.