PREPARATION OF ZINC OXIDE NANOSTRUCTURES AND HYBRID GRAPHENE/ZINC OXIDE NANOMATERIALS BY A POLYSACCHARIDE AQUEOUS-BASED METHOD

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Abstract

In this investigation, nanostructured ZnO as well as novel graphene/ZnO nanocomposites were developed and characterized. Nanostructured ZnO was prepared by an aqueous co-precipitation method assisted by a polysaccharide. The synthesis were carried out using three different ZnO:Polysaccharide ratios (1:0.5, 1:1, 1:3). Three different morphologies and sizes were obtained: nanoflowers, nanoalmonds and nanocrosses. XRD results showed that the materials present hexagonal wurtzite structure, with a crystallite size between 12 and 40 nm. The hybrid graphene/ZnO nanomaterials were prepared at three different concentrations of ZnO. The formation of hybrid nanomaterial was confirmed by XRD and SEM.

Introduction

Because of its diverse advantages such as its interesting characteristics, low price, to the numerous practical applications, ZnO has received exceptional attention among numerous semiconducting oxide materials. ZnO is a functional material exhibiting near ultra violet emission, transparent conductivity, semiconducting, magnetic, and piezoelectric properties [1]. Zinc oxide materials and differently shaped ZnO nanocrystals have attracted considerable attention due to their unique properties that strongly depend on their size and morphologies [2]. ZnO occurs naturally in the Earth's crust, and it exists in two main crystalline forms: wurtzite and zinc-blende. The wurtzite structure is the most common and stable form [3]. Therefore, numerous strategies have been attempted to design and fabricate ZnO nanostructures endowed with the suitability to fulfill each purpose for particular applications. Several methods for the fabrication of ZnO nanostructures have been reported, including hydrothermal synthesis [4,5], vapor–liquid–solid (VLS), vapor–solid (VS) [6] processes, metal–organic chemical vapor deposition (MOCVD) [7], chemical vapor deposition [8], solution-liquid-solid growth inorganic solvents [9], and template based methods [10–13]. Most reported synthesis techniques are complicated, time and energy consuming, and not environmentally friendly. In particular, when organometallic precursors are used, complex procedures, high temperatures and sophisticated equipment to control the growth process are involved.

On the other hand, as a new carbonaceous material, graphene has attracted tremendous attention in the past years, due to its unique electronic properties, excellent mobility of charge carriers (200,000 cm2 V−1 s−1), and extremely high theoretical specific surface area (∼2600 m2 g−1) [14]. It was reported that these features can be employed to improve electronic, optoelectronic, electrocatalytic and photocatalytic performance of semiconductor materials [15] as ZnO. Some investigations in graphene/ZnO were also attempted [16-18].

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Furthermore, graphene is an important building block in nanotechnology, so that hybrid strategy of graphene with ZnO has provided us with the opportunities for enhancing the intrinsic properties of ZnO in diverse manners. Synergistic effects in photocatalytic,[19-21] electrochemical, [22-24] and optical properties[25-27] have been successfully demonstrated in ZnO−graphene hybrid nanostructures. Because most of the multifunctional properties of ZnO are critically influenced by the behavior of its electrons, understanding the behavior of electrons in the ZnO-graphene hybrid system is of great significance to expand the opportunities in relevant applications.

A simple, inexpensive and green synthesis process is required. Here, we report a novel synthesis route for the preparation of ZnO nanostructures and ZnO−graphene hybrid nanostructures. The growth of shape-controlled ZnO nanostructures in large scale is achieved using a zinc nitrate aqueous solution by adjusting composition, concentration of the polysaccharide and growth temperature.

Experimental
Synthesis of ZnO NPs. First, a certain amount of zinc nitrate hexahydrate (Sigma Aldrich, 98%) and polysaccharide gum (purified in the lab) were dissolved in deionized water at room temperature under constant stirring for 3 h. Then, a certain amount of NaOH was added to the solution under constant stirring in order to raise the pH up to 10-12. After stirring for a few hours, the precipitate was recovered by centrifugation and washing cycles, and the solid was dried at room temperature.
Preparation of Graphene Dispersion. The raw materials are graphite, polysaccharide gum and deionized water. The mixture is processed with a high energy homogenizer (ultraturrax). Turbulent flow helps to delaminate sheets of graphite structure and the polysaccharide gum helps to prevent aggregation or agglomeration of the sheets.
Synthesis of Graphene@ZnO. Graphene nanosheets were used to load ZnO NPs for the production of G@ZnO hybrids via a simple route at room temperature. Briefly, the obtained ZnO powder was added to graphene colloidal suspension in 3 different ZnO concentrations (0.001 M, 0.0001 M, and 0.0005 M) with an identical proportion of polysaccharide gum. The suspension was vigorously stirred for 2 h, sonicated for 10 min and subsequently heated at 80° C to obtain the hybridized ZnO/graphene after evaporation the water.
Characterization. X-ray diffraction (XRD) data were obtained on a Panalytical Empyrean Power X-ray Diffraction (40 kV) with Cu−Kα radiation. The morphologies and structures of the samples were investigated by scanning electron microscopy (SEM) Nova Nano 200 FEI and the thermal analyses were with the equipment SDT Q600 from TA Instruments.

Results and Discussion
ZnO NP Results
ZnO nanoparticles produced by the method of precipitation assisted by a natural polysaccharide gum were analyzed by SEM. Figure 1 shows micrographs of the different morphologies obtained. In Figure 1 A) it can be observed that with a 1:1 ratio of zinc nitrate:natural polysaccharide gum, the morphology of nano-flower o nano-star is obtained, but if the concentration of polysaccharide gum is reduced as in the case of B) the size is increased and the morphology is modified to almond shape; when an excess of polysaccharide gum is added as in C) 0.5 micron size particles are obtained and a morphology of nano-cross is obtained.
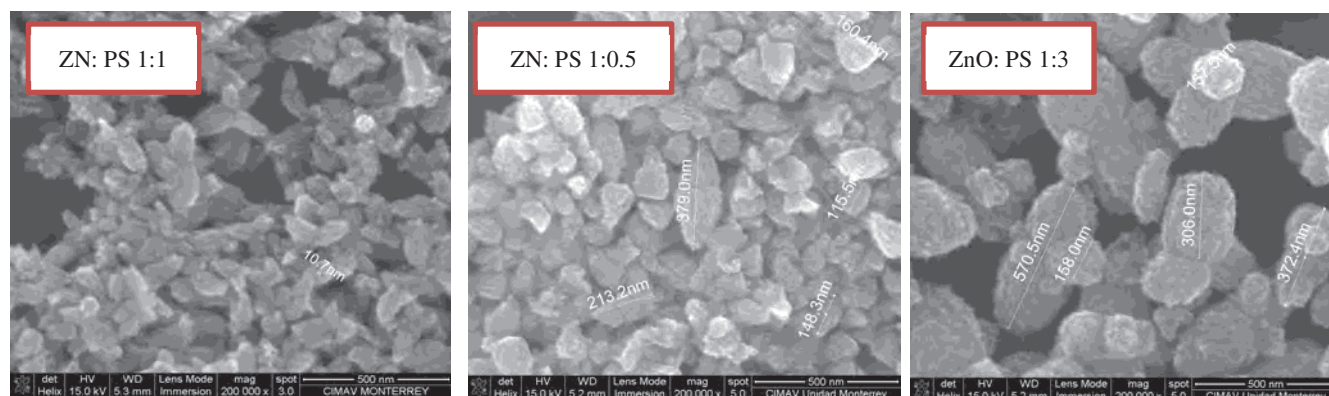
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Figure 1.- SEM Micrographs of ZnO nanoparticles obtained at different Zinc Precursor:Polysaccharide gum ratios: A)1:1; B) 1:0.5; and C) 1:3.

Graphene@ZnO Results

X-ray Diffraction

In figure 2 a diffractogram of the nanocomposite graphene@ZnO is shown; the main signals of hexagonal ZnO were evident, and these can be seen from 30°-38°; the wide signals from 0-30° were attributed to graphene natural structure.
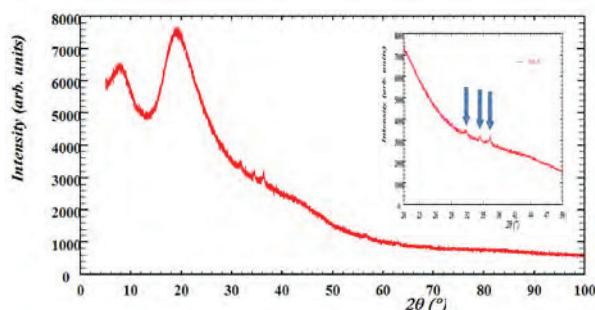

Figure 2.- X-ray diffractogram of Graphene@ZnO nanocomposite.

SEM and EDS Results.

A SEM micrograph of the hybrid material Graphene@ZnO is shown in figure 3; in A) a cluster is observed, however when analyzed at higher magnifications (B) it is possible to distinguish that the cluster is composed of smaller ZnO nanoflowers. Moreover the smoother areas are also distinguished, this layer is graphene.
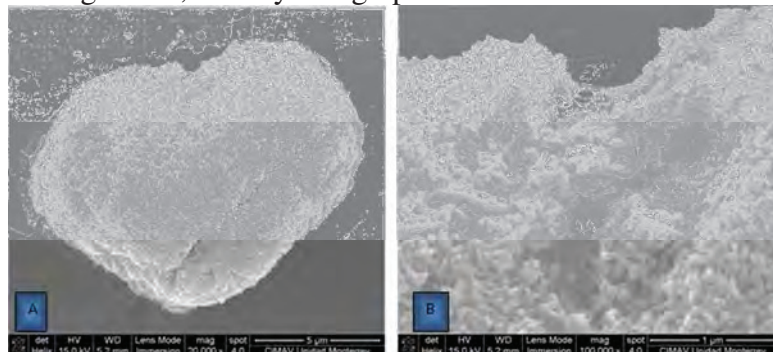

Figure 3.- Graphene@ZnO SEM micrograph: A) Cluster B) ZnO nanoflowers coating a Graphene layer.

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In the elemental analysis by EDS, it was found that as predicted, the smooth area is mainly graphene (figure 4, left) but ZnO is also present; and the rough area is ZnO nanoparticles (figure 4,right), but carbon is also detected.
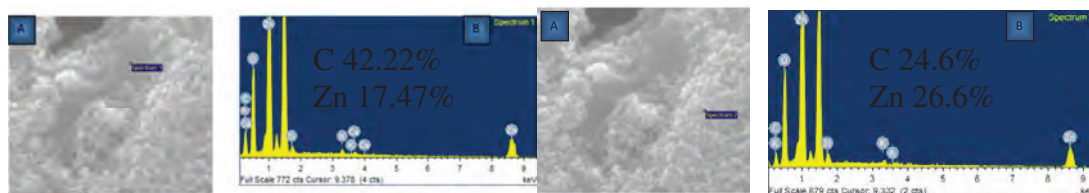

Figure 4.- Left.- Spectrum Analysis 1 "Smooth Area", Right.- Spectrum Analysis 2 "Rough Area".

TGA-DTA Results.

Three graphene-ZnO composite samples in different concentrations of the latter (0.001 M, 0.0001 M, 0.0005 M) were analyzed, and a similar behavior could be observed for the different samples due to the low concentration of ZnO nanoparticles in graphene, which is described below. The first mass loss is 5%, around 100 °C, which can be assigned to water molecules trapped within the structure of the graphene or in the samples. The rapid mass loss of about 40% occurring around 300 °C can be attributed to the pyrolysis of the groups containing oxygen in unstable forms of CO and CO_2. This differs from graphene oxide found in the literature [28-31]), this displacement of approximately 50 °C and it is attributed to the presence of the ZnO nanoparticles in graphene (figure 5). At the end of this characterization the remanent is about 20 % ash, the average amount of product testing with graphene.
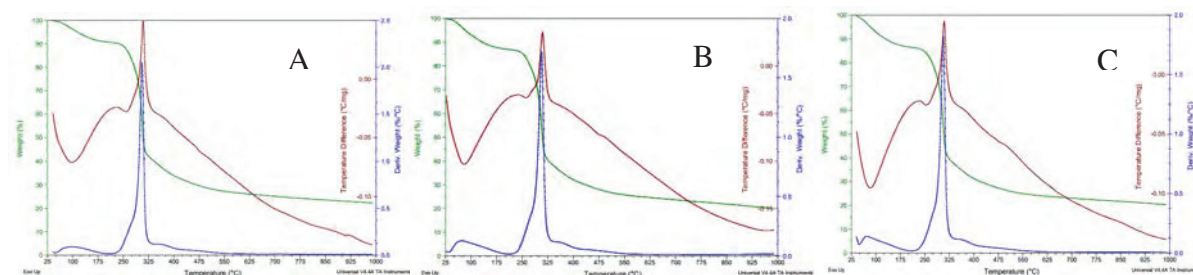

Figure 5.- TGA-DTA curves for Graphene@ZnO nanocomposite: A) ZnO concentration 0.001 M, B) ZnO concentration 0.0005 M, C) ZnO concentration 0.001 M.

Conclusions

It is possible to produce high quality ZnO nanoparticles by a co-precipitation method assisted by a natural polysaccharide gum. The concentration of this polysaccharide affects the morphology of the ZnO nanoparticles. It is possible to produce a composite of graphene@ZnO by the same method.

Acknowledgements

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