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Functionalization of MWCNTs with Ag-AuNPs by a green method and their catalytic properties

D. Mendoza-Cachú[a], J.L. López-Miranda[a], C. Mercado-Zúñiga[b], G. Rosas[a,*]

[a] Instituto de Investigaciones Metalúrgicas, UMSNH, edificio U., Ciudad Universitaria, C.P. 58000, Morelia, Michoacán, Mexico
[b] Tecnológico de Estudios Superiores de Coacalco, Av. 16 de Septiembre # 54, C.P. 55700, Col. Cabecera Municipal, Coacalco de Berriozábal, Edo. de México, Mexico

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ABSTRACT

Some new and notable applications of carbon nanotubes (CNTs) require previous treatment, whether they are stabilized or decorated. The present research aims to achieve a homogeneous decoration of multi-walled CNTs with Ag-AuNPs through an alternative process following a low-temperature green synthesis route. The MWCNTs were first stabilized using sodium dodecyl sulfate (SDS) as surfactant agent and evaluated using UV–Vis spectroscopy and scanning electron microscopy (SEM), showing a considerable decrease in nanotubes agglomeration. Subsequently, the synthesis of the Ag-AuNPs proceeded through the reduction of the $AgNO_3$ and $HAuCl_4$ salts, using the *A. triphylla* plant extract. UV–Vis, SEM, and transmission electron microscopy (TEM) analysis were helpful in determining the formation of the Ag-AuNPs, along with the appropriateness decoration of the MWCNTs. Finally, the evaluation of the catalytic activity of the decorated MWCNTs was conducted by using the degradation of methylene blue dye, showing positive results. This study was developed employing the UV–Vis technique.

1. Introduction

Since the discovery by Sumio Iijima in 1991 [1], when he found the CNTs for the first time, carbon structures have constituted the main work of various researchers. Numerous investigations about the synthesis of CNTs are available in present days using different techniques, including arc discharge and chemical vapor deposition (CVD), among others [2–5]. The structural characteristics of the products, as well as some important properties depend directly on the synthesis process. From this aspect, it is possible to synthesize two different types of nanotubes: (a) single-wall carbon nanotubes (SWCNTs), which have one single graphite layer, and multi-wall carbon nanotubes (MWCNTs), formed by multiple concentric graphite layers [6]. These structural differences influence their properties, such as excellent electrical and optical behavior for the SWCNTs [7,8] and extraordinary mechanical properties for the MWCNTs [9,10]. These features are suitable for many applications such as strain sensors, piezoresistive and organic vapor sensing [11–15], structural materials [16,17] stretchable electronic devices [18], wastewater treatment [19], dye-sensitized solar cells [20], and capacitors [21], among others [22,23].

On the other hand, the research field of the CNTs has spread due to its aptitude to be superficially modified, which is important for many of the newly discovered applications. For example, because the CNTs tend to agglomerate, one of the most widely used surface modification processes involves the use of various surfactants that keep them uncoupled, such as sodium dodecyl sulfate (SDS), oleic acid (OLA) and polyvinylpyrrolidone (PVP) [24–29]. Among them, many investigations show the effectiveness of SDS for this purpose. The advantage of using SDS instead of some other compounds is that the amount of SDS needed to obtain a stable dispersion is considerably lower compared to OLA and PVP. The main reason for this effect comes from the coordination of the surfactant molecules with the metal ions, which increases the amount of surfactant necessary to achieve homogeneous stabilization. Furthermore, within the possible surface treatment, the decoration of CNTs becomes especially important when it comes to improving the physical properties [30,31]. This decoration process consists in attaching some nanoparticles (NPs) along the entire surface of the nanotubes, which confers or enhances certain properties. To guarantee an adequate decoration, the NPs must be homogeneously distributed along the entire nanotube and with a little amount of agglomeration. Recently, there have been some studies on the decoration of CNTs with different kind of particles, such as metallic NPs, including Ag, Pt, and Ru [32–34], and some ceramics, specifically ZnO [35].

Depending on the nature of the particles chosen to decorate CNTs and according to their application area, the processing technique considerably changes. When using silver NPs, one of the mainly

* Corresponding author.
E-mail address: grtrejo@umich.mx (G. Rosas).

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investigated is the CVD, although some techniques such as ultraviolet irradiation and electrochemical processes are also suitable for this particular case [36–38]. Nevertheless, some information is available about the decoration of CNTs with AgNPs using simpler techniques such as chemical reduction. Moreover, the development of the green synthesis for obtaining metallic NPs is spreading rapidly [39–41]. These methods consist of using biological molecules from the plant extracts to obtain NPs. For example, some investigations using *A. tryphilla* plant extract are available, specifically for the synthesis of Ag and Au NPs [42]. Thus, there is the possibility to apply a relatively simple and cheaper technique and, at the same time, synthesize materials in the nanometric range, free from toxic and harmful to health compounds. In this manner, the opportunity to functionalize CNTs with metallic particles and employ an eco-friendly process extends the application field of these CNTs/metallic NPs nanocomposites.

Moreover, the catalysis process has an extensive field of research and a large number of applications. Some of them are in solar cells, energy storage and, more specifically, for the purification of wastewater in the elimination of dangerous quantities of toxic compounds, the decrease of the microbial load and, in general, the improvement of water quality treated. Currently, there are several works available that address this issue, using different catalysts, such as DoO-TiO_2, CNT and carbon nanodots, among others [43–46]. However, many of them are synthesized with chemical compounds that are dangerous to human health. In this aspect, the NPs obtained by green methods are suitable for use in this type of applications, since they are free of harmful compounds because the process is respectful of the environment. The AgNps and AuNps have shown an adequate catalytic behavior found in numerous research works. Among them are the green synthesis using different plants, such as *Tulsi leaves*, *Citrus maxima* and *Actinidia deliciosa* [47–49]. Furthermore, the application field of the AgNps and AuNps is quite large, they are used in the electronics industry [50], photocatalytic degradation [51], and medical treatments [52].

Therefore, the present research work is focused on the decoration of CNTs with bimetallic NPs and following a green synthesis route to obtain products with the characteristics necessary to be applied in areas of health and ecology. An application can be the remediation of wastewater, taking advantage of its properties in catalysis.

2. Experimental

The experimental procedure consists of various steps, each of them important because they may influence the process efficiency. In the first place, the MWCNTs were synthesized by the spray pyrolysis method and subjected to a previously established purification treatment [53].

Subsequently, for the dispersion of the purified MWCNTs, the surfactant sodium dodecyl sulfate (SDS) acted as deagglomerating agent. All the dispersion experiments were developed in aqueous solution. First, it proceeds with the measuring of 7 mL of distilled water, followed by the addition of the necessary amounts of SDS to obtain concentrations of 0.2 mg/mL, 0.3 mg/mL, 0.4 mg/mL, and 0.5 mg/mL. Afterward, 1 mg of MWCNTs was added and treated under an ultrasonic bath for 90 min. The MWCNTs dispersion was evaluated employing UV–Vis spectroscopy and scanning electron microscopy (SEM).

The nanotube decoration proceeded using a green route for the synthesis of the NPs to promote a simpler and cheaper method in comparison with the ones most used nowadays [54,55]. The silver nitrate salt ($AgNO_3$) acted as a precursor for the synthesis of the Ag seeds and chloroauric acid for Au ($HAuCl_4$). Also, the *A. triphylla* plant extract worked as a reduction agent. The preparation of the extract consists in weighing 2 g of the crushed plant and pouring it into a beaker with 100 mL of distilled water. The solution is placed on a magnetic stirrer for 30 min at a 60 °C temperature. Later, the liquid was filtered to remove any waste from the plant. After that, 10 mL of a 3 mM solution of $AgNO_3$ and 5 mL of plant extract were added to the dispersed MWCNTs. Finally, the addition of 5 mL of a 3 mM solution of $HAuCl_4$ promotes the formation of the bimetallic NPs, according to the procedure by López-Miranda, et al. [56]. UV–Vis spectroscopy (Lambda 25 Perkin-Elmer), MEB (JEOL JSM 7600F), and transmission electron microscopy (TEM, Philips Tecnai F-20) helped to evaluate the decoration of the MWCNTs with bimetallic Ag-AuNPs.

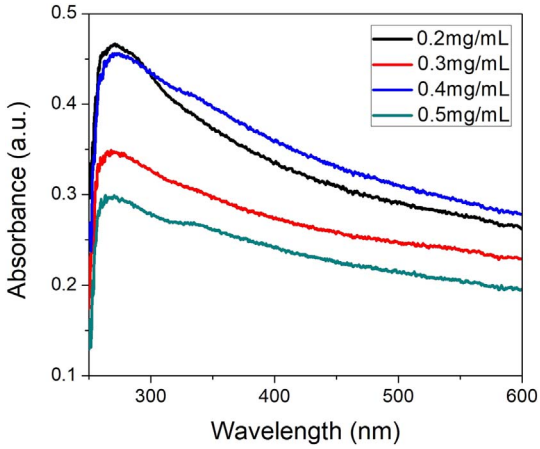

Fig. 1. UV–Vis spectra of the dispersion of MWCNTs, employing different amounts of SDS as surfactant agent.

Ultimately, the evaluation of the catalytic activity of the decorated MWCNTs proceeded using the degradation of the methylene blue (MB) dye. For this, 2 mL of a 2 mM solution of MB were mixed with 1 mL of the solution of MWCNTs decorated with Ag-AuNPs. Finally, the incorporation of 0.1 mL of a solution of $NaBH_4$ acted as catalyzer into the catalysis process. UV–Vis measurements were taken every 5 min up to a time of 20 min, where the capacity of degradation of MB dye was evaluated.

3. Results and discussion

Fig. 1 shows the UV–Vis spectra of the MWCNTs dispersion in aqueous solution, using SDS as surfactant agent and under different concentrations. The specific band corresponding to the MWCNTs at around 275 nm is present for every sample. As the surfactant concentration rises, the intensity of the band decreases, indicating a smaller amount of MWCNTs absorbing in this range, which is attributed to an excessive amount of surfactant that leads to flocculation. On the other hand, the narrower band corresponds to the lowest concentration and, qualitatively, the best results were obtained with a surfactant concentration of 0.2 mg/mL, which presents the most intense and narrow band in comparison with its higher values. These results are comparable with those reported by other authors [57,58].

Subsequently, an MEB study helped to corroborate the previous statement, and its results are shown in Fig. 2. Observations indicate the best dispersion for the use of a surfactant concentration of 0.2 mg/mL (Fig. 2a) presenting the lower pack degree of the MWCNTs; this is in agreement with the results of UV–Vis. Furthermore, the sample corresponding to a concentration of 0.4 mg/mL (Fig. 2c), have a similar behavior. Nevertheless, it presents an excessive amount of surfactant, determined by a loss of contrast in the image, which is not desirable for the decoration of MWCNTs. Similarly, in the case of the concentrations of 0.3 mg/mL and 0.5 mg/mL (Figs. 2b and d, respectively), it presents a low dispersion and an excess of surfactant. Thereby, the following two concentrations show better results suitable for the next experimental stages (0.2 mg/mL and 0.4 mg/mL).

Fig. 3 displays the UV–Vis spectra of the decoration of MWCNTs with Ag-AuNPs. The black line spectrum corresponds to the reduction process of $AgNO_3$ salt after 15 min of reaction (Fig. 3a), showing the typical AgNPs absorption band around 450 nm, indicating the efficient formation of the Ag seeds from which will proceed the formation of the