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Paraffin Removal in the Synthesis of Novel Janus Carbon Nano-Onions

A. Del Valle-Pérez[a], L. Rivera-Rivera[a], O. González-Sánchez[a], and L. Cunci[a].

[a] School of Natural Science and Technology, Universidad Ana G. Méndez, Gurabo, Puerto Rico

Recent research has demonstrated that Janus nanoparticles provide a novel strategy to prepare catalysts and biomaterials. This is because of the versatility of being able to modify both sides of a particle with different properties. Carbon nano-onions are an excellent material as a support for different applications such as metal nanoparticles due to their unique structure and good conductivity. Because of their physical and chemical properties, carbon nano-onions are an ideal material to create Janus nanoparticles for further amphiphillic modifications. This article aims to show a preparatory process to ensure the removal of paraffin efficiently. The main method to be able to create these particles is employing the Pickering emulsion process. Paraffin wax is used as the hydrophobic part of this mixture and serves to block one side of the CNOs to facilitate their modification only on one side. Therefore, its removal is essential to obtain this catalytic nanoparticle.

Introduction

Carbon nano onions (CNO) are spherical structures composed of multilayers of fullerenes, these layers are connected in a way that shows the shape of an onion. Research on CNOs began with the discovery of this material in 1985 by scientists Curl, Kroto, and Smalley (1). During this research, they were able to study in detail the structure of this carbon material which they identified as fullerene, C_{60}. They characterized the structure of this material as compared to a soccer ball. The C_{60} carbon structure is composed of 60 carbon atoms which form a truncated icosahedron, a polygon with 60 vertices and 32 faces that has 12 pentagonal and 20 hexagonal (1). However, in 1992, scientist Ugarte was able to obtain a new carbon material with a very special structure by laser irradiation of a graphite sample (11). This structure is composed of 5-8 layers of fullerene giving it the shape similar to an onion (11). Following this discovery, research has been carried out on this carbon material as a support for metals.

Carbon materials have been used extensively as support for catalysts. This is because they have been shown to help disperse metals on the surface, reduce particle agglomeration, and make better use of the metal during oxygen reactions in fuel cells (6,9,10). Janus nanoparticles are receiving increasing attention because both sides of the particle can be modified with different properties allowing its versatility for a variety of applications (3-5,7,8). The modifications on the surface of these nanoparticles can provide different chemical and physical properties. Research on Janus particles began after the publication of scientist C. Casagrande et al.(2) showing the modifications on both sides of a crystal sphere with different properties. Through this discovery, research in this topic has been increasing, especially in the biomedical area. Moreover, in 1991, Dr. Pierre-Gilles de Gennes won the Nobel Prize for his contribution to the development of an asymmetric nanoparticle and he implemented the word Janus to describe a particle with different properties on both sides (3). Furthermore, this has allowed new research on Janus particles to be extended to applications such as a support for electrocatalysts for fuel cells, especially in the oxygen reduction reaction (4-9).

However, one of the main problems when designing and fabricating Janus nanoparticles is to clean off the side of the nanoparticles that was covered for the modification process. Whether using paraffin wax such as in this work, or other strategy, the modification of the first face to be covered must be cleaned in order to keep the properties of the original nanoparticle, if that is the goal. Therefore, in this work, Janus nanoparticles were fabricated by a wax-paraffin Pickering emulsion process using CNOs on its surface (4,6) and the purpose of this article is to provide information on the process of efficiently removing paraffin for the creation of these particles. Paraffin wax is essential in the process of creating Janus particles. The purpose of paraffin in this process is to cover one side of the CNOs allowing the modification of the nanoparticles to be deposited on one side only. However, to finally obtain the Janus particles, the paraffin must to be removed.

Methods

Synthesis of CNOs

CNOs were prepared by a modified Hummer's Method using concentrated H_2SO_4 and six times the amount needed of $KMnO_4$ to oxidize the CNOs (14). This mixture was left for 4 days at a temperature of 50°C. After 4 days, the mixture was dispersed in 80 mL of deionized water and 3 mL of 35% H_2O_2, heated to boiling. Finally, it was centrifuged several times to obtain the CNOs completely dispersed in water.

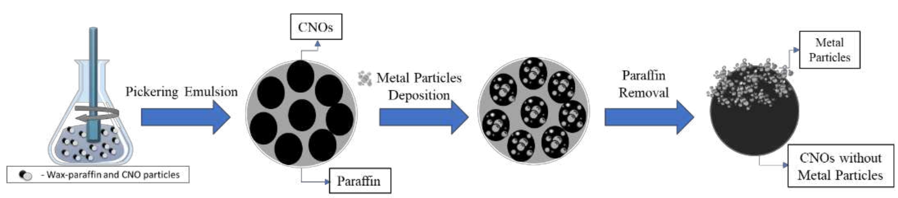

Figure 1 – Scheme of the Pickering emulsion and paraffin removal process.

Pickering Emulsion and Paraffin Removal

The Pickering emulsion process was carried out using a relationship of 5:1 paraffin wax and CNOs. Then dispersed in 0.1 M of H_2SO_4. This solution was homogenized for 5 minutes at 12,000 rpm in a water bath at 60 °C to finally obtain the wax-paraffin/CNO particles. The paraffin removal was carried out by dispersing 1 g of the particles in 4 mL of chloroform and heated in a water bath at 60°C for 30 minutes. Then, the slurry was centrifuged for 45 minutes to remove the chloroform with the paraffin dissolved. Finally, the solution was rinsed and sonicated in isopropanol to remove the remains of chloroform in the particles. A scheme of the Pickering emulsion process and paraffin removal is shown in Figure 1.

Characterization Techniques

X-ray diffraction (XRD) Rigaku SmartLab was used to identify changes in the crystalline structure that indicate complete paraffin removal. On the other hand, Raman Spectroscopy was also used to observe changes in the structure of CNOs. Scanning Electron Microscopy (SEM) JEOL JSM-6010LA was used to know the changes in the morphology of the particles in the paraffin removal process. Raman spectroscopy was done using a DXR 3 Raman imaging microscope from ThermoFisher Scientific.

Results and Discussion

SEM images of Wax/CNOs particles

SEM images were obtained to confirm the Pickering emulsion process was carried out. In Figure 2, we can see the image of the synthesized CNOs and the image of the particles formed from paraffin and CNOs. In Figure 2(left) it can be seen the morphology of the CNOs after drying, given that even though it is a powder, as it dries they agglomerate into what has the appearance of films. The particles in Figure 2 (right) shows the Paraffin/CNOs. As the emulsion process is carried out, we cannot appreciate the presence of the CNOs in SEM because of their size as well as due to the fact that paraffin forms spheres where CNOs attach. On the other hand, it can be seen in the SEM images that the paraffin spheres are not charging negatively as much as is typically seen in materials such as paraffin because of the conductivity of the CNOs on their surface that allows electrons to flow to ground. During the Pickering emulsion process, the homogenization of the paraffin together with the amphiphilic behaviour of the oxidized CNOs created these particles that can be seen with a spherical morphology. During the emulsion process, given that the CNOs have zones that are oxidized and areas where the the graphite is pristine, CNOs have the property of interacting with both hydrophobic and hydrophilic liquids (melted paraffin/water) acting as a surfactant and allowing the formation of these small wax particles. While areas that are less oxidized will turn to the paraffin, areas that are more oxidized will prefer to be exposed to water facilitating the process of metal deposition or any other modification (3,13).

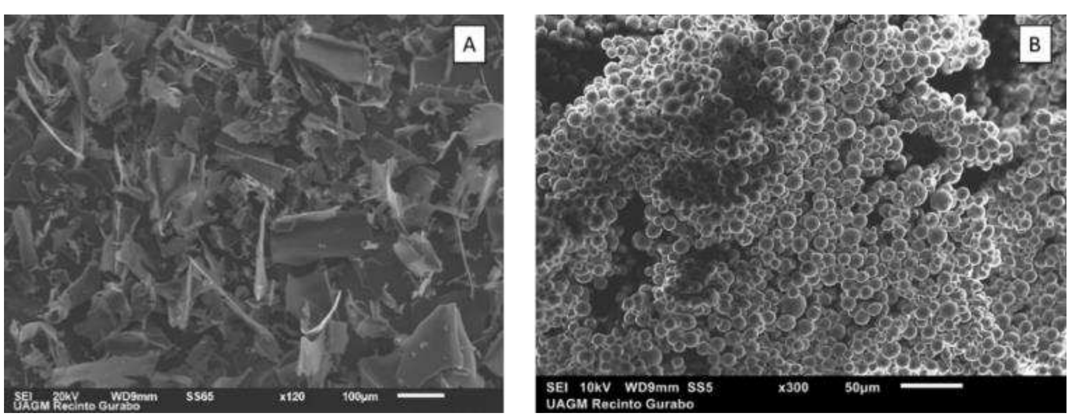

Figure 2 – SEM images of CNOs synthetized (Left) and after the Pickering emulsion process (Right).

On the other hand, Figure 3 shows the morphology of the nanoparticles after the different chloroform treatments that were carried out to remove paraffin from the Janus particles. The paraffin removal process ranged from two chloroform treatments and increasing them to six. When characterizing these samples, we observed significant changes in the morphology of the particles. The first characteristic that can be noticed is the presence of layers of agglomerated CNOs that can be identified unlinke in Figure 2 (right) where the presence of CNOs was not appreciated due to the formation of the paraffin spheres. In the three SEM images shown in Figure 3, the layers of agglomerated CNOs can be seen. As the number of chloroform treatments for paraffin removal increased, the morphology changed greatly. In Figure 3A, it can be seen that there were still paraffin residues which indicated that with only two chloroform treatments it was not enough to be able to remove paraffin effectively. This was also observed due to the charging in some areas of the sample, which did not have spherical morphology due to chloroform dissolving the paraffin. However, by increasing the number of chloroform treatments it can be seen that the material looks much cleaner compared to the first two treatments. In Figure 3B, layers of CNOs are seen after the removal process that includes four treatments with chloroform. In some of the areas of the image, charging can still be seen while much lower than Figure 3A. Finally, in Figure 3C, a completely different structure can be seen after the removal process that was comprised of six chloroform treatments. Differently from the other treatments, layers with holes were easily observed in this sample. The size of the holes is about 10 µm diameter, which is similar to the size of paraffin particles seen in Figure 2.

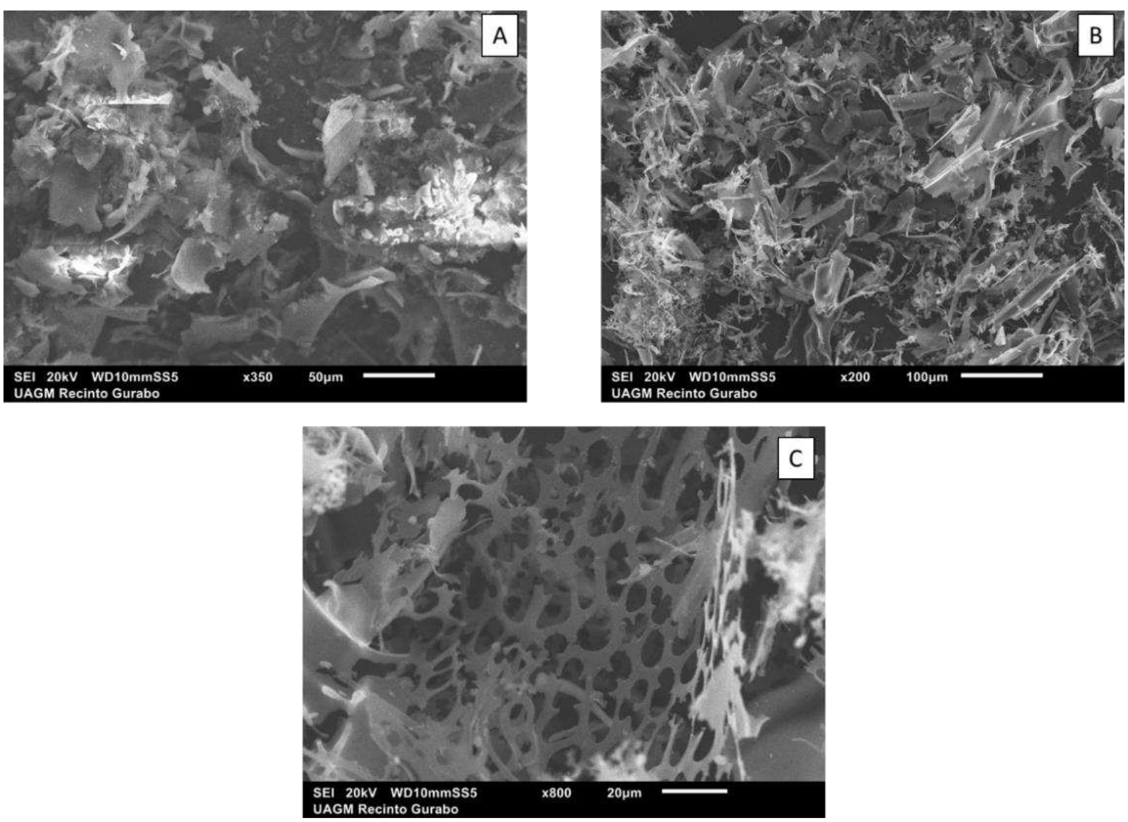

Figure 3 – SEM Images of three process of paraffin removal. (A) 2 treatments of chloroform, (B) 4 treatments of chloroform, and (C) 6 treatments of chloroform.

Physical Characterization after Paraffin Removal

After surface modification, paraffin must be removed to finally obtain the amphiphilic particle (4). The paraffin is only needed to cover one side of the CNOs and allow the deposition of metal nanoparticles or other surface modifications to take place on the exposed side of the CNOs. For this reason, a preparatory paraffin removal process was initiated to ensure that the paraffin has been completely removed and will not serve as an obstacle in creating the Janus nanoparticle. To corroborate that the paraffin can be efficiently removed, it was tested to remove the paraffin from the CNOs before any surface modification in order to optimize a protocol to be used after the modification of the surface. The diffractogram of the CNOs was used as a standard to be able to determine that it was possible to remove paraffin completely due to the high peaks produced by the cristallites formed when paraffin solidifies. XRD characterizations can be seen in Figure 4. Using this technique, changes in the crystalline structure of CNOs were studied.

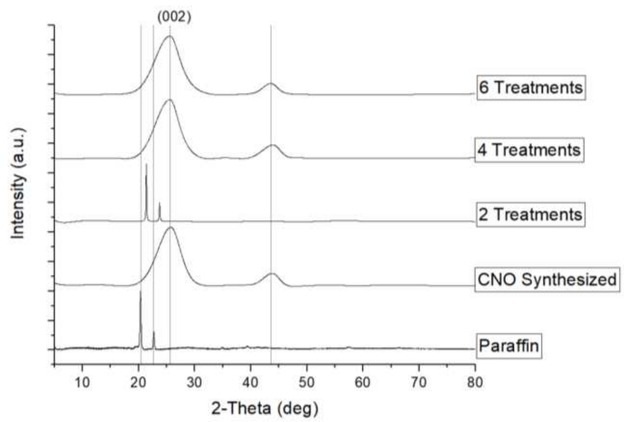

Figure 4 – X-ray diffractograms of paraffin, CNOs, and paraffin/CNOs after paraffin removal with two, four, and six treatments with chloroform.

The diffractograms showed the different treatments that were performed to remove paraffin comparing to the diffractograms of CNOs and paraffin to confirm its elimination. In Figure 4, we can see the comparison between the diffractogram of the paraffin, CNOs, and the paraffin/CNOs samples after two, four, and six paraffin removal treatments. By observing the diffractograms in detail, the characteristic peaks of paraffin at ~20.4° and ~22.7° can be seen in the same position as those in the sample after two removal processes. Comparing the diffractograms of the samples with the CNOs and paraffin, it can be confirmed that two treatments with chloroform is not enough to remove paraffin since the sample presented the diffractogram similar to that of paraffin. However, the diffractogram of the sample with four chloroform treatments and six treatments showed to be similar to the diffractogram of CNOs. In the diffractograms, it can seen that the characteristic peaks appear at ~25.7° and ~43.6° that describe the crystalline structure of the CNOs. The peak at ~25.7° corresponds to the basal atomic planes (002) and it is wider because of the much smaller crystallite size of the CNOs compared to paraffin as was also seen in Figure 4 (10). XRD results confirmed that four chloroform treatments can efficiently remove paraffin. Moreover, a paraffin removal process with six chloroform treatments was also done in order to compare the process between four and six treatments to ensure the cleanliness of the sample with regard to paraffin removal. The sample of paraffin/CNOs after four and six treatments showed the same diffractogram implying that both samples had the paraffin removed.

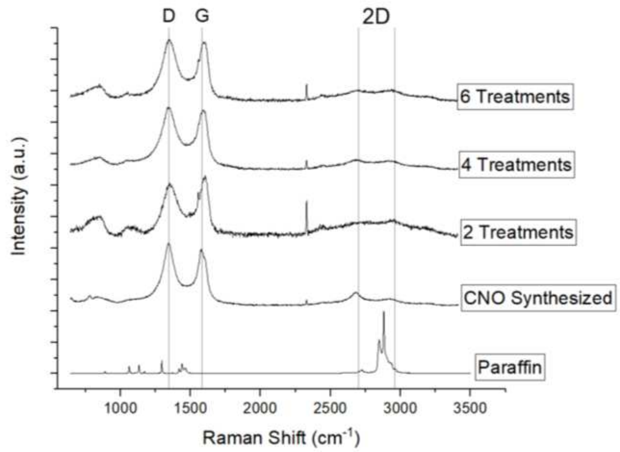

Figure 5 – Raman spectra of paraffin, CNOs, and paraffin/CNOs after paraffin removal with two, four, and six treatments with chloroform.

In order to further study the changes in the structure of CNOs in the paraffin removal process, Raman spectroscopy characterizations were performed. Figure 5 shows the Raman spectra of the samples and the comparison between them with the paraffin and CNOs spectra. The paraffin Raman spectrum can be seen with the characteristic peaks and the main peaks at ~2,850 cm^{-1} and ~2,890 cm^{-1}. These peaks represent the "stretching" vibrations of the methylene groups in the paraffin carbon chain (12). After two chloroform treatments, it can be seen that a peak can be seen at ~1,350cm^{-1} (D peak) which is suppressed compared to the G peak at ~1,580cm^{-1} when shown together with the Raman spectrum of CNOs. This may be because the order of the sp^3 bonds is lower which may indicate that there was no major rupture of the sp^2 bonds and minor defect of the graphitic structure (10). However, the spectra of four and six treatments showed that, as the paraffin removal treatments increase, peak D increases while peak G decreases. Therefore, spectra after four and six treatments look similar to the Raman spectrum of CNOs before the paraffin/CNOs sample preparation.

Conclusion

The paraffin removal process is crucial to create amphiphilic particles when using this strategy for the fabrication of Janus particles. Paraffin is necessary to carry out the Pickering process but it must be removed efficiently to obtain the Janus nanoparticles. The results obtained by XRD confirmed the efficient paraffin removal with at least four chloroform treatments. However, SEM imaging characterizations show that chloroform treatments can drastically change their morphology with thinner layers of CNOs. On the other hand, Raman spectra showed that as chloroform treatments increased, the ratio of D to G peaks is increased. These results suggest that the changes in the disorders and defects of the carbon structure of the CNOs are minimal. The next step is to perform the procedure of deposition or modification of the CNOs and apply the treatment presented to create the amphiphilic particle. In this way, we can study in detail its structure, morphology, and initiate experiments that allow us to study their catalytic activity. This detailed preparatory paraffin removal process will be fundamental for future research into producing Janus nanoparticles as fuel cell catalysts.

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