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SYNTHESIS AND CHARACTERIZATION OF PLATINUM NANOCOMPOSITES

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ABSTRACT

This work related to fabrication of platinum nano particles, reveals considerably outstanding catalytic and electrical properties and preparation of Pt- PS nano composite. For this study Pt nano particles were synthesized by wet chemical method. Pt particles with 0.25%, 0.5%, 1% and 2% concentration amounts were added into the polystyrene solution, acquired by recycled PS. Three different composites which possess a distinct percentage of platinum were produced. Fibers were fabricated by electro spinning method afterward. Pt particles which were produced by wet chemical method and fibers were analyzed by SEM-EDS. There were various test and measurement methods performed to determine the characteristics of the platinum nano composite.

Keywords: Platinum, Nanocomposites, Electro spinning, Fibers

1. INTRODUCTION

Nanotechnology, products called "Advanced Functional Materials" are developed which have a high surface area and exhibit unusual properties that differ from their initial characteristics. [1]

Precious metals, especially Platinum, are the most suitable metal to be used as a catalyst because of its properties. [2] Platinum is a member of the noble metals which are commonly used as catalysts. [3, 4] In particular, platinum is important in many applications because of their extraordinary physical and chemical features that have high surface area, low density, and usable nano scale inner space. [5] Additionally, Pt is one of the least reactive metals, with resistance high temperature and corrosion, dense, malleable and ductile. Pt is generally subject to wet chemical method, [6] which mostly applies with aqua regia solution in order to making the solution process. After the process, precipitation of the Pt powder can be obtained by several methods. [7] However, in partially ammonium chloride is used to precipitate the platinum. Moreover, hydrazine hydrate, potassium chloride and some patented chemical material precipitate platinum as a platinum powder. In this work, nano scale platinum powders were produced by dissolving method aqua regia. Thus, bulk metal transformed to nano size metal powders in order to enhance its potential and applications. [8] By using platinum in the nano size, we will reduce the cost in proportion to the amount of precious metal platinum used by this project. [9]

Electro spinning is a practical approach to produce very unique fibers which possess down to the nano scale. [10] To obtain nano size fiber, electro spinning is one of the most versatile methods. [11] Also, different types of fibers which are composed of either polymer or synthetic, organic-inorganic materials can be produced. [9] In the electrospray process, electric current is applied to the droplet of the polymer solution suspended at the end of a needle attached to a syringe or at the end of the ports. [12] The electrode is either immersed in the polymer solution or connected to the ends of the capillaries.

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In this work, recycled PS was used as a polymer source to produce fiber. Platinum sheet were transformed to platinum nano powders by wet chemical method. Platinum nano composites by electro spinning technology were fabricated within the scope of this project, and platinum nano composites were obtained by mixing platinum nano powder and recycled polystyrene.

2. EXPERIMENTAL

2.1. Materials

In order to fabricate platinum metal powder we used a pure platin sheet (from the exchange bank in Istanbul, Turkey) which included one gram, HCl (hydrochloric acid, Sigma Aldrich Chemical Co) and HNO_3 (nitric acid, Sigma Aldrich Chemical Co) used to dissolve platinum. Additionally, NaOH (from Merck) was used to adjust the pH of the solution, Hydrazine hydrate (from Merck) to precipitate the metal. Also, a foam polystyrene (PS) plate that ensured laboratory equipment from ICU Nanotechnology Lab, synthesized polymer solution, DMF (dimethylformamide, from Merck) solvent to dissolve the polymer were used to fabricate polymer solution. The solutions were directly used for the electro spinning process and machine (NE200 Electro spinning Device, purchased by Inovensa in Istanbul, Turkey). All chemicals were of analytical grade and were used without further purification.

2.2. Producing Hexachloroplatinic Acid

Platinum sheet, which is approximately 0.987g, was purchased from the exchange bank. The sheet was rolled to increase the surface area. Then the platinum sheet was put inside the 500 ml beaker and HCl and HNO_3 acids, which are called aqua regia, were added in the beaker. This experiment uses highly corrosive chemicals and produces toxic gases. Thus, we performed the process with gloves in a fume hood (purchased from Green Lab. Equipment in Istanbul, Turkey) Firstly, 40 ml of HCl and also 10 ml of HNO_3 were added on the platinum sheet under the fume hood. As soon as pouring the solutions, the chemical reaction showed up and then the color of the solution turned from white to orange while platinum metal was being dissolved. The reaction occurred as soon as the platinum added into the solution even at the room temperature, yet increasing of the temperature reaction is faster than the room temperature. Beaker was put on the magnetic heater (from MSH20D DAIHAN Scientific) and magnetic stirrer bar was also stirred to the solution in order to accelerate the reaction.

The reaction happened when the platinum is reacting with nitric acid to produce platinum ions. The following reactions occurred:

$$Pt + 4HNO_3 + 4H^+ \rightarrow Pt4^+ + 4NO_2 + 4H_2O$$
$$Pt^{4+} + 6HCl \rightarrow H2PtCl6 + 4H^+$$
$$Pt + 4HNO_3 + 6HCl \rightarrow H2PtCl6 + 4NO_2 + 4H_2O$$

Finally, the overall reactions produce hexachloroplatinic acid, also known as a chloroplatinic acid.

2.3. Precipitation of Platinum Powder

After dissolving, the pH of the solution was brought to 2 with caustic solution (NaOH, Merck), the concentration of caustic solution may be 10 M. After the pH adjustment was made, 10 ml of hydrazine hydrate was added and the solution was heated to constant temperature (60° C) for 15 minutes to yield blackish Pt powder. The hydrazine addition should have at least a 500-1000 ml beaker, for the possibility of overfilling the solution. After filtration, filtration is carried out and powdered platinum was obtained. Filtration can be done with Sartorius filter paper; do not leave ashes during the drying process.

When we added the hydrazine hydrate, the color of the solution which obtains platinum powder turned from orange to grey. This reaction of the solution and hydrazine hydrate took very little time. After adding the desirable amount of hydrazine, platinum begun to precipitate. After the precipitation process begun, the magnetic heater was turned off and waited over a night in order to precipitate the platinum completely. A result of the waiting overnight, platinum powders separated absolutely from the solution and precipitated under the solution. Filtration process was applied with the filtration paper afterward. As a result of the long drying step, we totally dried powder on the heater when heated about 70°C. The dried powders were grounded with a mortar and pestle in order to obtain smaller particles.

2.4. Preparation of the PS/Pt Nanocomposites

Besides all, PS (polystyrene) plate particles were initially dissolved in dimethylformamide (DMF) and pure PS solution was obtained. It was then stirred for 1 hour using a magnetic stirrer in order to obtain a homogeneous polymer solution. After that, the dried platinum particles were added in to this polymeric solution in proportion to 0.25%, 0.5%, 1% and 2% of the all weight, respectively. Then, combination of the platinum and polymer solution was mixed by using a magnetic stirrer during one day at the magnetic heater with 1000 RPM and at 30°C. Finally, PS/Pt composites which have a black color were ready to place into the electro spinning machine. As shown in the Table 1. when DMF is constant for each composites, Pt and PS amounts are inversely proportional to each other.

Table 1. Composition of PS/Pt Nanocomposites

Composition	Composite 1	Composite 2	Composite 3	Composite 4
DMF (wt %)	80	80	80	80
PS (wt %)	19.95	19.9	19.8	19.6
Pt contents (wt %)	0.05	0.1	0.2	0.4

2.5. Electro Spinning

In the electrospinning process, an electric current is applied to the droplet of the polymer solution suspended at the end of a needle attached to a syringe or at the end of the ports. Prepared platinum-polymer composites were poured inside of the 10 ml syringes, respectively. Then the syringe was placed in the Inovensa Electro spinning Machine. Indeed, all working steps for the electro spinning machine are the same except for the spinning parameters which mostly possess special features for every composites and solutions. For example: spinning parameters for the 1% platinum composite: Distance between the needle and collector was 30 cm, the DC voltage was 25 kV and the pump speed of the electro spinning was 2 ml /hour.

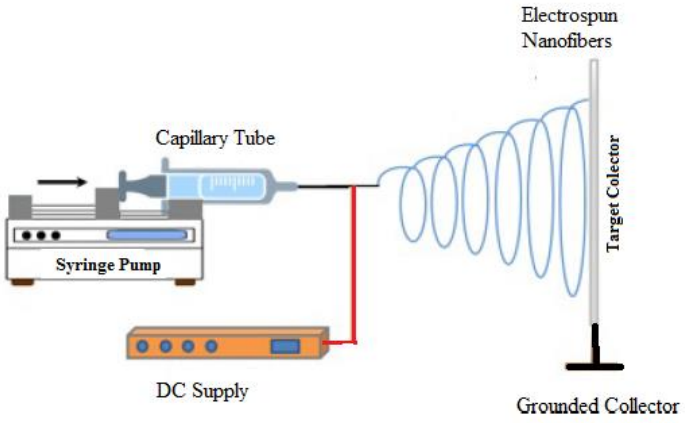

Figure 1. Schematic illustration of electro spinning process [13]

3. RESULTS

3.1. Observation of the Morphology of the Platinum Nano Powders

The morphology of the Pt nano powders were observed by using a Scanning Electron Microscopy (SEM, ZEISS SIGMA at Yıldız Technical University Center Lab, Istanbul) with 50.00kx magnification SEM-EDS results were also demonstrated in order to demonstrate the purification of platinum.

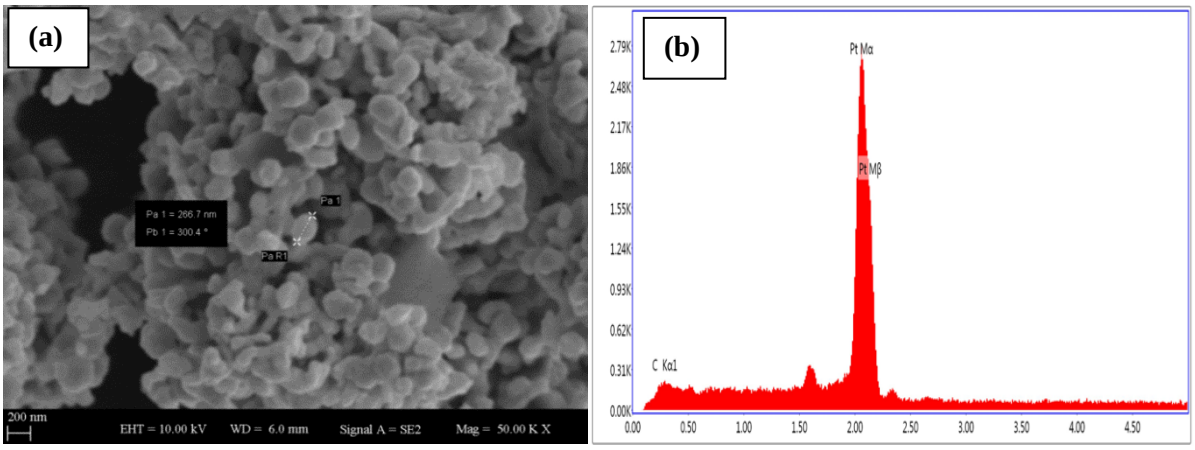

Figure 2. (a) Morphology of platinum nanopowders by SEM. **(b)** Elemental analyze of platinum nanopowders by SEM-EDS.

As shown in the Figure 2. (a) and (b) the diameter of platinum powders were measured about 200 nm and only platinum pick demonstrated that pure platinum powders were synthesized under the laboratory conditions. These obtained platinum nano powders were used to produce nanocomposite after the platinum precipitation step. Because of the heating of the nanopowder in order to remove residual impurity, heating caused agglomeration as shown in the Figure 2a.

3.2. Observation of the Morphology of the Nanocomposites

Nanocomposites surfaces were coated with Au-Pd in order to ensure the conductive surface and the morphologies of the PS/Pt nanocomposites were observed by using Scanning Electron Microscopy (SEM, ZEISS SIGMA at Yıldız Technical University Center Lab, Istanbul). SEM-EDS results were also demonstrated in order to observe chemical composition of the composites.

As shown in the Figure 5. average fiber diameter of Pt nanofibers were calculated 975 nm that measured by Image J software. Platinum nanopowders, which were coated on the fibers, were demonstrated SEM images in Figure 3. Also, morphology of PS/Pt nanocomposites with different amounts of platinum (a) 0.25% Pt; (b) 0,5% Pt; (c) 1% Pt and (d) 2% Pt were denoted, respectively.

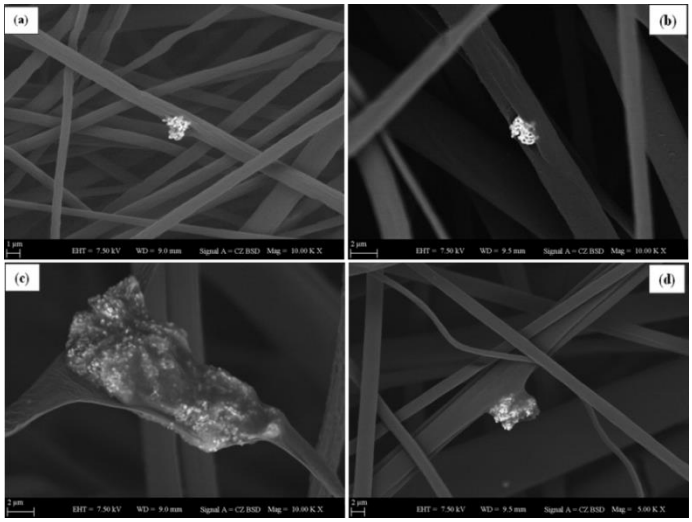

Figure 3. Morphology of PS/Pt nanocomposites by SEM. Description of different amounts of platinum (a) 0.25% Pt; (b) 0,5% Pt; (c) 1% Pt and (d) 2% Pt, respectively.

The %0.5 PS/Pt fibers are demonstrated in Figure 3. (b) by SEM image. Also, added platinum powders embedded in the fibers and metal powders coated by fiber's wall are shown Figure 3. (c). All figures were observed with 10.000K X magnification, except Figure 3. (d) Which possesses 5.00 K X magnification.

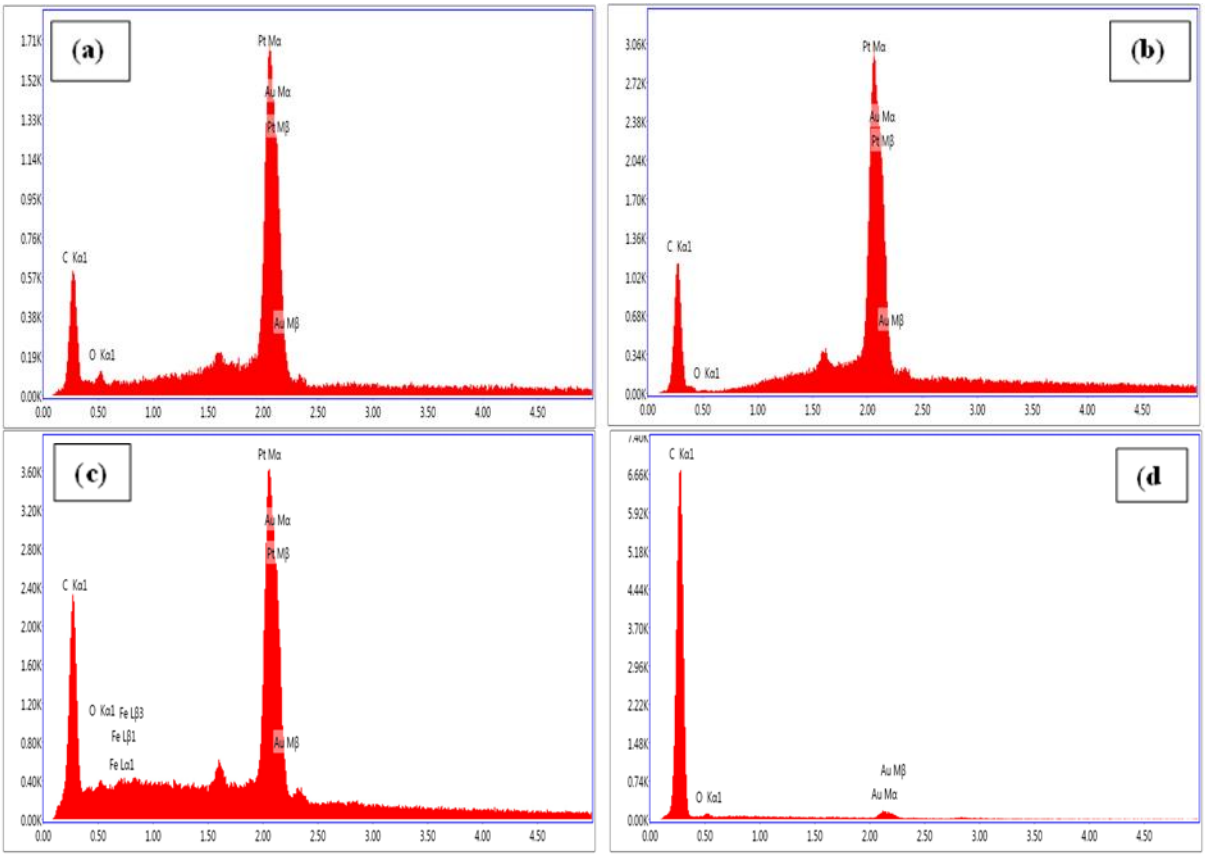

Figure 4. SEM-EDS results of PS/Pt nanocomposites and pure PS (a), (b) and (c) are 0.25% Pt, 0.5% Pt and 1% **Pt**, respectively and (d) pure PS result.

For the SEM-EDS calculations, both of four PS/Pt composites and pure PS composite were measured to demonstrate the difference between ratios of the chemical compositions. According to SEM-EDS results, pure PS has only C element picks but PS/Pt composites possess different amounts of platinum and carbon picks to depend on their retained platinum quantity as show in the Figure 4.

4. DISSCUSSION

Platinum powders were successfully added in the fibers and PS/Pt nanofibers were fabricated and tested via SEM and SEM-EDS methods. Pure platinum powders were demonstrated based on the SEM-EDS analysis. Composite samples coated with Au were used to analyze by SEM. Error bars were calculated according to standard deviations of fibers as shown in Figure 5.

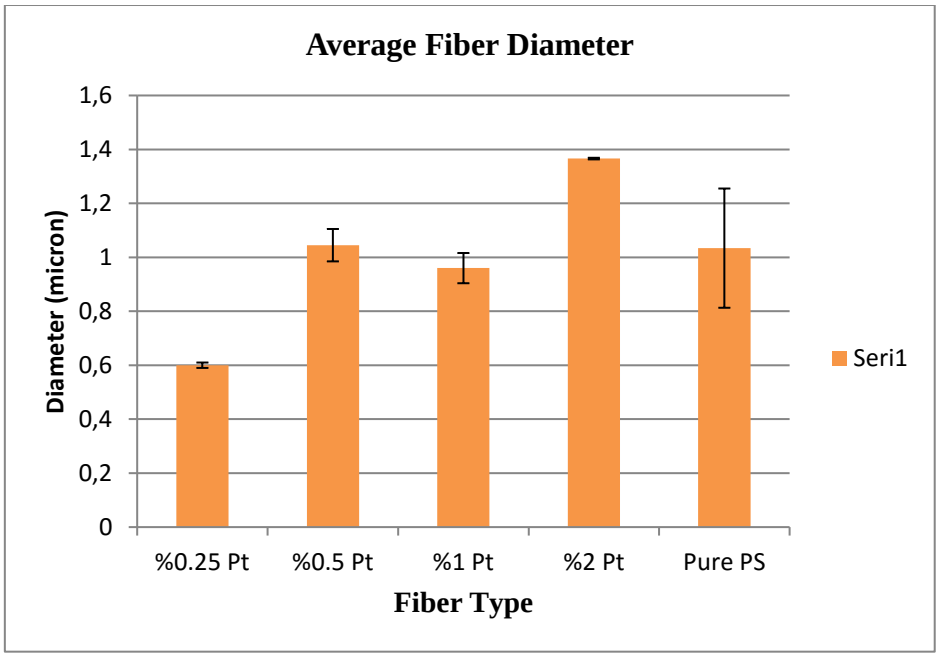

Figure 5. Average fiber diameters of the fibers with error bars.

According to Figure 5, the smallest fiber diameter was observed from the 0.25% Pt/PS nanofiber. When the amount of platinum powders increased, fiber diameters generally were increased. Furthermore, 2% Pt loaded fiber possesses the highest fiber diameter.

Also in Figure 2. certain results would be observed that platinum powders were agglomerated because of the high temperature purification step. Nevertheless, platinum metal was succeeded to synthesize as a nano size.

5. CONCLUSION

Nano platinum powders were produced from the pure platinum sheet after the dissolving and precipitating steps. Platinum powders were subjected to SEM and SEM-EDS analyses in order to demonstrate the size and purification of the powders. Platinum loaded nanofibers were succesfully fabricated by using an electro spinning machine. Moreover, the results revealed that platinum nano powders were coated by the fibers. Because of the platinum powder agglomeration, some powders were embedded inside the fibers.

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