

(19)



LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie

(11)

N° de publication :

LU501479

(12)

BREVET D'INVENTION**B1**

(21)

N° de dépôt: LU501479

(51)

Int. Cl.:

H01M 4/90, H01M 8/16

(22)

Date de dépôt: 15/02/2022

(30)

Priorité:

(72)

Inventeur(s):

YAO Juanjuan - Chine, FU Guokai - Chine, CHANG Ruiting - Chine, BAI Yun - Chine, ZHA Zhengtai - Chine, SHI Xueping - Chine, CAI Fangfang - Chine, ZHANG Zhi - Chine, YUAN Zhang - Chine, ZHOU Yuanhang - Chine, ZHOU Yingying - Chine, HU Xueli - Chine, CHEN Shihao - Chine, ZHOU Shun - Chine

(43)

Date de mise à disposition du public: 16/08/2022

(47)

Date de délivrance: 16/08/2022

(73)

Titulaire(s):

CHONGQING UNIVERSITY - 400044 Chongqing city (Chine)

(74)

Mandataire(s):

Patent42 SA - 4081 Esch-sur-Alzette (Luxembourg)

(54)

Preparation method of nitrogen self-doped porous graphite carbon MFCs air cathode catalyst.

(57)

The invention discloses a method of preparing nitrogen self-doped porous graphite carbon MFCs air cathode catalyst. According to the invention, the waste mangosteen peel is used to prepare porous graphite biomass carbon, the nitrogen element contained in the biomass materials is used for doping without adding nitrogen source, combining the activation of KOH and Co²⁺ catalytic graphitization, the preparation process is simple, and the mangosteen peel biomass is successfully converted into a high-performance ORR catalyst for MFCs air cathode.

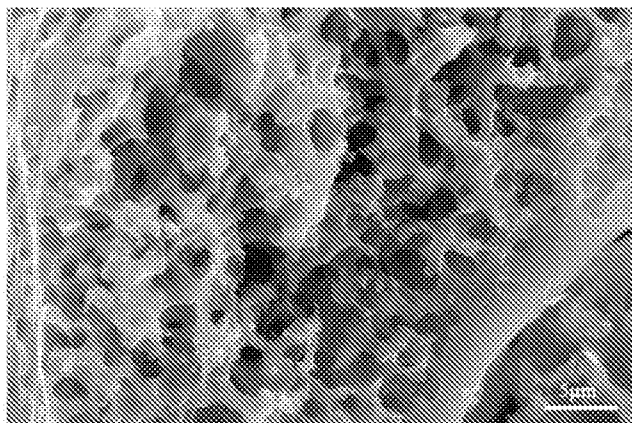


Figure 5

Description

LU501479

Preparation method of nitrogen self-doped porous graphite carbon MFCs air cathode catalyst**TECHNICAL FIELD**

The invention relates to the field of Microbial Fuel Cells (MFCs), in particular to a method of preparing nitrogen self-doped porous graphite carbon MFCs air cathode catalyst.

BACKGROUND

MFCs is a "green" technology that can not only treat wastewater organics but also generate electricity, which is of great significance for sustainable and new energy development field.

Air cathode MFCs is one of the important research directions of MFCs because of its simple structure and low cost. However, the existing air cathode MFCs have sluggish oxygen reduction reaction (ORR) kinetics process due to the mass transfer resistance of oxygen. Therefore, it is crucial for the large-scale application of MFCs to exploit an ORR catalyst with high efficiency, low cost and excellent stability.

Various ORR catalysts have been widely exploited, Pt based catalysts has high electrocatalytic activity and widely studied and applied as ORR catalysts in MFCs. . While the cost of Pt is high, so it is difficult for large-scale application of air-cathode MFCs Carbon-based catalysts are considered as ideal candidate materials for Pt-based catalysts due to their cheap, large surface area, reasonable electrocatalytic activity, and easy preparation.

The specific surface area and pore structure of carbon-based catalyst are important factors that affect the performance of ORR. Carbon-based materials are usually activated by chemical activators to obtain porous structures with high specific surface area, but adding the chemical activators will damage the graphitization degree of materials, thus weakening the electrical conductivity, several methods for preparing porous graphite carbon materials have been recorded, such as the sacrificial template method using silica or surfactant, however, this method needs expensive precursor materials and the preparation process is complicated, so it is difficult for large-scale application of ORR catalysts.

Biomass, as precursors of carbon-based materials, low-cost and plentiful. Its unique natural structure and abundant element composition including oxygen, nitrogen, and other elements play an important role in the synthesis of carbon materials.

Therefore, it is important to propose a low-cost and environmentally friendly way of preparing appropriate porous structure and high graphitization degree carbon materials from natural biomass, and used them as ORR catalysts for MFCs field. LP501479

SUMMARY

The objective of the present invention is to overcome the above problems, and propose a strategy of synthesizing nitrogen self-doped porous graphite carbon with low cost and high efficiency by using mangosteen peel as carbon source and nitrogen source, coupled with KOH activation and Co^{2+} catalytic graphitization.

The technical scheme disclosed by the invention is as follows:

the method of preparing nitrogen self-doped porous graphite carbon MFCs air cathode catalyst comprises the following steps:

S1, repeatedly washing mangosteen peel with deionized water, drying at 100-120°C, and crushing the dried mangosteen peel into powder to obtain product A;

S2, heating the product A to 400°C at a heating rate of 5-8°C/min under the protection of nitrogen, then pyrolyzing for 2-3 hours to obtain a dark black product, and grinding the dark black product to obtain product B;

S3, adding product B into CoCl_2 aqueous solution, soaking for 6-10h under stirring condition, then separating solid phase from liquid, drying, adding the solid phase into KOH solution, reacting for 6-10h under stirring condition, separating the solid phase again, and drying it to obtain product C;

S4, heating the product C to 600-850°C at a heating rate of 5-8°C/min under the protection of nitrogen, and then calcining for 2-3 hours to obtain a black product D;

S5, immersing the product D in HCl solution to react for 8-12 hours, then separating the solid phase, repeatedly washing with deionized water to neutrality, and drying to obtain nitrogen self-doped porous graphite carbon.

As an improvement, the drying step in S1 is carried out in an oven for 10-12 hours.

As an improvement, the concentration of CoCl_2 aqueous solution in S3 is 0.05mol/L, and the mass ratio of product B to CoCl_2 is 1:1-2:1.

As an improvement, the concentration of KOH solution in S3 is 0.1g/mL, and the mass ratio of product B to KOH is 1:1-1:2.

As an improvement, the product washed to neutrality by deionized water in S5 is dried at 60-80°C for 10-12 hours. bU501479

The invention has the following advantages:

According to the invention, the waste mangosteen peel is used to prepare porous graphite biomass carbon, the nitrogen element contained in the biomass materials is used for doping without adding additional nitrogen source, coupled with the KOH activation and Co^{2+} catalytic graphitization, the preparation process is simple, and the mangosteen peel is successfully converted into a high-performance ORR catalyst for MFCs air cathode.

BRIEF DESCRIPTION OF THE FIGURES

Fig. 1 is a 5 μm electron micrograph of embodiment 1 of the present invention;
 Fig. 2 is a 5 μm electron micrograph of embodiment 2 of the present invention;
 Fig. 3 is a 5 μm electron micrograph of embodiment 3 of the present invention;
 Fig. 4 is a 2 μm electron micrograph of embodiment 4 of the present invention;
 Fig. 5 is a 5 μm electron micrograph of embodiment 4 of the present invention;
 Fig. 6 is a 5 μm electron micrograph of embodiment 5 of the present invention;
 Fig. 7 is an XPS full spectrum diagram of embodiments 1-5 of the present invention;
 Fig. 8 is the nitrogen adsorption-desorption isotherm of embodiments 1-5 of the present invention;
 Fig. 9 is a power density and polarization curve of embodiments 1-5 of the present invention;
 Fig. 10 is a Raman curve of embodiments 1-5 of the present invention.

DESCRIPTION OF THE INVENTION

Next, the invention will be further explained with specific embodiments. It should be understood that the embodiments of the present invention are only used to illustrate the present invention and not to limit the scope of the present invention. In addition, after reading the content of the present invention, those skilled in the art can make changes or modifications to the present invention, and the equivalent forms also fall within the scope defined by the claims of this application.

Embodiment 1

This embodiment discloses a method of preparing nitrogen self-doped porous graphite carbon MFCs air cathode catalyst, which comprises the following steps:

S1, repeatedly washing mangosteen peel with deionized water, drying at 100°C for 12 hours,^{LU501479} and crushing the dried mangosteen peel into powder to obtain product A;

S2, putting the product A into a tube furnace, gradually raising the temperature to 400°C at a heating rate of 5°C/min under the protection of nitrogen, then pyrolyzing for 2 hours to obtain a dark black product, and grinding to obtain product B;

S3, adding 10g of product B into 200mL of 0.05mol/L CoCl_2 aqueous solution, soaking for 8h under the condition of magnetic stirring, then separating solid phase from liquid, drying in an oven at 60°C, adding 200ml of KOH solution with a concentration of 0.1g/mL, soaking for 8h under stirring, separating the solid phase again, and drying to obtain product C;

S4, putting the product C into a tube furnace, heating to 600°C at a heating rate of 5°C/min under the protection of nitrogen, and then calcining for 1 hour to obtain a black product D;

S5, immersing the product D in HCl solution for 8 hours, then performing solid-liquid separation by suction filtration, repeatedly washing with deionized water until the solution is neutral, drying at 70°C for 12 hours, and then obtaining nitrogen self-doped porous graphite carbon.

Embodiment 2

This embodiment discloses a method of preparing nitrogen self-doped porous graphite carbon MFCs air cathode catalyst, which comprises the following steps:

S1, repeatedly washing mangosteen peel with deionized water, drying at 100°C for 12 hours, and crushing the dried mangosteen peel into powder to obtain product A;

S2, putting the product A into a tube furnace, gradually raising the temperature to 400°C at a heating rate of 5°C/min under the protection of nitrogen, then pyrolyzing for 2 hours to obtain a dark black product, and grinding to obtain product B;

S3, adding 10g of product B into 200mL of 0.05mol/L CoCl_2 aqueous solution, soaking for 8h under the condition of magnetic stirring, then separating solid phase from liquid, drying in an oven at 60°C, adding 200ml of KOH solution with a concentration of 0.1g/mL, soaking for 8h under stirring, separating the solid phase again, and drying to obtain product C;

S4, putting the product C into a tube furnace, heating to 700°C at a heating rate of 5°C/min under the protection of nitrogen, and then calcining for 2 hours to obtain a black product D;

S5, immersing the product D in HCl solution for 8 hours, then performing solid-liquid separation by suction filtration, repeatedly washing with deionized water until the solution is

neutral, drying at 70°C for 12 hours, and then obtaining nitrogen self-doped porous graphite carbon. LU501479

Embodiment 3

This embodiment discloses a method of preparing nitrogen self-doped porous graphite carbon MFCs air cathode catalyst, which comprises the following steps:

S1, repeatedly washing mangosteen peel with deionized water, drying at 100°C for 12 hours, and crushing the dried mangosteen peel into powder to obtain product A;

S2, putting the product A into a tube furnace, gradually raising the temperature to 400°C at a heating rate of 5°C/min under the protection of nitrogen, then pyrolyzing for 2 hours to obtain a dark black product, and grinding to obtain product B;

S3, adding 10g of product B into 200mL of 0.05mol/L CoCl_2 aqueous solution, soaking for 8h under the condition of magnetic stirring, then separating solid phase from liquid, drying in an oven at 60°C, adding 200ml of KOH solution with a concentration of 0.1g/mL, soaking for 8h under stirring, separating the solid phase again, and drying to obtain product C;

S4, putting the product C into a tube furnace, heating to 750°C at a heating rate of 5°C/min under the protection of nitrogen, and then calcining for 2 hours to obtain a black product D;

S5, immersing the product D in HCl solution for 8 hours, then performing solid-liquid separation by suction filtration, repeatedly washing with deionized water until the solution is neutral, drying at 70°C for 12 hours, and then obtaining nitrogen self-doped porous graphite carbon.

Embodiment 4

This embodiment discloses a method of preparing nitrogen self-doped porous graphite carbon MFCs air cathode catalyst, which comprises the following steps:

S1, repeatedly washing mangosteen peel with deionized water, drying at 100°C for 12 hours, and crushing the dried mangosteen peel into powder to obtain product A;

S2, putting the product A into a tube furnace, gradually raising the temperature to 400°C at a heating rate of 5°C/min under the protection of nitrogen, then pyrolyzing for 2 hours to obtain a dark black product, and grinding to obtain product B;

S3, adding 10g of product B into 200mL of 0.05mol/L CoCl_2 aqueous solution, soaking for 8h under the condition of magnetic stirring, then separating solid phase from liquid, drying in an oven at 60°C, adding 200ml of KOH solution with a concentration of 0.1g/mL, soaking for 8h under stirring, separating the solid phase again, and drying to obtain product C;

S4, putting the product C into a tube furnace, heating to 800°C at a heating rate of 5°C/min^{LU501479} under the protection of nitrogen, and then calcining for 2 hours to obtain a black product D;

S5, immersing the product D in HCl solution for 8 hours, then performing solid-liquid separation by suction filtration, repeatedly washing with deionized water until the solution is neutral, drying at 70°C for 12 hours, and then obtaining nitrogen self-doped porous graphite carbon.

Embodiment 5

This embodiment discloses a method of preparing nitrogen self-doped porous graphite carbon MFCs air cathode catalyst, which comprises the following steps:

S1, repeatedly washing mangosteen peel with deionized water, drying at 100°C for 12 hours, and crushing the dried mangosteen peel into powder to obtain product A;

S2, putting the product A into a tube furnace, gradually raising the temperature to 400°C at a heating rate of 5°C/min under the protection of nitrogen, then pyrolyzing for 2 hours to obtain a dark black product, and grinding to obtain product B;

S3, adding 10g of product B into 200 mL of 0.05mol/L CoCl_2 aqueous solution, soaking for 8h under the condition of magnetic stirring, then separating solid phase from liquid, drying in an oven at 60°C, adding 200 ml of KOH solution with a concentration of 0.1g/mL, soaking for 8h under stirring, separating the solid phase again, and drying to obtain product C;

S4, putting the product C into a tube furnace, heating to 850°C at a heating rate of 5°C/min under the protection of nitrogen, and then calcining for 2 hours to obtain a black product D;

S5, immersing the product D in HCl solution for 8 hours, then performing solid-liquid separation by suction filtration, repeatedly washing with deionized water until the solution is neutral, drying at 70°C for 12 hours, and then obtaining nitrogen self-doped porous graphite carbon.

According to Figures 1-6, the material calcined at 600°C (embodiment 1) shows a smooth surface, some large holes are formed, and most of its structure is not activated. With the increase of activation temperature, the surface becomes more and more rough and porous, until at 800°C, the material presents a three-dimensional honeycomb-like porous structure with interconnected pores, thus increasing the specific surface area of the material. With the activation temperature further increased to 850°C, the pore structure of the material began to collapse.

According to figure 7, embodiments 1-5 can successfully dope nitrogen into graphite carbon.

According to figure 8, it can be concluded that the same type I isotherm is shown in

embodiment 1 and embodiment 2, which indicates that the material has a large number of microporous structures and limited mesopores and macropores. While in embodiments 3-5, the isotherms of the materials observed at moderate relative pressure ($0.4 < P / P_0 < 0.9$) are type I and type IV, and H4 hysteresis loop appears, which proves the existence of micropore and mesopore structure. At the same time, the adsorption isotherm curve of embodiment 4 shows a slight upward trend at higher relative pressure ($P/P_0 > 0.90$), which corresponds to the existence of macropores, indicating that the material at this activation temperature realizes the coexistence structure of micropores, mesopores and macropores.

According to figure 9, it can be concluded that the power density of MFCs in embodiment 4 is slightly higher than that of Pt catalyst, and other embodiments is lower than that of Pt catalyst.

According to figure 10, in embodiments 1-5, the ratio of D peak to G peak decreases with the increase of activation temperature, and the graphitization degree also increases, and a distinct 2D peak at $\sim 2700 \text{ cm}^{-1}$ was observed in embodiments 3-5, which are typical peaks of graphite carbon.

Based on the above conclusions, it can be concluded that embodiment 4 is the preferred embodiment.

The specific embodiments of the present invention have been described in detail above, but they are only examples, and the present invention is not equivalent to the specific embodiments described above. For those skilled in the field, any equivalent modifications and substitutions of the present invention are also within the scope of the present invention. Therefore, equal changes and modifications made without departing from the spirit and scope of the present invention should be covered within the scope of the present invention.

CLAIMS

1. A method for preparing nitrogen self-doped porous graphite carbon MFCs air cathode catalyst, characterized by comprising the following steps:

S1, repeatedly washing mangosteen peel with deionized water, drying at 100-120°C, and crushing the dried mangosteen peel into powder to obtain product A;

S2, heating the product A to 400°C at a heating rate of 5-8°C/min under the protection of nitrogen, then pyrolyzing for 2-3 hours to obtain a dark black product, and grinding the dark black product to obtain product B;

S3, adding product B into CoCl_2 aqueous solution, soaking for 6-10h under stirring condition, then separating solid phase from liquid, drying, adding the solid phase into KOH solution, soaking for 6-10h under stirring condition, separating the solid phase again, and drying it to obtain product C;

S4, heating the product C to 600-850°C at a heating rate of 5-8°C/min under the protection of nitrogen, and then calcining for 2-3 hours to obtain a black product D;

S5, immersing the product D in HCl solution to react for 8-12 hours, then separating the solid phase, repeatedly washing with deionized water to neutrality, and drying to obtain nitrogen self-doped porous graphite carbon.

2. The method of preparing nitrogen self-doped porous graphite carbon MFCs air cathode catalyst according to claim 1, which is characterized in that the drying in S1 is carried out in an oven for 10-12 hours.

3. The method of preparing nitrogen self-doped porous graphite carbon MFCs air cathode catalyst according to claim 1, which is characterized in that the concentration of CoCl_2 aqueous solution in S3 is 0.05mol/L, and the mass ratio of product B to CoCl_2 is 1:1-2:1.

4. The method of preparing nitrogen self-doped porous graphite carbon MFCs air cathode catalyst according to claim 1, which is characterized in that the concentration of KOH solution in S3 is 0.1g/mL, and the mass ratio of product B to KOH is 1:1-1:2.

5. The method of preparing nitrogen self-doped porous graphite carbon MFCs air cathode catalyst according to claim 1, which is characterized in that the product washed to neutrality by deionized water in S5 is dried at 60-80°C for 10-12 hours.

PATENTANSPRÜCHE

1. Verfahren zur Herstellung von mit Stickstoff selbstdotiertem porösem Graphit-Kohlenstoff-MFCs-Luftkathodenkatalysator, dadurch gekennzeichnet, dass das die folgenden Schritte umfasst:

S1, wiederholtes Waschen der Mangostan-Schale mit deionisiertem Wasser, Trocknen bei 100-120°C und Zerkleinern der getrockneten Mangostan-Schale zu Pulver, um Produkt A zu erhalten;

S2, Erhitzen des Produkts A auf 400°C mit einer Heizrate von 5-8°C/min unter Stickstoffschutz, dann Pyrolysieren für 2-3 Stunden, um ein dunkelschwarzes Produkt zu erhalten, und Mahlen des dunkelschwarzen Produkts, um Produkt B zu erhalten;

S3, Zugabe von Produkt B in wässrige CoCl_2 -Lösung, Einweichen für 6-10 h unter Rührbedingungen, dann Trennen der festen Phase von der Flüssigkeit, Trocknen, Zugabe der festen Phase in KOH-Lösung, Einweichen für 6-10 h unter Rührbedingungen, erneutes Abtrennen der festen Phase und Trocknen, um Produkt C zu erhalten;

S4, Erhitzen des Produkts C auf 600-850°C mit einer Heizrate von 5-8°C/min unter Stickstoffschutz und anschließendes Kalzinieren für 2-3 Stunden, um ein schwarzes Produkt D zu erhalten;

S5, Eintauchen des Produkts D in HCl-Lösung zur Reaktion für 8-12 Stunden, dann Abtrennen der festen Phase, wiederholtes Waschen mit deionisiertem Wasser bis zur Neutralität und Trocknen, um mit Stickstoff selbstdotierten porösen Graphitkohlenstoff zu erhalten.

2. Verfahren zur Herstellung von mit Stickstoff selbstdotiertem porösem Graphit-Kohlenstoff-MFCs-Luftkathodenkatalysator nach Anspruch 1, dadurch gekennzeichnet, dass das Trocknen in S1 in einem Ofen für 10-12 Stunden durchgeführt wird.

3. Verfahren zur Herstellung von mit Stickstoff selbstdotiertem porösem Graphit-Kohlenstoff-MFCs-Luftkathodenkatalysator nach Anspruch 1, dadurch gekennzeichnet, dass die Konzentration der wässrigen CoCl_2 -Lösung in S3 0,05 mol/l beträgt und das Massenverhältnis von Produkt B zu CoCl_2 ist 1:1-2:1.

4. Verfahren zur Herstellung von mit Stickstoff selbstdotiertem porösem Graphit-Kohlenstoff-MFCs-Luftkathodenkatalysator nach Anspruch 1, dadurch gekennzeichnet, dass die Konzentration der KOH-Lösung in S3 0,1 g/ml beträgt und das Massenverhältnis von Produkt B zu KOH beträgt 1:1-1:2.
5. Verfahren zur Herstellung von mit Stickstoff selbstdotiertem porösem Graphit-Kohlenstoff-MFCs-Luftkathodenkatalysator nach Anspruch 1, dadurch gekennzeichnet, dass das Produkt, das in S5 mit entionisiertem Wasser bis Neutralität gewaschen wird, bei 60-80°C für 10-12 Stunden getrocknet wird.

FIGURES

LU501479

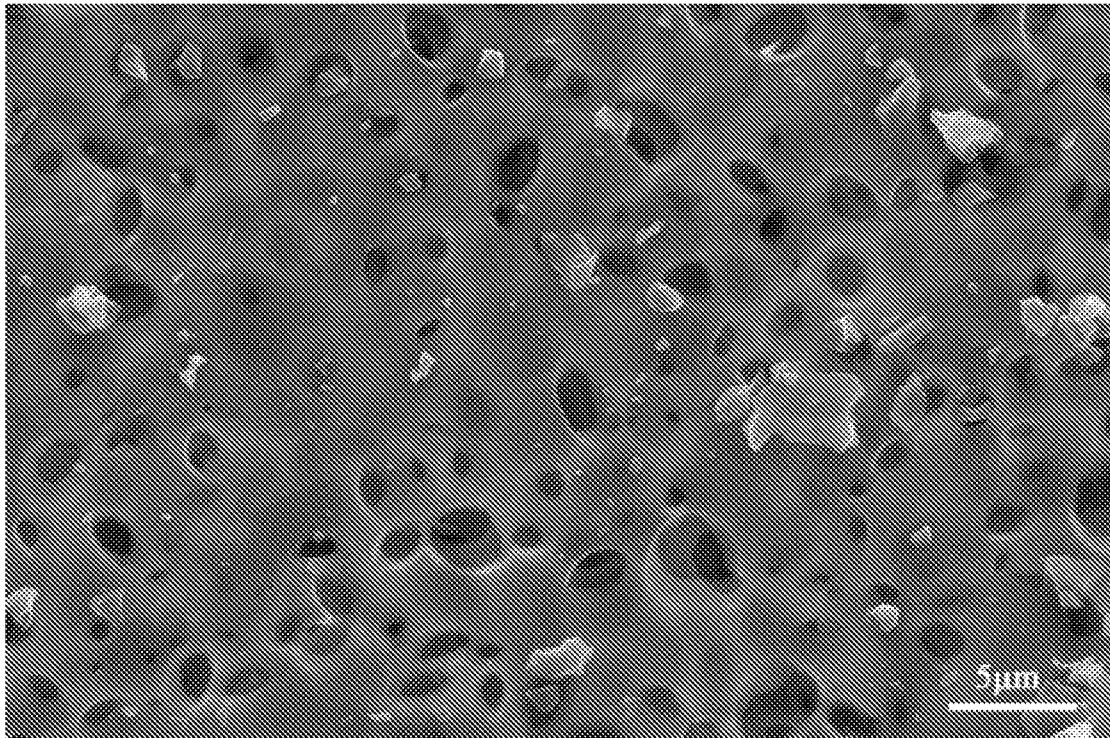


Figure 1

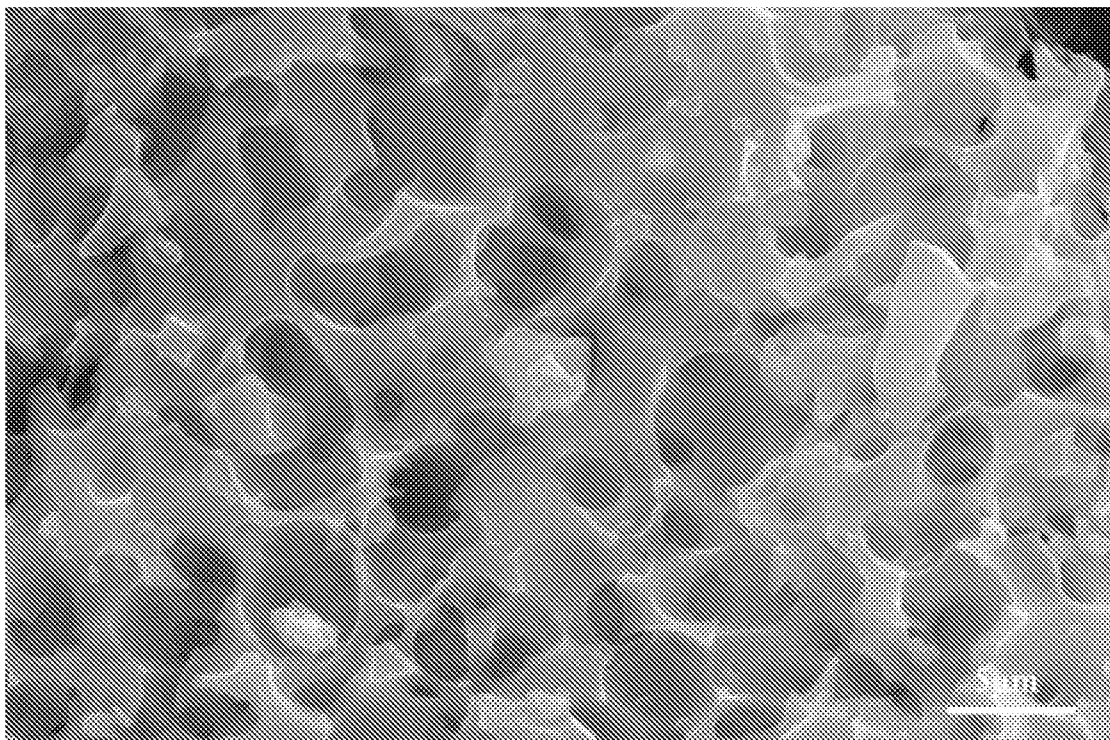


Figure 2

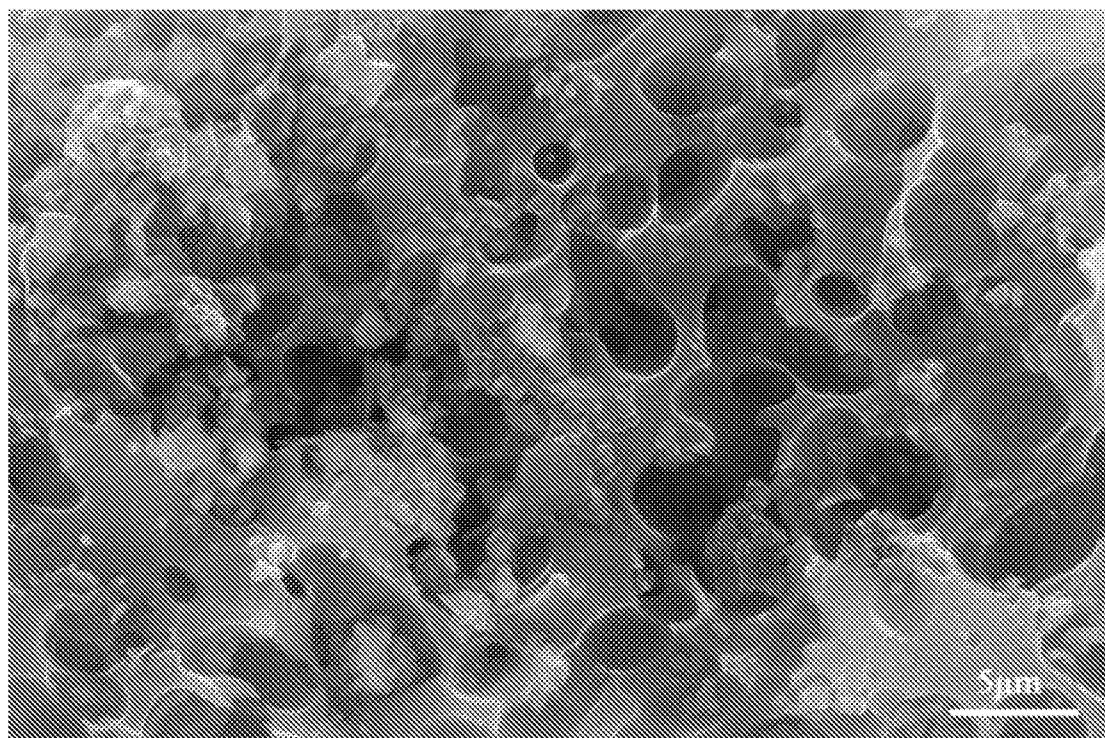


Figure 3

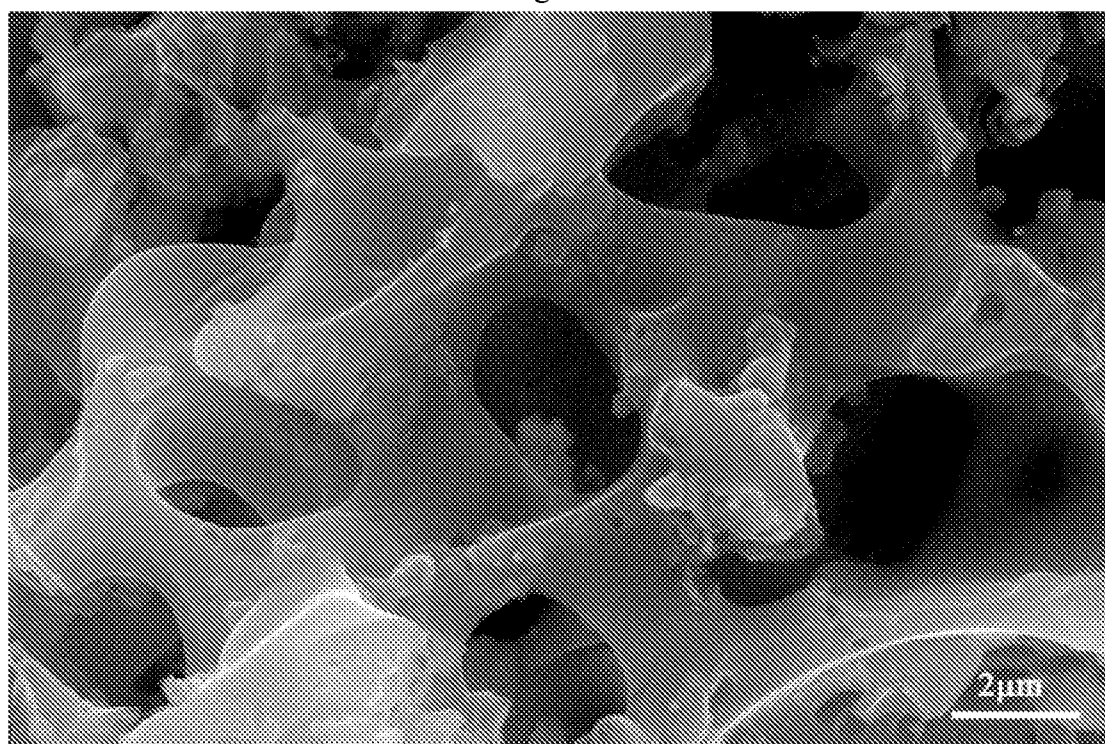


Figure 4

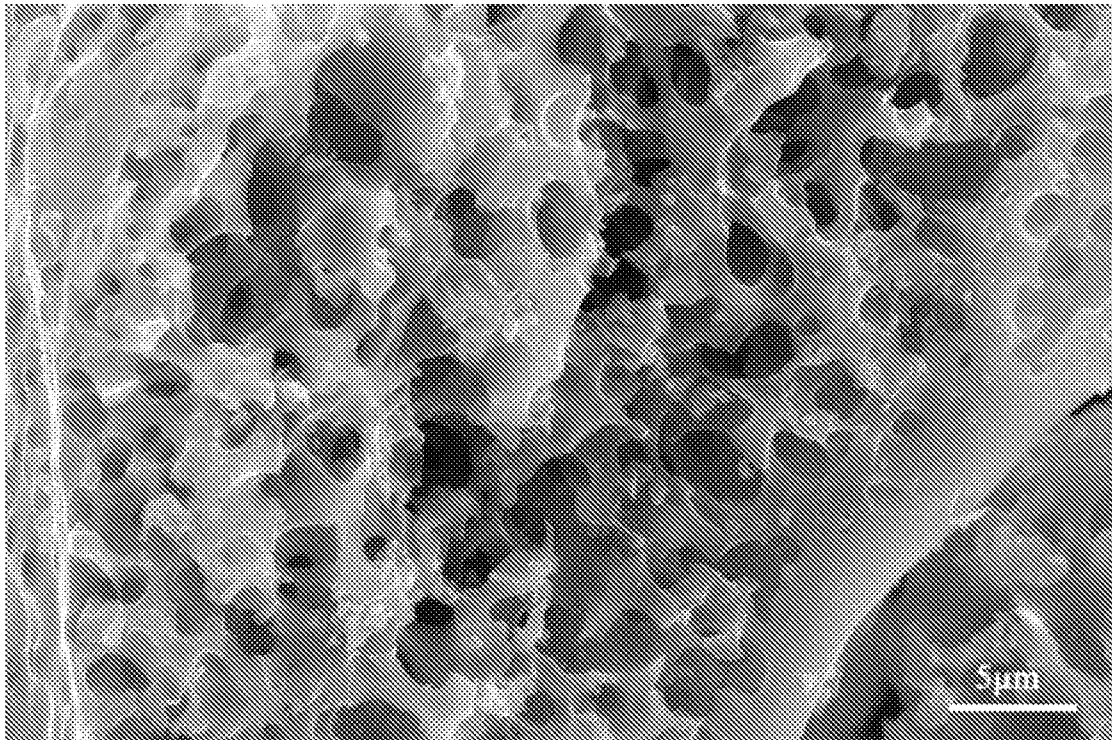


Figure 5

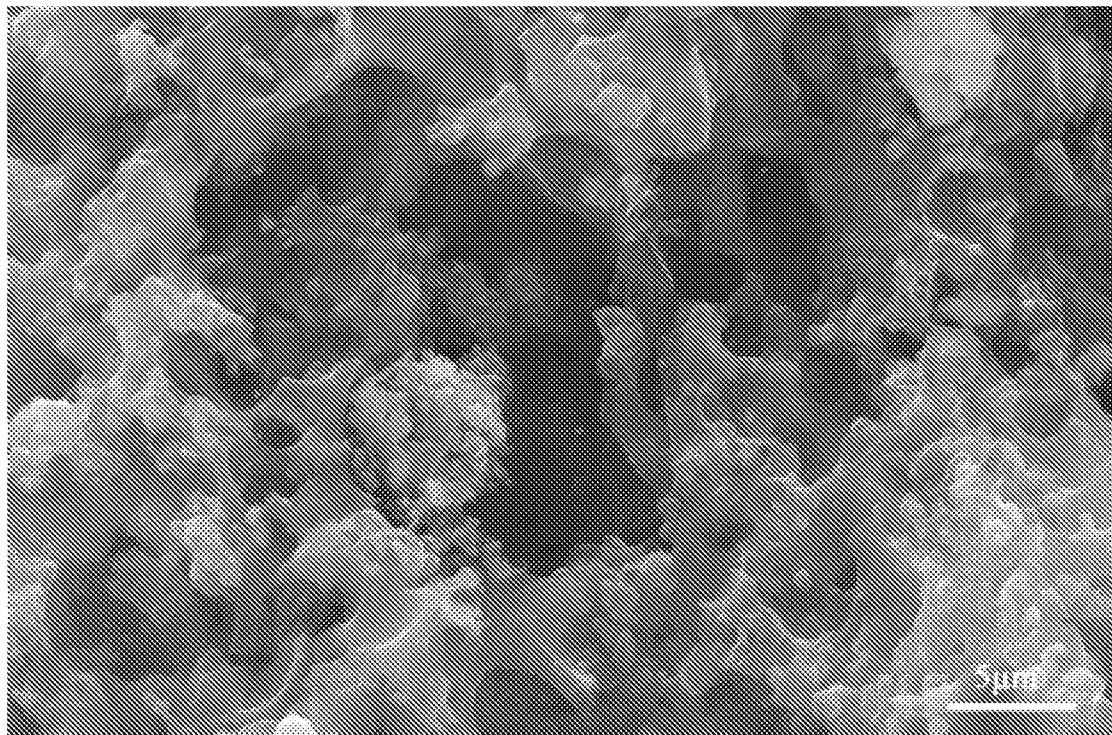


Figure 6

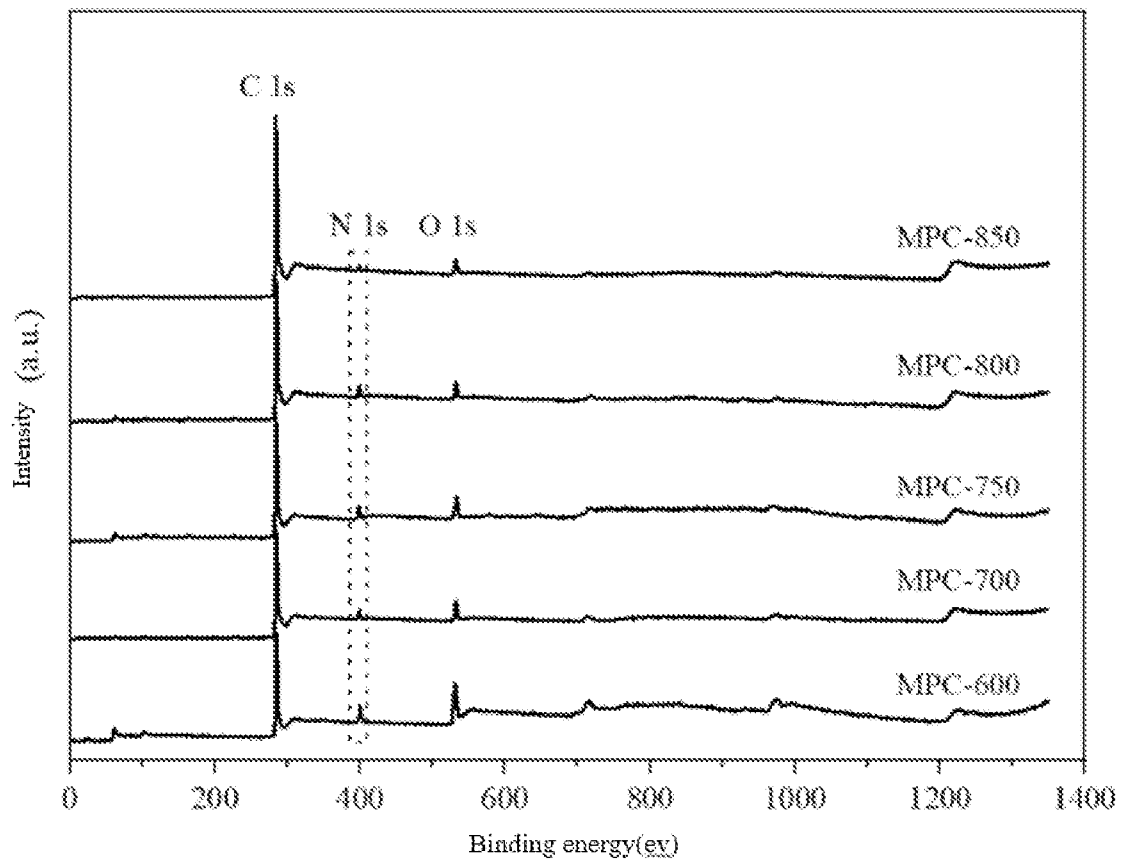


Figure 7

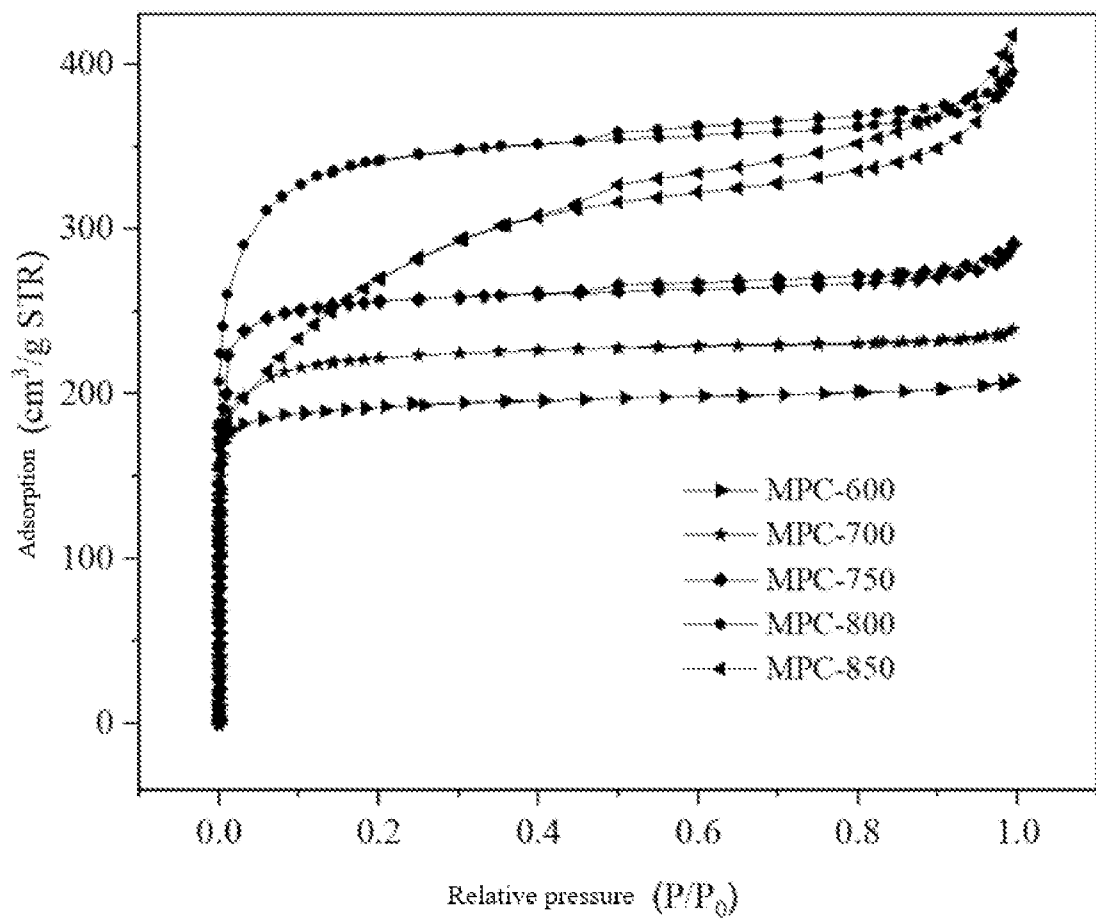


Figure 8

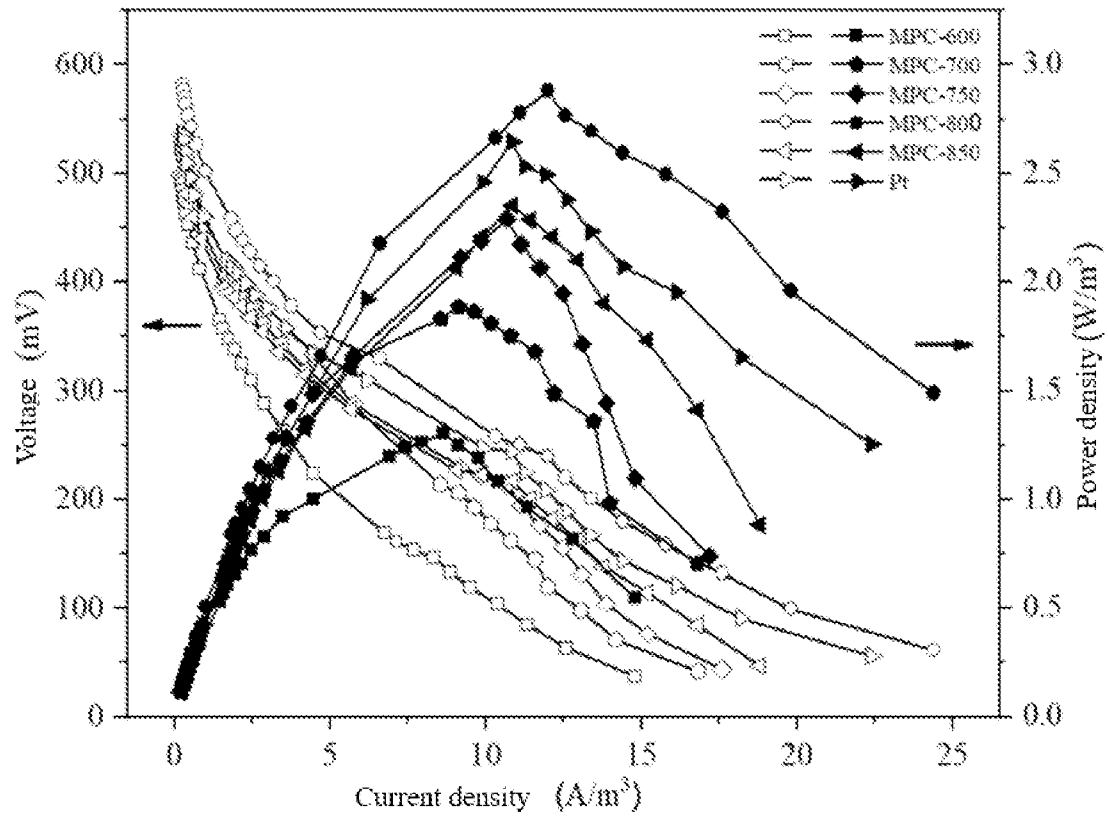


Figure 9

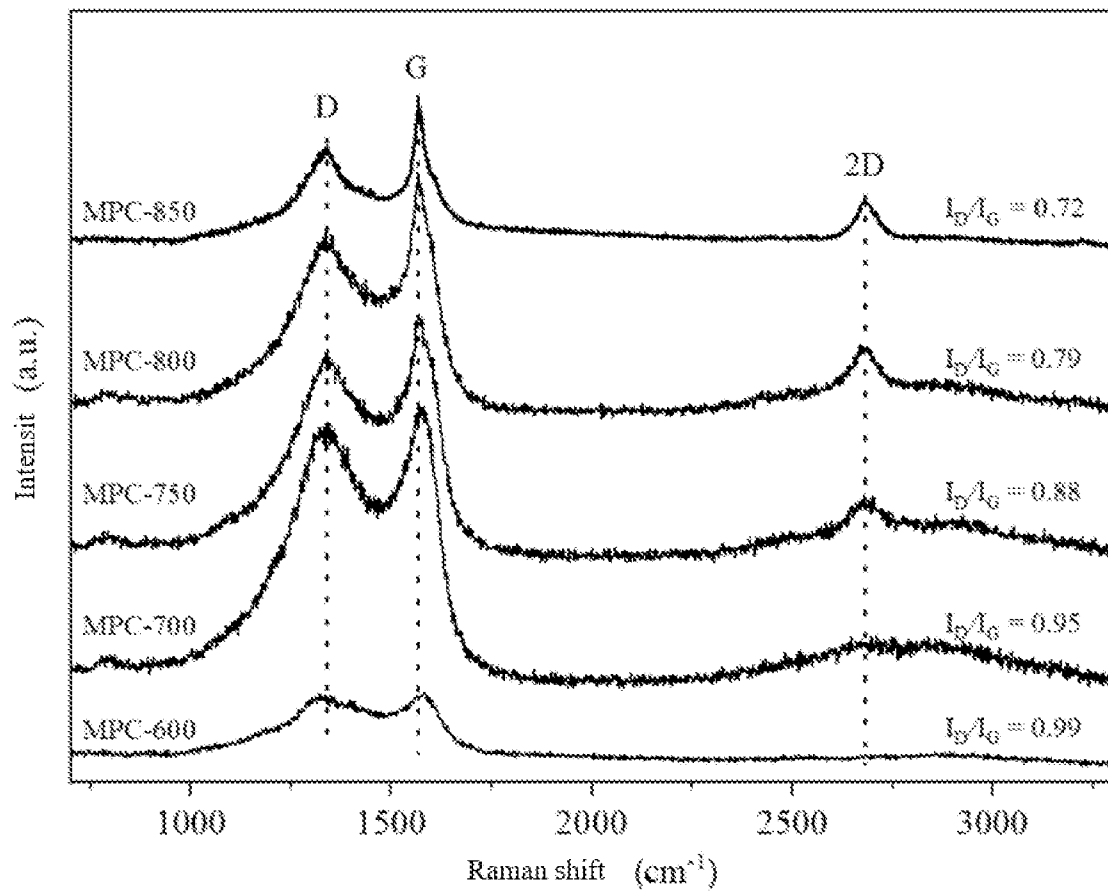


Figure 10