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(71) Applicant (for all designated States except US):
DONGJIN SEMICHEM CO. LTD. [KR/KR]; 472-2
Gajwa-dong, Seo-ku, Incheon-city 445-931 (KR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **JANG, Jyongsik**
[KR/KR]; Department of Chemical Engineering, College
of Engineering, Seoul National University, San 56-1
Shillim-dong, Kwanak-gu, Seoul 151-742 (KR). **HA,**
Jung-Suk [KR/KR]; Samho garden 3-cha apt. A-305,
Banpo-dong, Seocho-gu, Seoul 137-040 (KR).

(74) Agent: **LEE, Sang-Hun**; Suite 303, Back-Ak Bldg.,
828-53 Yoksam-dong, Kangnam-ku, Seoul 135-080 (KR).

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(54) Title: METHOD FOR PREPARING POLYANILINE NANOPARTICLES USING MICRO-EMULSION POLY-MERIZA-
TION



(57) Abstract: A method for preparing polyaniline nanoparticles having var-
ious shapes and high conductivity using microemulsion polymerization is dis-
closed. The method for preparing polyaniline nanoparticles includes the steps
of adding a surfactant into a reaction solvent, and stirring the surfactant to form
a micelle; adding aniline monomer into a reaction solution containing the mi-
celle, and polymerizing the aniline monomer with a dopant and an oxidizing
agent to form polyaniline; and adding excess organic solvent to the reaction
solution to separate the polyaniline and the micelle.

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Description

METHOD FOR PREPARING POLYANILINE NANOPARTICLES USING MICRO-EMULSION POLYMERIZATION

Technical Field

- [1] The present invention relates to a method for preparing polyaniline nanoparticles, and more particularly, to a method for preparing polyaniline nanoparticles having various shapes and high conductivity using micro-emulsion polymerization.

Background Art

- [2] With the rapid development of electronic and information technology, the application areas of a conductive material have been diversified, and researches on a conductive polymer which is capable of replacing a conductive metallic material have been actively carried out. The conductive polymer can be utilized in various areas, such as an electromagnetic shielding, an alternative material of Indium tin oxide(ITO), an alternative material of carbon fiber, a magnetic recording medium, an optical storage, a light emitting device(LED), a cathode material of lithium ion battery, a light transmission material, and so on.
- [3] When the conductive polymer is produced in the form of nanoparticles, the polymer has more desirable physical properties due to the small sizes of the nanoparticles than a conductive polymer of a bulk form. The nanoparticle is a material having the size of between a molecule and a bulk solid, and generally has the size of 1 to 100 nanometers. The nanoparticle has different magnetic, optical and electrical properties from a molecule and/or a bulk solid, and the specific properties of the nanoparticle are sometimes called as 'Quantum size effect'. Thus, the nanoparticle is also sometimes called as 'Quantum dot'.
- [4] Polyaniline, one of the representative conductive polymers, is a black colored polymer which is produced by oxidation-polymerization of aniline monomer in acidic solution, and conventionally called as 'aniline black'. In the middle of nineteen eighties, it is discovered that the conductivity of polyaniline dramatically increases when protonic acid is doped into the polyaniline. After that discovery, polyaniline have attracted much attention in the art as a desirable conductive polymer. Meanwhile, polyaniline and its derivatives have further advantages in that they are easy to produce, inexpensive, and have desirable atmospheric and thermal stabilities. When an electromagnetic shielding is produced by dispersing polyaniline into other non-conductive

polymer matrix, polyaniline should be uniformly dispersed into the matrix, and the two materials should form a uniform complex without inducing phase separations between the two polymers. If polyaniline in the form of nanoparticles is used for this purpose, polyaniline is more uniformly dispersed in the matrix than polyaniline of micro-size particles, and more uniform polyaniline filler/matrix complex can be formed. In addition, as the conductivity of polyaniline filler increases, the conductivity of the complex increases, and more desirable electromagnetic shielding can be obtained. Therefore, there is an increasing need in the art for polyaniline of high conductivity and nanoparticle size.

Disclosure of Invention

Technical Problem

- [5] Therefore, it is an object of the present invention to provide a method for preparing polyaniline nanoparticles having various shapes and high conductivity.
- [6] It is other object of the present invention to provide a method for preparing polyaniline nanoparticles by using microemulsion polymerization.
- [7] It is another object of the present invention to provide a method for preparing polyaniline nanoparticles which are useful as electrical and magnetic materials, such as electromagnetic shielding, a magnetic recording medium, and so on.

Technical Solution

- [8] In order to achieve these and other objects, the present invention provides a method for preparing polyaniline nanoparticles by using microemulsion polymerization, which comprises the steps of adding a surfactant into a reaction solvent, and stirring the surfactant to form a micelle; adding aniline monomer into a reaction solution containing the micelle, and polymerizing the aniline monomer with a dopant and an oxidizing agent to form polyaniline; and adding excess organic solvent to the reaction solution to separate the polyaniline and the micelle. Preferably, the surfactant can be selected from the group consisting of octyltrimethylammonium bromide, decyltrimethylammonium bromide, dodecyltrimethylammonium bromide, sodium dodecylsulfate, sodium dioctylsulfosuccinate and the mixtures thereof. In addition, when the reaction solvent is water, the surfactant can be an anionic and/or a cationic surfactant. When the reaction solvent is hexane, the preferable surfactant is sodium dioctylsulfosuccinate. The dopant can be selected from the group consisting of hydrochloric acid, sulfuric acid, phosphoric acid and the mixtures thereof, and the preferable oxidizing agent is ammonium persulfate. The preferable organic solvent can be selected from the group consisting of methanol, acetone and the mixtures thereof.

Description of Drawings

- [9] Fig. 1 is a transmission electron microscopy photograph for showing the polyaniline nanoparticles produced according to an example of the present invention.

Mode for Invention

- [10] Hereinafter, the preferable examples of the present invention are provided for better understanding of the present invention. However, the following examples are to illustrate the present invention, and the present invention is not limited by the following examples.
- [11] A more complete appreciation of the invention, and many of the attendant advantages thereof, will be better appreciated by reference to the following detailed description.
- [12] The method for preparing polyaniline nanoparticles according to the present invention utilizes microemulsion polymerization, and the shape and conductivity of the polyaniline nanoparticle can be controlled by adjusting the microemulsion polymerization conditions. In order to produce the polyaniline nanoparticles according to the present invention, micelles should be produced by using a surfactant, such as a cationic surfactant, an anionic surfactant, and the mixtures thereof in the step of microemulsion or inverse microemulsion polymerization. The micelles can be formed by adding a cationic surfactant or an anionic surfactant of various concentrations into a solvent, such as water, preferably distilled water, organic solvent or so on, and stirring the surfactant for 20 to 40 minutes, preferably for about 30 minutes at the temperature of 1 to 70 ° C, preferably at the temperature of 3 to 60 ° C. The concentration of the surfactant can be determined with reference to CMC 1 and CMC 2 of the surfactant. The term 'CMC' represents 'Critical Micelle Concentration' which is a concentration capable of forming micelle by surfactant association, and the shape of the micelle varies according to the type and concentration of the surfactant. Generally, when the concentration of the surfactant is more than CMC1, sphere shaped micelles are formed, and when the concentration of the surfactant is more than CMC2, rod shaped or hexagonal shaped micelles are formed. Meanwhile, when the concentration of the surfactant is between the CMC1 and CMC2, the produced micelles are transparent in the solution and invisible by a naked eye. When the concentration of the surfactant is more than CMC2, the produced micelles are invisible by the naked eye and the solution becomes opaque. Namely, the shapes of the micelles are difficult to determine by the naked eye. Therefore, the shape of the polymer polymerized in the micelles is observed with apparatus, such as TEM(Transmission Electron Microscope),

SEM(Scanning Electron Microscope) and so on, to determine the concentration of the surfactant. In case that the CMC 1 and CMC 2 of a surfactant at room temperature are known, the CMC 1 and CMC 2 can be utilized for the purpose of the present invention. The interior space of such micelle is used as a nano-reactor to produce nanoparticles.

- [13] When the solvent to form the micelles is water, the preferable cationic surfactant includes octyltrimethylammonium bromide (OTAB), decyltrimethylammonium bromide (DeTAB), dodecyltrimethylammonium bromide (DTAB), or the mixtures thereof. The more preferable cationic surfactant is decyltrimethylammonium bromide, which increases the conductivity of the produced polyaniline nanoparticles. The preferable anionic surfactant includes sodium dodecylsulfate(SDS), sodium dioctylsulfosuccinate and the mixtures thereof. Particularly, in the inverse microemulsion polymerization, which uses organic solvent such as hexane, the more preferable surfactant is sodium dioctylsulfosuccinate (AOT). The preferable amount of the surfactant is 5 to 15 weight part for 100 weight part of the solvent. When the amount of the surfactant is less than 5 weight part, the micelle may not be properly formed. When the amount of the surfactant is more than 15 weight part, the micelle may be transformed into an undesirable phase. In addition, when the temperature of the solvent is less than 1 ° C, the polymerization rate may decrease, and freezing of solution may occur. When the temperature of the solvent is more than 70 ° C, the decomposition of micelles may occur.

- [14] After forming micelles with the surfactant, stirring of the reaction solution is carried out while adding aniline monomer as the monomer of the conductive polymer. In addition, a dopant and an oxidizing agent are added thereto to initiate the polymerization reaction. The preferable amount of the aniline monomer is about 1.25 to 5 weight part for 100 weight part of the solution containing micelles. When the amount of the aniline monomer is less than 1.25 weight part, all of the micelle may not be used as the nano-reactor. When the amount of the aniline monomer is more than 5 weight part, the micelles may not receive all of the aniline monomer, and the deformation of micelles may occur.

- [15] The dopant is used to increase the conductivity of the polymerized polyaniline, and to adjust the acidic condition of the reaction solution for rapid and stable reaction. Exemplary dopant includes protonic acid such as hydrochloric acid, sulfuric acid, phosphoric acid, the mixtures thereof, and so on. For increasing the conductivity of the produced polymer, sulfuric acid is more preferable than hydrochloric acid as the dopant. The preferable amount of the dopant is 1 to 3 moles for 1 mole of the aniline

monomer. When the amount of the dopant is less than 1 mole, the conductivity of the produced polymer may not be satisfactory. When the amount of the dopant is more than 3 moles, the conductivity of the produced polymer does not additionally increase, but the phase of the polymer may be deformed.

- [16] The oxidizing agent is used to polymerize the aniline monomer, and the examples of the oxidizing agent includes ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$), potassium peroxydisulfate ($\text{K}_2\text{O}_8\text{S}_2$), and so on. The preferable amount of the oxidizing agent is 0.2 to 0.8 mole for 1 mole of the aniline monomer, and the more preferable amount is about 0.5 mole for 1 mole of the aniline monomer. When the amount of the oxidizing agent is less than 0.2 mole, the polymerization of the aniline monomer may not be satisfactory. Even when the amount of the oxidizing agent is more than 0.8 mole, the polymerization speed of the aniline monomer and the polymerization efficiency may not further increase. The oxidizing agent can be added to the reaction solution containing the aniline monomer and the dopant. Alternatively, the oxidizing agent can be dissolved with a dopant, such as hydrochloric acid, sulfuric acid, and so on, and the mixture of the oxidizing agent and the dopant can be added to the reaction solution containing the aniline monomer. More preferably, the oxidizing agent and the dopant are added to the reaction solution after stirring the solution containing micelles and the aniline monomer for about 30 minutes. During the stirring, the aniline monomers are fully incorporated into the interior of the micelles. The reaction time of the polymerization reaction is about 2 to 4 hours, and preferably about 3 hours, and the reaction temperature is preferably maintained to be same with the reaction initiation temperature. In order to increase the conductivity of the produced polyaniline, it is preferable to maintain the polymerization temperature at low temperature.

- [17] After completing the aniline polymerization, the surfactant is removed to separate the polyaniline nanoparticles produced in the micelles. In order to remove the surfactant and reaction by-products, the reaction solution is poured into a separatory funnel, and excess organic solvent such as methanol, acetone, the mixtures thereof, and so on, is added thereto. Then the surfactant and the reaction by-products dissolve and are moved into the organic layer. By discarding the upper organic layer, an aqueous solution containing precipitated polyaniline nanoparticles is obtained. Then, by evaporating the aqueous solution at room temperature, the target polyaniline nanoparticles can be obtained. For easy removing of the micelles and effective increasing of the conductivity of the polyaniline, acetone is preferable than methanol as the organic solvent.

- [18] From the TEM(Transmission Electron Microscopy) analysis of the obtained polyaniline nanoparticles, it is confirmed that nanoparticles having various morphologies and sizes can be formed according to the reaction conditions. Specifically, when the concentration of the surfactant is maintained between CMC 1 and CMC 2, the produced polyaniline nanoparticles have the size of 10 to 100 nanometers, and have the shape of a sphere or an elliptical sphere. When the concentration of the surfactant is maintained more than CMC 2, the produced polyaniline nanoparticles have the shape of rod or wire, and have the size of several hundreds nanometers. It is also discovered that octyltrimethylammonium bromide and/or decyltrimethylammonium bromide are more preferable as the surfactant, and hydrochloric acid is more preferable as the dopant for producing sphere shaped polyaniline nanoparticles with high yield. In addition, the polyaniline nanoparticles may have the various conductivities according to the reaction conditions.
- [19] Hereinafter, the preferable examples of the present invention are provided for better understanding of the present invention. However, the following examples are to illustrate the present invention, and the present invention is not limited by the following examples.
- [20] [Example 1] Manufacture of polyaniline nanoparticles using cationic surfactant and sulfuric acid dopant at the reaction temperature of 3 ° C
- [21] The reaction temperature was maintained to 3 ° C with a water bath, and 40 ml of distilled water was used as a reaction medium. 3g of cationic surfactant, such as octyltrimethylammonium bromide, decyltrimethylammonium bromide, or dodecyltrimethylammonium bromide, was used with the concentration of between CMC 1 and CMC 2. After stirring the surfactant in the distilled water to form micelles, 1g of aniline monomer was dropwisely added to the reaction solution by a pipette. The added aniline monomer further stirred for 30 minutes to fully insert the aniline monomer into the interior of the micelles. Meanwhile, 1.125g of ammonium persulfate(oxidizing agent) was dissolved with 10 ml of 2M sulfuric acid (mole ratio of aniline/ ammonium persulfate = 1/0.5), and the mixture was added to the reaction solution. While maintaining the reaction temperature to the reaction initiation temperature, the reaction solution was stirred for 3 hours to polymerize the aniline monomer. After completing the polymerization reaction, the reaction solution was poured into a separatory funnel, and excess acetone was added thereto to dissolve the surfactant and reaction by-products. To obtain the precipitated polyaniline nanoparticles, the upper layer of the reaction solution, i.e., the acetone layer was

removed by using a pipette, and the remaining layer containing nanoparticles was evaporated at room temperature. The formation of the polyaniline nanoparticles was confirmed with FT-IR analysis. From the TEM(Transmission Electron Microscopy) analysis of the obtained polyaniline nanoparticles, it is confirmed that nanoparticle having the size of 10 to 100 nanometers and the shape of a sphere or an elliptical sphere was produced (See Fig. 1). The conductivity of the obtained nanoparticle was 80 to 100 S/cm, which is much higher than the conductivity of 5 to 10 S/cm of conventional polyaniline.

[22] [Example 2] Manufacture of polyaniline nanoparticles using anionic surfactant and hydrochloric acid dopant at the reaction temperature of 60 ° C

[23] Except for maintaining the reaction temperature to 60 ° C, using sodium dodecylsulfate(anionic surfactant) as the surfactant, using 20 ml of 1.5M hydrochloric acid as the dopant instead of 10 ml of 2M sulfuric acid, and using excess methanol to dissolve the surfactant and the reaction by-products instead of acetone, polyaniline nanoparticles were produced according to the method described in Example 1. The formation of the polyaniline nanoparticles was confirmed with FT-IR analysis. From the TEM(Transmission Electron Microscopy) analysis of the obtained polyaniline nanoparticles, it is confirmed that nanoparticle having the size of 50 to 100 nanometers and the shape of a sphere or an elliptical sphere was produced. The conductivity of the obtained nanoparticle was 60 to 70 S/cm.

[24] [Example 3] Manufacture of polyaniline nanoparticles using inverse microemulsion polymerization at the reaction temperature of 3 ° C

[25] The reaction temperature was maintained to 3 ° C with a water bath, and 40 ml of hexane was used as a reaction medium. Sodium dioctylsulfosuccinate was used at the concentration of more than CMC 2 as the surfactant. In addition, 20 ml of 1.5M hydrochloric acid was used as the dopant instead of 10 ml of 2M sulfuric acid, and excess methanol was used to dissolve the surfactant and the reaction by-products instead of acetone. Except for the above conditions, polyaniline nanoparticles were produced according to the method described in Example 1. The formation of the polyaniline nanoparticles was confirmed with FT-IR analysis. From the TEM(Transmission Electron Microscopy) analysis of the obtained polyaniline nanoparticles, it is confirmed that nanoparticle having the size of several hundreds nanometers and the shape of a rod or a wire was produced.

Industrial Applicability

[26] As described above, the polyaniline nanoparticle produced according to the method

of the present invention has high conductivity and various shapes, and is particularly useful as an electro-magnetic material, such as an anti-static agent, an electromagnetic shielding, a magnetic recording medium, a gas sensor, an electron transport layer of a light emitting device, and so on.

Claims

- [1] A method for preparing polyaniline nanoparticles, comprising the steps of:
adding a surfactant into a reaction solvent, and stirring the surfactant to form a micelle;
adding aniline monomer into a reaction solution containing the micelle, and
polymerizing the aniline monomer with a dopant and an oxidizing agent to form polyaniline; and
adding excess organic solvent to the reaction solution to separate the polyaniline and the micelle.
- [2] The method for preparing polyaniline nanoparticles according to claim 1, wherein the surfactant is selected from the group consisting of octyltrimethylammonium bromide, decyltrimethylammonium bromide, dodecyltrimethylammonium bromide, sodium dodecylsulfate, sodium dioctylsulfosuccinate and the mixtures thereof.
- [3] The method for preparing polyaniline nanoparticles according to claim 1, wherein the reaction solvent is water, and the surfactant is an anionic and/or a cationic surfactant.
- [4] The method for preparing polyaniline nanoparticles according to claim 1, wherein the reaction solvent is water, and the surfactant is an anionic and/or a cationic surfactant.
- [5] The method for preparing polyaniline nanoparticles according to claim 1, wherein the concentration of the surfactant is between CMC 1 and CMC 2.
- [6] The method for preparing polyaniline nanoparticles according to claim 1, wherein the dopant is selected from the group consisting of hydrochloric acid, sulfuric acid, phosphoric acid and the mixtures thereof.
- [7] The method for preparing polyaniline nanoparticles according to claim 1, wherein the oxidizing agent is selected from the group consisting of ammonium persulfate, potassium peroxodisulfate and the mixtures thereof.
- [8] The method for preparing polyaniline nanoparticles according to claim 1, wherein the organic solvent is selected from the group consisting of methanol, acetone and the mixtures thereof.
- [9] The method for preparing polyaniline nanoparticles according to claim 1, wherein the surfactant is octyltrimethylammonium bromide and/or decyltrimethylammonium bromide, and the dopant is hydrochloric acid.

[Fig. 1]



INTERNATIONAL SEARCH REPORT

national application No.
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A. CLASSIFICATION OF SUBJECT MATTER**IPC7 C08G 73/02, C08G 73/00**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 C08G 73/02, C08G 73/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean patents and applications for inventions since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CA-on CD, KIPASS, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	Kim, B.-J.; Oh, S.-G.; Han, M.-G.; Im, S.-S. "Synthesis and characterization of polyaniline nanoparticles in SDS micellar solutions", Synthetic metals 2001, 122(2), pp. 297-304	1-4, 6-8
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A	US 5,324,453 A (NESTE OY) 28 Jun 1994 see the whole documents	1-9

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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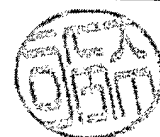
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Information on patent family members

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