

TEA LEAF DREGS GRAPHENE-CUCEMOF-PVB COMPOSITE MATERIAL AND PREPARATION METHOD AND USE THEREFOR

TECHNICAL FIELD

5 The present invention belongs to the technical field of graphene composite materials, and particularly relates to a tea leaf dregs graphene-CuCeMOF-PVB composite material, and a preparation method and use thereof.

BACKGROUND

China's tea gardens are distributed in 18 provinces. The tea areas are mainly divided into
10 Southwest China, East China, Jiangnan and Jiangbei tea areas. Due to differences in regional climate, land and other resources, the characteristic tea produced in each tea area and the local tea culture also vary, enriching the content of Chinese tea culture.

China is rich in tea, and its output and export volume are increasing day by day. In addition, China attaches great importance to the planting industry. In terms of tea output, from 2000 to
15 2010, its output increased from 683,300 tons to 1,475,060 tons. In 2015, China's tea production reached 2.092 million tons, and the export volume was only 301,500 tons, accounting for approximately 14.3% of the output. This shows that the total amount of domestic sales and the amount of discarded tea are large. If the tea leaf dregs are recycled and used to prepare graphene, it will not only benefit the environment, but also provide new products for the new material
20 industry.

Chinese patent No. CN201710196300.5 in the prior art discloses a CeMOF photocatalytic material as well as a preparation method and application thereof. CeMOFs of dipyrroindedicarboxylic acid generally have excellent optical properties, but their wet stability is poor.

Graphene thermally conductive films and anti-corrosion coatings used in the market, especially organic polymer materials as thermally conductive films, do not have broad spectrum absorption and low emission functions. Therefore, there are no products with thermally conductive films and anti-corrosion coatings on the market having broad spectrum absorption and low emission functions.

SUMMARY

In view of the above problems in the prior art, an object of the present invention is to provide a tea leaf dregs graphene-CuCeMOF-PVB composite material and a preparation method and application thereof, in which the production process is safe and environmentally friendly, low in cost and easy to operate, and the prepared tea leaf dregs graphene-CuCeMOF-PVB composite material has broad spectrum absorption and low emission.

The technical content of the present invention is as follows.

A tea leaf dregs graphene-CuCeMOF-PVB composite material is provided, which is prepared from raw materials including waste tea leaf dregs, CeMOF and a copper source substance. The composite material has broad spectrum absorption and low emission function.

The present invention also provides a preparation method for a tea leaf dregs graphene-CuCeMOF-PVB composite material, which includes the steps of:

1) preparing a PVB ethanol slurry;

2) preparing tea leaf dregs graphene: taking dry powder of tea leaf dregs, heating up under nitrogen conditions (at a nitrogen rate of 10 ml/min) to undergo a heating reaction, then cooling to obtain tea leaf dregs charcoal, adding CH_3COOK and mixing well, heating up under nitrogen conditions to undergo a heating reaction, and then cooling to obtain tea leaf dregs graphene;

3) preparing tea leaf dregs graphene-CuCeMOF composite: taking CeMOF, tea leaf dregs graphene and copper source substance and mixing evenly, then centrifuging and washing the same such that CeMOF changes from light yellow to gray blue, adding DMAC, DMSO and glucose, heating up to undergo a heating reaction, cooling to room temperature, and washing, centrifuging, and drying a resulting product to obtain the tea leaf dregs graphene-CuCeMOF composite; and

4) preparing the tea leaf dregs graphene-CuCeMOF-PVB composite material, comprising mixing the PVB ethanol slurry and the tea leaf dregs graphene-CuCeMOF composite evenly to obtain the tea leaf dregs graphene-CuCeMOF-PVB composite material.

The PVB ethanol slurry in step 1) is a mixture of PVB and ethanol, and a use ratio of PVB to ethanol is 1:10-40.

A use ratio of the PVB ethanol slurry to the tea leaf dregs graphene-CuCeMOF composite in step 4) is 1:1-10.

After the heating up in step 2), the temperature is maintained for 1 to 5 hours.

The copper source substance in step 3) comprises copper acetate.

The temperature of the heating reaction in step 3) is 110-140°C, and the temperature is maintained for 12-24 hours.

Preparation of CeMOF in step 3) comprises taking $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and 2,2'-dipyridine-5,5'-phthalate and mixing to be added to DMF and DMSO, stirring evenly with a glass rod at room temperature, heating up to undergo a heating reaction, and then cooling to obtain a light yellow precipitate, and washing, centrifuging, and drying the precipitate to obtain CeMOF.

The present invention also provides use of the tea leaf dregs graphene-CuCeMOF-PVB composite material in preparing thermally conductive materials and anticorrosive coatings.

The beneficial effects of the present invention are as follows:

The tea leaf dregs graphene-CuCeMOF-PVB composite material of the present invention uses waste tea leaf dregs as raw materials, which is low in cost and of universal raw materials, and solves the problem of resource waste caused by waste tea leaf dregs being disposed as garbage. The composite material also has broad spectrum absorption and low emission functions and thermal conductivity. It can be used to prepare thermally conductive materials (including thermally conductive films) and anti-corrosion coatings. Thermally conductive films can be used for thermal conduction of electronic devices, which solves the problem that graphene composite materials in the prior art contain heavy metals that are harmful to the environment, without the functions of broad spectrum absorption and low emission and the like.

The composite material of the present invention has simple preparation process, low price, safety and environmental protection, is suitable for continuous industrial production, expanding its application field, can be used in national defense, and has broad market application prospects.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a Raman spectrum of a tea leaf dregs graphene obtained in Example 1;

FIG. 2 shows a broad absorption spectrum of a tea leaf dregs graphene-CuCeMOF-PVB composite material; and

5 FIG. 3 shows a low emission spectrum of the tea leaf dregs graphene-CuCeMOF-PVB composite material.

DETAILED DESCRIPTION

The present invention will be described in further detail through specific examples and the accompanying drawings. It should be understood that these embodiments are only used to
10 illustrate the present invention and not to limit the scope of protection of the present invention. After reading the present invention, various equivalent modifications made by those skilled in the art to the present invention fall within the scope of the appended claims of the present application.

Unless otherwise specified, all the raw materials and reagents of the present invention are
15 the raw materials and reagents in the conventional market.

Example 1

Preparation of a tea leaf dregs graphene-CuCeMOF-PVB composite material includes:

- 1) preparing a PVB ethanol slurry: dissolving PVB powder in ethanol to form the PVB ethanol slurry;
- 20 2) preparing tea leaf dregs graphene: taking dry powder of tea leaf dregs, heating up under nitrogen conditions (at a nitrogen rate of 10 ml/min) from room temperature to 500-850°C at a rate of 1°C/min, keeping for 1-5 hours in order to fully decompose dioxins produced by combustion and remove heteroatoms, and then cooling to room temperature at a rate of 5°C/min to obtain tea leaf dregs charcoal; and
- 25 adding CH₃COOK (to reduce the corrosive effect on the furnace, and reduce the amount of acid and alkali in the production process), grinding uniformly with the tea leaf dregs charcoal, heating up under nitrogen conditions at a rate of 1°C/min from room temperature to 900 - 1150°C, keeping for 1-5 hours in order to further remove heteroatoms to facilitate the formation

of graphene, and then cooling to room temperature at a rate of 5°C/min to obtain tea leaf dregs graphene;

3) preparing tea leaf dregs graphene-CuCeMOF composite: taking $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and 2,2'-bipyridine-5,5'-dicarboxylic acid and adding to a 100 mL PTFE-lined hydrothermal reactor, adding to a mixed solvent of DMF and DMSO in turn, stirring evenly with a glass rod at room temperature, transferring the PTFE-lined hydrothermal reactor to an oven, heating up to 110-140°C within 3 hours, keeping for 9-18 hours, and cooling to room temperature at a cooling rate of 3°C/h to obtain a light yellow precipitate, washing and centrifuging the precipitate twice with DMF, soaking in dichloroethane for 8-12 h, and centrifuging; and placing the same in a vacuum drying oven and setting the drying temperature to 80-90°C, and drying for 12-24 hours to obtain CeMOF; and

adding copper acetate and tea leaf dregs graphene to CeMOF, fully stirring for 12 h to allow CeMOF and Cu^{2+} to reach adsorption equilibrium, then centrifuging the mixture, washing twice with a DMAC solvent, centrifuging to remove the residue Cu^{2+} on the surface of the complex CeMOF, such that the originally light yellow complex CeMOF presents a gray blue color;

adding the gray blue complex CeMOF to a mixed solvent of DMAC and DMSO, adding a molar amount of glucose, placing the PTFE liner in a stainless steel hydrothermal reactor, with a heating temperature of 110-140°C, a holding time of 12 -24 h, and a cooling time of 12 h, and cooling to room temperature, washing the product with the DMAC solvent, and then centrifuging at a high speed (9600 rpm) with a centrifuge five times with 15 minutes each time, and finally, placing the product in the vacuum drying oven at a temperature of 80-100°C and drying for 12-24 hours to obtain the tea leaf dregs graphene-CuCeMOF composite; and

4) preparing the tea leaf dregs graphene-CuCeMOF-PVB composite material: mixing the PVB ethanol slurry and the tea leaf dregs graphene-CuCeMOF composite fully to obtain the tea leaf dregs graphene-CuCeMOF-PVB composite material.

FIG. 1 shows a Raman spectrum of tea leaf dregs graphene, in which a D peak is around 1365cm^{-1} , a G peak appears at 1685cm^{-1} , and the stacking method of graphene appears at a 2D peak at 2685cm^{-1} .

Instrument name: Micro Raman spectrometer, model: LabRAM Aramis, Manufacturer:

French H.J.Y company.

Example 2

Preparation of a tea leaf dregs graphene-CuCeMOF-PVB thermally conductive material includes:

- 5 taking and dissolving PVB in ethanol at a ratio of 1:10 and letting it stand for 1 hour; then adding the tea leaf dregs graphene-CuCeMOF composite at a ratio of 1:1 and stirring evenly, letting it stand for 1 hour until no bubbles are generated, and placing a film in a fume hood, and after 2 hours, drying to form a film in an oven.

After testing, the thermal conductivity passed the thermal conductivity measuring
10 instrument (TC3000D, Xi'an Xiaxi Electronic Technology Co., Ltd.), and the thermal conductivity is 5.5 W/mK.

Example 3

Preparation of a tea leaf dregs graphene-CuCeMOF-PVB thermally conductive material includes:

- 15 taking and dissolving PVB in ethanol at a ratio of 1:20 and letting it stand for 1 hour; then adding the tea leaf dregs graphene-CuCeMOF composite at a ratio of 1:2 and stirring evenly, and letting it stand for 1 hour until no bubbles are generated, and placing a film in a fume hood, and after 2 hours, drying to form a film in an oven.

After testing, the thermal conductivity is 5.8W/mK.

20 Example 4

Preparation of a tea leaf dregs graphene-CuCeMOF-PVB thermally conductive material includes:

- 25 taking and dissolving PVB in ethanol at a ratio of 1:25 and letting it stand for 1 hour; then adding the tea leaf dregs graphene-CuCeMOF composite at a ratio of 1:5 and stirring evenly, and letting it stand for 1 hour until no bubbles are generated, and placing a film in a fume hood, and after 2 hours, drying to form a film in an oven.

After testing, the thermal conductivity is 6.7W/mK.

Example 5

- 30 Preparation of a tea leaf dregs graphene-CuCeMOF-PVB thermally conductive material includes:

taking and dissolving PVB in ethanol at a ratio of 1:30 and letting it stand for 1 hour; then adding the tea leaf dregs graphene-CuCeMOF composite at a ratio of 1:7 and stirring evenly, and letting it stand for 1 hour until no bubbles are generated, and placing a film in a fume hood, and after 2 hours, drying to form a film in an oven.

5 After testing, the thermal conductivity is 7.1W/mK.

Example 6

Preparation of a tea leaf dregs graphene-CuCeMOF-PVB thermally conductive material includes:

10 taking and dissolving PVB in ethanol at a ratio of 1:40 and letting it stand for 1 hour; then adding the tea leaf dregs graphene-CuCeMOF composite at a ratio of 1:10 and stirring evenly, and letting it stand for 1 hour until no bubbles are generated, and placing a film in a fume hood, and after 2 hours, drying to form a film in an oven.

After testing, the thermal conductivity is 7.5W/mK.

15 FIG. 2 shows a broad absorption spectrum of the tea leaf dregs graphene-CuCeMOF-PVB composite material (using the Japanese Hitachi UV-Vis spectrophotometer U3010, quoting BaSO₄, the UV-visible diffuse reflectance data is in the 200-900 nm spectral region), showing high absorption from 300 nm to 900 nm. It can be seen that the tea leaf dregs graphene-CuCeMOF-PVB composite material has a broad spectrum absorption function.

20 FIG. 3 shows a low emission spectrum of the tea leaf dregs graphene-CuCeMOF-PVB composite material (on a Hitachi F-4500 fluorescence spectrophotometer, with 450 W xenon lamp as the excitation light source, photoluminescence (PL) measurement at room temperature). The wavelength of the excitation light is 300 nm or 350 nm. It can be seen that the tea leaf dregs graphene-CuCeMOF-PVB composite material has a low emission function.

What is claimed is:

1. A tea leaf dregs graphene-CuCeMOF-PVB composite material, characterized in that,
5 the composite material is prepared from raw materials comprising waste tea leaf dregs, CeMOF, and a copper source substance.

2. A preparation method for a tea leaf dregs graphene-CuCeMOF-PVB composite material, characterized in that, the preparation method comprises the steps of:

10 1) preparing a PVB ethanol slurry;

2) preparing tea leaf dregs graphene: taking dry powder of tea leaf dregs, heating up under nitrogen conditions to undergo a heating reaction, then cooling to obtain tea leaf dregs charcoal, adding CH_3COOK and mixing well, heating up under nitrogen conditions to undergo a heating reaction, and then cooling to obtain tea leaf dregs graphene;

15 3) preparing tea leaf dregs graphene-CuCeMOF composite: taking CeMOF, tea leaf dregs graphene and a copper source substance and mixing evenly, then centrifuging and washing such that CeMOF changes from light yellow to gray blue, adding DMAC, DMSO and glucose, heating up to undergo a heating reaction, cooling to room temperature, and washing, centrifuging, and drying a resulting product to obtain the tea leaf dregs graphene-CuCeMOF
20 composite; and

4) preparing the tea leaf dregs graphene-CuCeMOF-PVB composite material: mixing the PVB ethanol slurry and the tea leaf dregs graphene-CuCeMOF composite evenly to obtain the tea leaf dregs graphene-CuCeMOF-PVB composite material.

25 3. The preparation method for the tea leaf dregs graphene-CuCeMOF-PVB composite material according to claim 2, wherein the PVB ethanol slurry in step 1) is a mixture of PVB and ethanol, and a use ratio of PVB to ethanol is 1:10-40.

4. The preparation method for the tea leaf dregs graphene-CuCeMOF-PVB composite
30 material according to claim 2 or 3, wherein a use ratio of the PVB ethanol slurry to the tea leaf dregs graphene-CuCeMOF composite in step 4) is 1:1-10.

5. The preparation method for the tea leaf dregs graphene-CuCeMOF-PVB composite material according to claim 4, wherein, after the heating up in step 2), the temperature is maintained for 1 to 5 hours.

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6. The preparation method for the tea leaf dregs graphene-CuCeMOF-PVB composite material according to claim 5, wherein the copper source substance in step 3) comprises copper acetate.

10 7. The preparation method for the tea leaf dregs graphene-CuCeMOF-PVB composite material according to claim 6, wherein the temperature of the heating reaction in step 3) is 110-140°C, and the temperature is maintained for 12-24 hours.

15 8. The preparation method for the tea leaf dregs graphene-CuCeMOF-PVB composite material according to claim 7, wherein preparation of CeMOF in step 3) comprises taking $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and 2,2'-dipyridine-5,5'-phthalate and mixing to be added to DMF and DMSO, stirring evenly with a glass rod at room temperature, heating up to undergo a heating reaction, and then cooling to obtain a light yellow precipitate, and washing, centrifuging, and drying the precipitate to obtain CeMOF.

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9. Use of the tea leaf dregs graphene-CuCeMOF-PVB composite material according to claim 1 in preparing thermally conductive materials and anticorrosive coatings.