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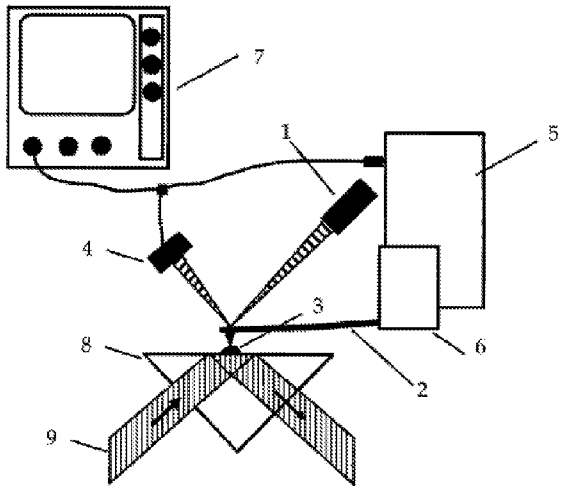


Figure 1

(57) Abstract: A method for identifying the information about a polymer sample utilizing an atomic force microscope comprises: a) providing a polymer sample; b) contacting a probe of the atomic force microscope with the polymer sample; c) irradiating at a first wavelength on the polymer sample with a beam of radiation at an incident location; d) allowing the probe to remain at the incident location; e) collecting the deflection data from the probe; f) repeating the data collection of step e) by varying radiation wavelength to create a spectrum about the polymer sample.

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A METHOD FOR INFRARED SPECTROSCOPIC ANALYSIS OF A POLYMER UTILIZING AN ATOMIC FORCE MICROSCOPE

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FIELD OF THE INVENTION

[0001] The present disclosure relates to a method for identifying information about a polymer sample, particular to compositional and/or structural information, utilizing an atomic force microscope.

BACKGROUND OF THE INVENTION

[0002] Identification of a polymer in different scales is of great practical importance. There are many tools to characterize micro-structures of polymers. For example, infrared spectroscopy (IR) and atomic force microscope (AFM) are useful tools. Conventional IR is a widely used technique to measure the characteristics of polymers. In many cases the unique signatures of IR spectra can be used to identify unknown polymer materials. However, conventional IR is limited by optical diffraction and has resolution on the scale of many microns.

[0003] The development of Photo-Thermal Induced Resonance (PTIR) technique has increased the spatial resolution of IR to about 50-100 nm scale. This technique can measure information about a sample's chemical composition with resolution down to the micron and nanometer scale, and thus provide highly localized IR spectra and absorption on a sample surface utilizing an AFM.

[0004] It would be desirable to extend applications of IR techniques in polymer materials, particular to those polymers with complex structures due to lack of noticeably distinguishable IR absorption peaks of the polymers, and develop a simple and effective method to identify information about a polymer sample.

[0005] It would be particularly useful to perform IR on a highly localized scale, at various locations on a surface of polymer sample. Such method would be useful to provide compositional and structural information at different incident locations of the polymer sample.

BRIEF SUMMARY OF THE INVENTION

[0006] The present disclosure relates to a method for identifying information about a polymer sample utilizing an atomic force microscope, the method comprising:

a) providing a polymer sample;

b) contacting a probe of an atomic force microscope with the polymer sample;

c) irradiating at a first wavelength on the polymer sample with a beam of radiation at an incident location;

d) allowing the probe to remain at the incident location; while

e) collecting deflection data from the probe; then

f) repeating the data collection of step e) by varying radiation wavelength to create a spectrum about the polymer sample.

[0007] The method can further comprise a step to compare the spectrum to reference spectrum library of known polymers to determine compositional information about the polymer sample. The method can also comprise a step to move the probe to a different incident location of the polymer sample to determine structural information about the polymer sample.

[0008] The present disclosure also relates to a use of an atomic force microscope for determining information about a polymer sample, wherein the atomic force microscope is set up with a radiation source.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] **Figure 1** Illustrates an exemplary PTIR technique as used herein (as disclosed in US 8,001,830).

[0010] **Figure 2** Shows morphology of an Impact Polypropylene Copolymer (ICP) measured by PTIR, where three different incident locations of the ICP were selected.

[0011] **Figure 3** Shows PTIR spectra on a sample of ICP acquired at three selected incident locations: the core (a), intermediate layer (b) and matrix of polypropylene (c).

[0012] **Figure 4** Shows applicability of compositional analysis utilizing PTIR through polypropylene homopolymer and three ethyelene-propylene copolymer samples with known ethylene content.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0013] Selected embodiments will now be described in more detail, but this description is not meant to foreclose other embodiments within the broader scope of this disclosure.

[0014] Each of the following terms written in singular grammatical form: "a" , "an", and "the" as used herein, may also refer to, and encompass, a plurality of the stated entity or object, unless otherwise specifically defined or stated herein, or, unless the context clearly dictates otherwise.

[0015] The "polymer sample" as used herein refers to a polymer in the form of films and having two or more of the same or different mer units. A "homopolymer" is a polymer

having mer units that are the same. A "copolymer" is a polymer having two or more mer units that are different from each other. A "terpolymer" is a polymer having three mer units that are different from each other. "Different" as used to refer to mer units indicates that the mer units differ from each other by at least one atom or are different isomerically. Accordingly, the definition of copolymer, as used herein, includes terpolymers and the like. An "ethylene polymer" or "ethylene copolymer" is a polymer or copolymer comprising at least 50 mole% ethylene derived units, a "propylene polymer" or "propylene copolymer" is a polymer or copolymer comprising at least 50 mole% propylene derived units, and so on.

[0016] Throughout the illustrative description, the examples, and the appended claims, a numerical value of a parameter, feature, object, or dimension, may be stated or described in terms of a numerical range format. It is to be fully understood that the stated numerical range format is provided for illustrating implementation of the embodiments disclosed herein, and is not to be understood or construed as inflexibly limiting the scope of the embodiments disclosed herein.

[0017] It is to be understood that the various embodiments disclosed herein are not limited in their use to the details of the order or sequence, and number, of steps or procedures, and sub-steps or sub-procedures, of operation or implementation of embodiments of the methods or to the details of type, composition, construction, arrangement, and order thereof, set forth in the following illustrative description and examples, unless otherwise specifically stated herein. The identification method disclosed herein can be practiced or implemented according to various other alternative forms and in various other alternative ways.

[0018] PTIR spectroscopy utilizes an AFM probe to detect the local thermal expansion caused by IR absorption of certain wavelengths, and therefore achieve the resolution below the diffraction limit. The IR source of variable wavelength infrared (IR) radiation is broadly and continuously tunable over the "fingerprint region" that allows for highly sensitive discrimination and even identification of polymers. As used herein, the "fingerprint region" covers wavelength ranges from roughly 7 to 17 μm, with the richest region for chemical information being above 10 μm.

[0019] In any embodiment, the PTIR spectroscopy system shown schematically in Figure 1, as disclosed in US 8,001,830, can be used in the present invention. The polymer sample 3 is mounted on a ZnSe prism 8, or prism made from other suitable materials, which does not absorb the radiation of interest. A pulsed IR source 9 is directed into the prism. The prism is made at an angle such that the beam is in Total Internal Reflection in order for the beam to be propagative in the sample and evanescent in the air, thus only the polymer sample is

significantly exposed to the laser radiation. The probe 2 which is standard commercialized Silicon or Silicon Nitride AFM probes suitable for contact mode imaging, is placed at a point on the sample by the scanner 6. The tip of the AFM probe 4 is in constant contact with the polymer sample, the deflection caused by the contact is controlled by feedback electronics 5. Both the vertical and lateral deflection signal as well as the feedback signal, are may be monitored at computer 7.

[0020] Identification of unknown polymer materials is a critical need for research and industry. The present invention provides a method for identifying information about a polymer sample, the method comprising:

a) providing a polymer sample;

b) contacting a probe of an atomic force microscope with the polymer sample;

c) irradiating at a first wavelength on the polymer sample with a beam of radiation at an incident location;

d) allowing the probe to remain at the incident location; while

e) collecting deflection data from the probe; then

f) repeating the data collection of step e) by varying radiation wavelength to create a spectrum about the polymer sample.

[0021] The method can be used to identify unknown polymer materials with sub-micron resolution. Due to the thermal expansion of the polymer materials caused by the absorption of incident radiation at a specific wavelength, a thermal expansion will occur in the polymer sample within the total volume of the radiation. In the meanwhile, the AFM probe is in contact with the sample at a specific incident location, the AFM probe will collect such thermal expansion in form of an exciting oscillation of such area of the sample. In this way, the absorption data can be collected. Particularly, the method can be used to obtain IR spectra from highly localized regions/domains of a polymer sample, allowing discrimination and/or identification of the composition of a polymer sample.

[0022] In any embodiment, the method can further comprise a step to compare the spectrum to reference spectrum library of known polymers to determine compositional information about the polymer sample.

[0023] In a series of preferred embodiments of the invention, the first wavelength of the radiation is about 900 cm^{-1}, and the radiation wavelength can be varied within a range from 900 to 1500 cm^{-1}.

[0024] In any embodiment, the method can further comprise a step to move the probe to a different incident location on the polymer sample to determine structural information about

the polymer sample. The present method can be used for mapping the variations in IR absorption over a wider area of a polymer sample, in particular those polymers with complex structures, such as multiple-phase structures, core-shell structures, by imaging the energy absorbed at one or more wavelengths. From these absorption maps, chemometric maps of a polymer sample can be established. Specifically, chemometric maps can indicate the localization of different polymer materials by using localized IR absorption to assign a color, for example, to each major chemical component in an image.

[0025] In a series of preferred embodiments of the invention, the frequency of the radiation can be chosen to be at or near an oscillation frequency of a probe; the spectrum can comprise an absorption spectrum; the beam of radiation in step c) can comprise a radiation from a pulsed infrared source; or the polymer sample can be substantially opaque to infrared light.

[0026] The polymer sample in the present invention can be a homopolymer or copolymer. Preferably, the polymer sample can be an ethylene polymer/copolymer or propylene polymer/copolymer. For example, the polymer sample can be an impact polypropylene copolymer (ICP). Impact polypropylene copolymer (ICP) or high-impact polypropylene (HIPP) is a kind of polymer comprising at least two distinguishable phases: a matrix phase and dispersed phase. In a more preferred embodiment, the impact polypropylene copolymer has polypropylene-rich rubber particles, preferably has a particle size in a range of from 50 to 100 nm.

[0027] In some embodiments, the polymer sample has a sub-micron domain in a scale of from 50 to 100nm, and thus the probe can contact the sub-micron domain of the polymer sample in step b).

[0028] The polymer samples were prepared in a shape of films with a thickness in the range of from 100 to 1000nm, in order to make sure it is substantially opaque to the radiation. The radiation can illuminate from either side of the films. In a preferred embodiment, the radiation source is on the same side of the polymer sample as the probe and can cause radiation to be incident on the top surface of the polymer sample near covering the point of the probe so that the probe can detect the expansion or contraction of the polymer sample as a result of exposure to the radiation.

[0029] In any embodiment, for the purpose of polymer material identification, it is often desirable to compare a PTIR spectrum to those in a reference library. Many commercially available software packages allow the comparison of spectra and suggest candidate materials based on the quality of the match between the reference spectrum and the experimental

spectrum. Because the present method can measure spectra with sub-micron resolution, it is also possible to identify material locally with sub-micron resolution. Thus, the method can further comprise a step to compare the spectrum to reference spectrum library of known polymers to determine compositional information about the polymer sample.

[0030] The present invention also provides a use of an atomic force microscope for determining information about a polymer sample, wherein the atomic force microscope is set up with a radiation source. In any embodiment, the radiation source comprises a radiation from a pulsed infrared source, and the polymer sample may have multi-phase structures. The determined information obtained from such use includes compositional information and/or structural information.

[0031] Now, having described the various features of the identification method, described here in numbered embodiments is:

1. A method for identifying information about a polymer sample utilizing an atomic force microscope, the method comprising:

    a) providing a polymer sample;

    b) contacting a probe of an atomic force microscope with the polymer sample;

    c) irradiating at a first wavelength on the polymer sample with a beam of radiation at an incident location;

    d) allowing the probe to remain at the incident location; while

    e) collecting deflection data from the probe; then

    f) repeating the data collection of step e) by varying radiation wavelength to create a spectrum about the polymer sample.

2. The method of numbered paragraph 1, wherein further comprising: comparing the spectrum to reference spectrum library of known polymers to determine compositional information about the polymer sample.

3. The method of numbered paragraphs 1-2, wherein the first wavelength is about 900 cm-1.

4. The method of numbered paragraphs 1-3, wherein the radiation wavelength in step f) is within a range from 900 to 1500 cm-1.

5. The method of numbered paragraphs 1-4, wherein further comprising: moving the probe to a different incident location of the polymer sample to determine structural information about the polymer sample.

6. The method of numbered paragraphs 1-5, wherein a frequency of the radiation is chosen to be at or near an oscillation frequency of a probe.

7. The method of numbered paragraphs 1-6, wherein the beam of radiation of step c) comprises a radiation from a pulsed infrared source.

8. The method of numbered paragraphs 1-7, wherein the spectrum comprises an absorption spectrum.

9. The method of numbered paragraphs 1-8, wherein the polymer sample is substantially opaque to infrared light.

10. The method of numbered paragraphs 1-9, wherein the polymer sample has a sub-micron domain in a scale of from 50 to 100nm.

11. The method of numbered paragraphs 1-10, wherein the probe contacts the sub-micron domain of the polymer sample in step b).

12. The method of numbered paragraphs 1-11, wherein the polymer sample has multi-phase structures.

13. The method of numbered paragraphs 1-12, wherein the polymer sample comprises an impact polypropylene copolymer.

14. The method of numbered paragraphs 1-13, wherein the impact polypropylene copolymer has polypropylene-rich rubber particles.

15. The method of numbered paragraphs 1-14, wherein the polypropylene-rich rubber particles are in a range of from 50 to 100 nm.

16. A use of an atomic force microscope for determining information about a polymer sample, wherein the atomic force microscope is set up with a radiation source.

17. The use of numbered paragraph 16, wherein the radiation comprises a radiation from a pulsed infrared source.

18. The use of numbered paragraphs 16-17, wherein the polymer sample comprises multi-phase structure.

19. The use of numbered paragraphs 16-18, wherein the information determination comprises compositional information or structural information.

20. The use of numbered paragraphs 16-19, wherein the information determination comprises compositional information and structural information.

Examples

Polymer Samples:

[0032] The ICP, polypropylene homopolymer and three ethyelene-propylene copolymer samples were all commercial grade products available from ExxonMobil Chemical Company, Houston, Texas, USA. Films of the polymer samples with a thickness in the range from 400-700nm were prepared for the PTIR experiments.

Equipment:

[0033] Conventional IR spectra were collected on a Bruker Vertex-70 spectrometer equipped with a DTGS detector and an ATR accessory (ZnSe crystal, 45) at 4 cm^{-1} resolution. PTIR experiments were carried out on a nano-IR PTIR instrument (commercially available from Anasys Instruments).

Identification Procedure:

[0034] The sample was placed on a ZnSe prism and an AFM image was acquired in contact mode using EX-C450 tips (commercially available from Anasys Instruments) to identify the morphology, then the polymer sample was illuminated from underneath by total internal reflection with a Ekspla optical parametric oscillator laser with a 900-1500 cm^{-1} tuning range and a spectral resolution of 4 cm^{-1}. PTIR spectra were generated by measuring with the AFM probe the thermal expansion of the polymer sample as a function of the IR laser wavelength normalized by the laser intensity. IR images were acquired by moving the AFM probe across the surface of the polymer samples while illuminating the polymer sample at a specific wavelength (e.g., 1378 cm^{-1}).

Example 1

[0035] The ICP samples were analyzed by PTIR as shown in Figure 2. There are three different incident locations (Figure 2a) showing structure of the ICP contains polypropylene in the matrix phase and dispersed phase are rubber particles with multilayered core-shell structure, and the cores (a) are rigid whereas the intermediate layers (b) are soft. The core of the particle (c) is quite bright, indicating a high content of polypropylene in the core, which is not clearly understood previously due to lacking of effective identification tools.

[0036] Figure 3 presents a PTIR spectra in the C-H bending region acquired at the color-coded locations in the core (a) and intermediate layer (b) as well as in the matrix (c), respectively. The peak at about 1378 cm^{-1} is the symmetric C-H bending of methyl group, characteristic of polypropylene, whereas both polypropylene and polyethlene in the ICP contribute to the symmetric C-H bending band of methylene group, observed at about 1460 cm^{-1}. From the relative intensity of the 1378 band, it shows that all three phases contain significant amounts of polypropylene, which provide structural information about the ICP as well.

[0037] To determine compositional information about the ICP, polypropylene and polyethylene with known IR spectrum in a reference library are used to correlate the ethylene content in the copolymers with the peak area ratio of the CH_2 and CH_3 bending bands at about 1460 and about 1378 cm^{-1}, respectively. The intermediate layers (b) and cores of

rubber particles (a) as well as the matrix (c) in multiple microtomed films of the ICP sample were analyzed by PTIR, and the composition of each incident location was analyzed.

[0038] Lambert-Beer's Law was used to perform the calculation of C_2 content: $A=a\cdot b\cdot c$, where A is the IR absorbance, "a" is the extinction coefficient, "b" is the optical path length (sample thickness), and "c" is the molar concentration. Peaks at 1378 cm^{-1} and 1460 cm^{-1} wavelengths were selected to as the peak at 1378 cm^{-1} is the δ_s ($-CH_3$) and 1460 cm^{-1} is the δ ($-CH_2-$) band. The ratio of the peak intensity of 1460 cm^{-1} peak over 1378 cm^{-1} peak was used to derive the C2 wt% to eliminate the sample thickness factor. The correlation should follow: $r=C+(C_E/C_p)\cdot k$, $C_E+C_p=1$, where r is the peak intensity ratio, C_E and C_p are the wt% of C2 and C3, C and k are fitting parameters. The compositioal information is listed in Table 1.

Table 1. Composition of Different Incident Locations on the ICP

Incident Location	Average Ethylene Content (wt.%)
Matrix (c)	2.0
Intermediate layer (b)	38.8
Core (a)	17.2

[0039] It can be seen that the ethylene content in the matrix is only 2.0 %, which is quite low and demonstrates that the matrix is polypropylene. The intermediate layer has a high ethylene content of about 39 wt%, showing it is ethylene-propylene random copolymers (EPR) and/or ethylene-propylene block copolymers (EbP). The cores contain only about 17 wt% ethylene units, which confirms the above finding by PTIR mapping, that the cores in the rubber particles are rich in polyproylene.

Example 2

[0040] Polypropylene homopolymer and three ethyelene-propylene copolymer samples with known ethylene content were analyzed by PTIR, and the average peak ratios, each from at least 15 replicates, are shown in Figure 4. The results shows applicability of the present method can be used in compostion analysis of a polymer sample.

[0041] It will be apparent to those skilled in the art that modifications may be made to embodiments described herein without departing from the spirit and scope of the invention. Other features not mentioned in the specification, but known to one skilled in the art may be integrated as well without departing from the spirit and scope of the present invention. In particular, many of the embodiments may be used independent of the PTIR technique with

alternative embodiments of AFM-based IR spectroscopy or more generally in IR spectroscopy and imaging, all within the scope of the invention. The methods and uses of the present invention should therefore be afforded the broadest possible scope under examination. As such, the invention taught herein by specific examples is limited only by the scope of the claims that follow.

CLAIMS

What is claimed is:

1. A method for identifying information about a polymer sample utilizing an atomic force microscope, the method comprising:
   a) providing a polymer sample;
   b) contacting a probe of an atomic force microscope with the polymer sample;
   c) irradiating at a first wavelength on the polymer sample with a beam of radiation at an incident location;
   d) allowing the probe to remain at the incident location; while
   e) collecting deflection data from the probe; then
   f) repeating the data collection of step e) by varying radiation wavelength to create a spectrum about the polymer sample.

2. The method of claim 1, wherein further comprising: comparing the spectrum to reference spectrum library of known polymers to determine compositional information about the polymer sample.

3. The method of claim 1, wherein the first wavelength is about 900 cm^{-1}.

4. The method of claim 1, wherein the radiation wavelength in step f) is within a range from 900 to 1500 cm^{-1}.

5. The method of claim 1, wherein further comprising: moving the probe to a different incident location of the polymer sample to determine structural information about the polymer sample.

6. The method of claim 1, wherein a frequency of the radiation is chosen to be at or near an oscillation frequency of the probe.

7. The method of claim 1, wherein the beam of radiation in step c) comprises a radiation from a pulsed infrared source.

8. The method of claim 2, wherein the spectrum comprises an absorption spectrum.

9. The method of claim 1, wherein the polymer sample is substantially opaque to infrared light.

10. The method of claim 1, wherein the polymer sample has a sub-micron domain in a scale of from 50 to 100nm.

11. The method of claim 10, wherein the probe contacts the sub-micron domain of the polymer sample in step b).

12. The method of claim 1, wherein the polymer sample has multi-phase structures.

13. The method of claim 1, wherein the polymer sample comprises an impact polypropylene copolymer.

14. The method of claim 13, wherein the impact polypropylene copolymer has polypropylene-rich rubber particles.

15. The method of claim 14, wherein the polypropylene-rich rubber particles are in a range of from 50 to 100 nm.

16. A use of an atomic force microscope for determining information about a polymer sample, wherein the atomic force microscope is set up with a radiation source.

17. The use of claim 16, wherein the radiation source comprises a radiation from a pulsed infrared source.

18. The use of claim 16, wherein the polymer sample has multi-phase structures.

19. The use of claim 16, wherein the information determination comprises compositional information or structural information.

20. The use of claim 16, wherein the information determination comprises compositional information and structural information.

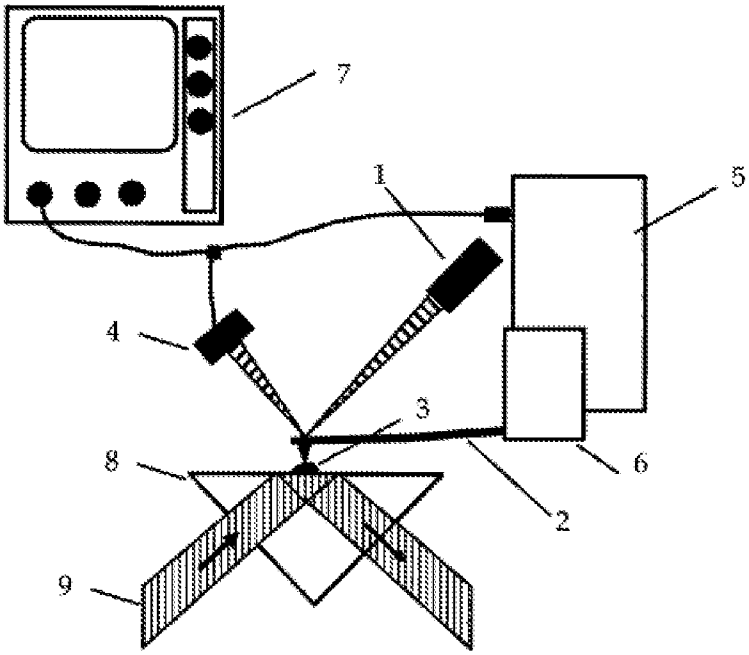


Figure 1

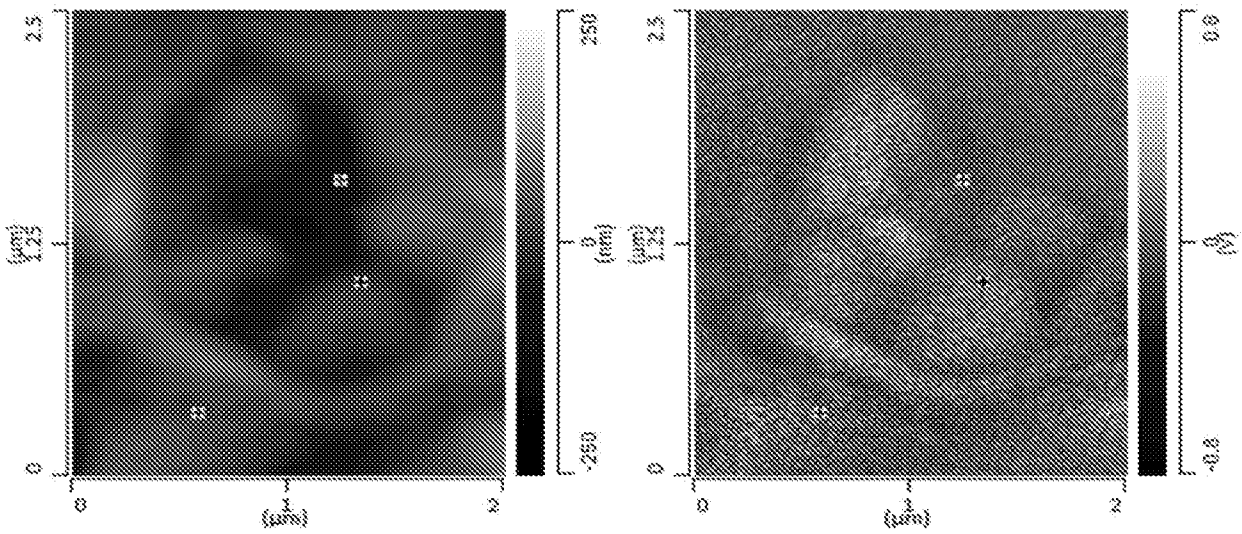


Figure 2

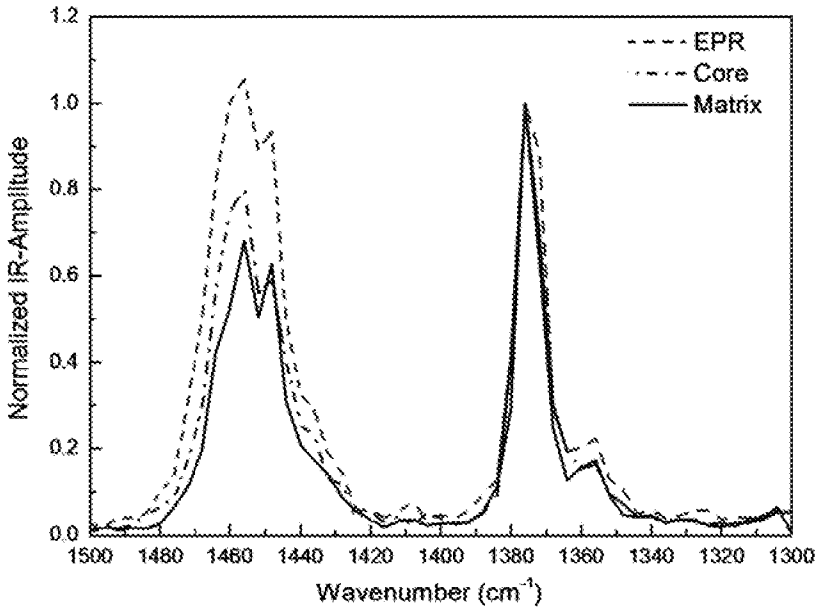


Figure 3

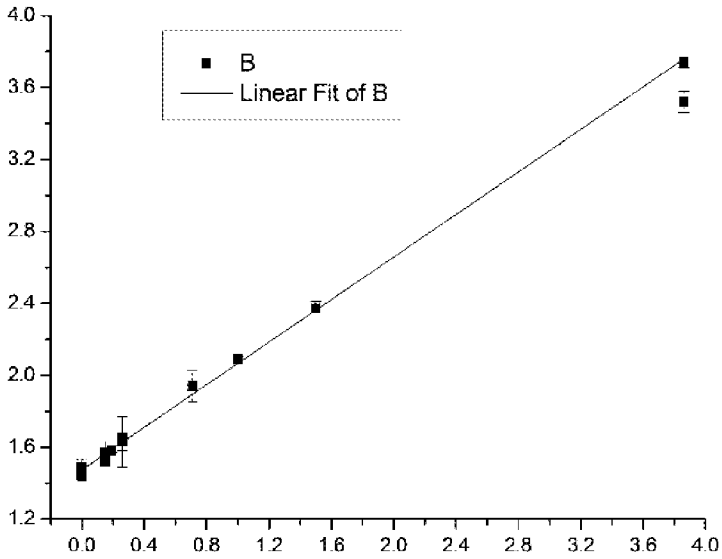


Figure 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2015/094547

A. CLASSIFICATION OF SUBJECT MATTER

G01Q 60/24(2010.01)i

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)

G01Q60, G01N3

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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

CNKI, CNABS, CNTXT, WPI, EPODOC, atomic force microscope, AFM, deflection, IR radiation, wavelength

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/0283428 A1 (ANASYS INSTRUMENTS, INC.) 17 November 2011 (2011-11-17) description, paragraphs[0007], [0010]-[0013], and figure 2	1-20
A	US 2003/0115939 A1 (MITSUBISHI DENKI KK) 26 June 2003 (2003-06-26) the whole document	1-20
A	CN 103645348 A (INST ELECTRICAL ENG CHINESE ACAD SCI) 19 March 2014 (2014-03-19) the whole document	1-20
A	CN 103792393 A (CHANG CHUN APPLIED CHEM INST CHINESE ACAD) 14 May 2014 (2014-05-14) the whole document	1-20

☐ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
30 June 2016	**08 August 2016**

Name and mailing address of the ISA/CN	Authorized officer
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Facsimile No. **(86-10)62019451**	Telephone No. **(86-10)62085649**

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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