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(54) METHOD FOR SYNTHESIZING GRAPHENE-BASED NANOCOMPOSITE AND GRAPHENE-BASED NANOCOMPOSITE SYSTNESIZED USING THE METHOD

(71) Applicant: **Industry-Academic Cooperation Foundation, Yonsei University**, Seoul (KR)

(72) Inventors: **KwangBum Kim**, Goyang-si (KR); **JongPil Jegal**, Daejeon-si (KR); **Hyun Kyung Kim**, Chungju-si (KR); **SeungBum Yoon**, Seoul (KR); **MyeongSeong Kim**, Seoul (KR)

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CPC *C25D 5/54* (2013.01)

USPC **428/323**; 428/408; 205/159

(57) **ABSTRACT**

A method of rapidly fabricating a graphene-based nanocomposite using oxidation-reduction and a graphene-based nanocomposite fabricated by the same method. A solution in which a graphene oxide is dispersed is prepared. A source material for a metal oxide is added into the solution in which the graphene oxide is dispersed. A nanocomposite is formed by forming the metal oxide on at least one surface of graphene that is reduced using oxidation-reduction between the graphene oxide and the source material for the metal oxide. The reduction voltage of the source material for the metal oxide is 1.0 V or less.

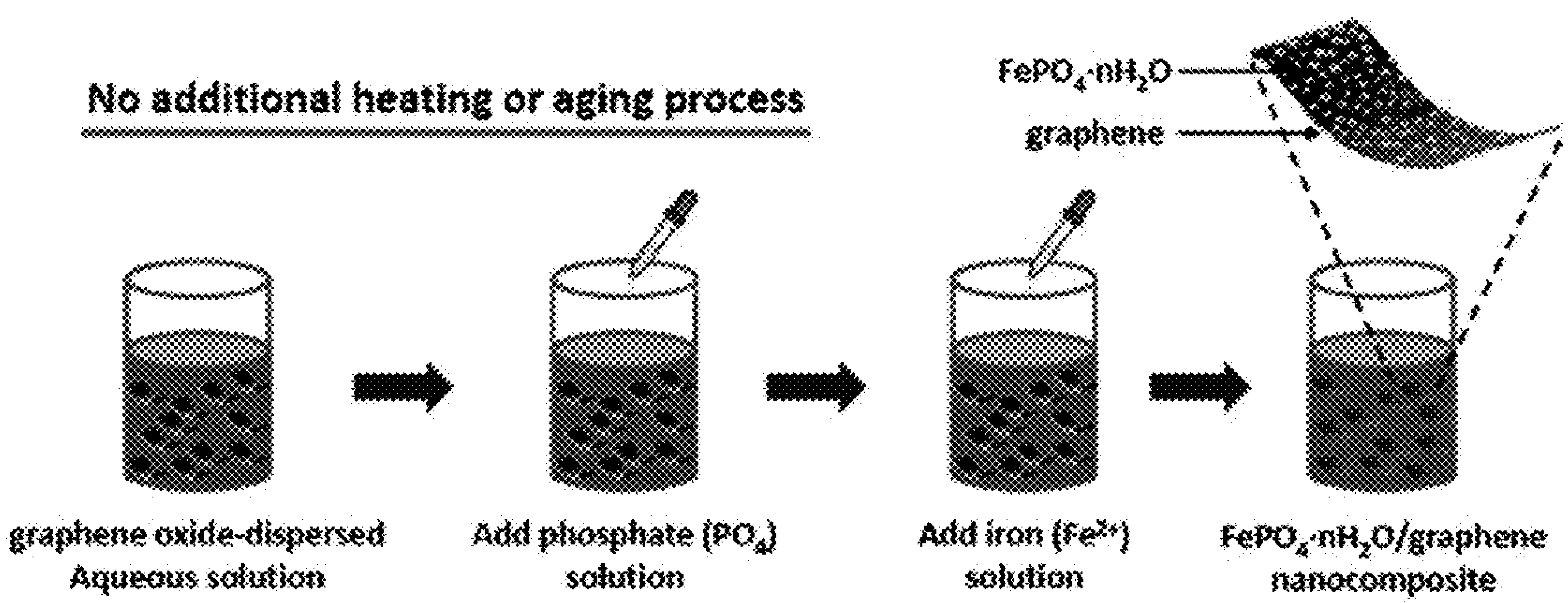


Fig.1

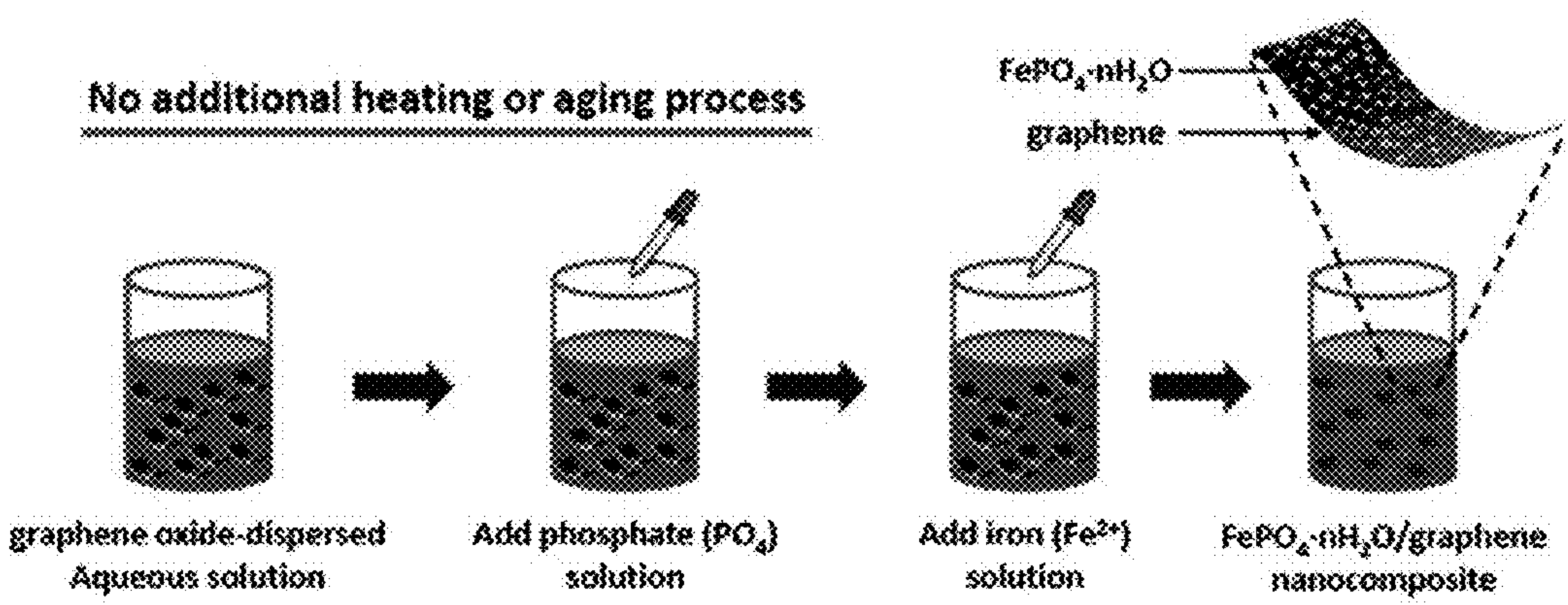

No additional heating or aging process
$FePO_4 \cdot nH_2O$
graphene
graphene oxide-dispersed Aqueous solution
Add phosphate (PO_4) solution
Add iron (Fe^{2+}) solution
$FePO_4 \cdot nH_2O$/graphene nanocomposite

Fig. 2

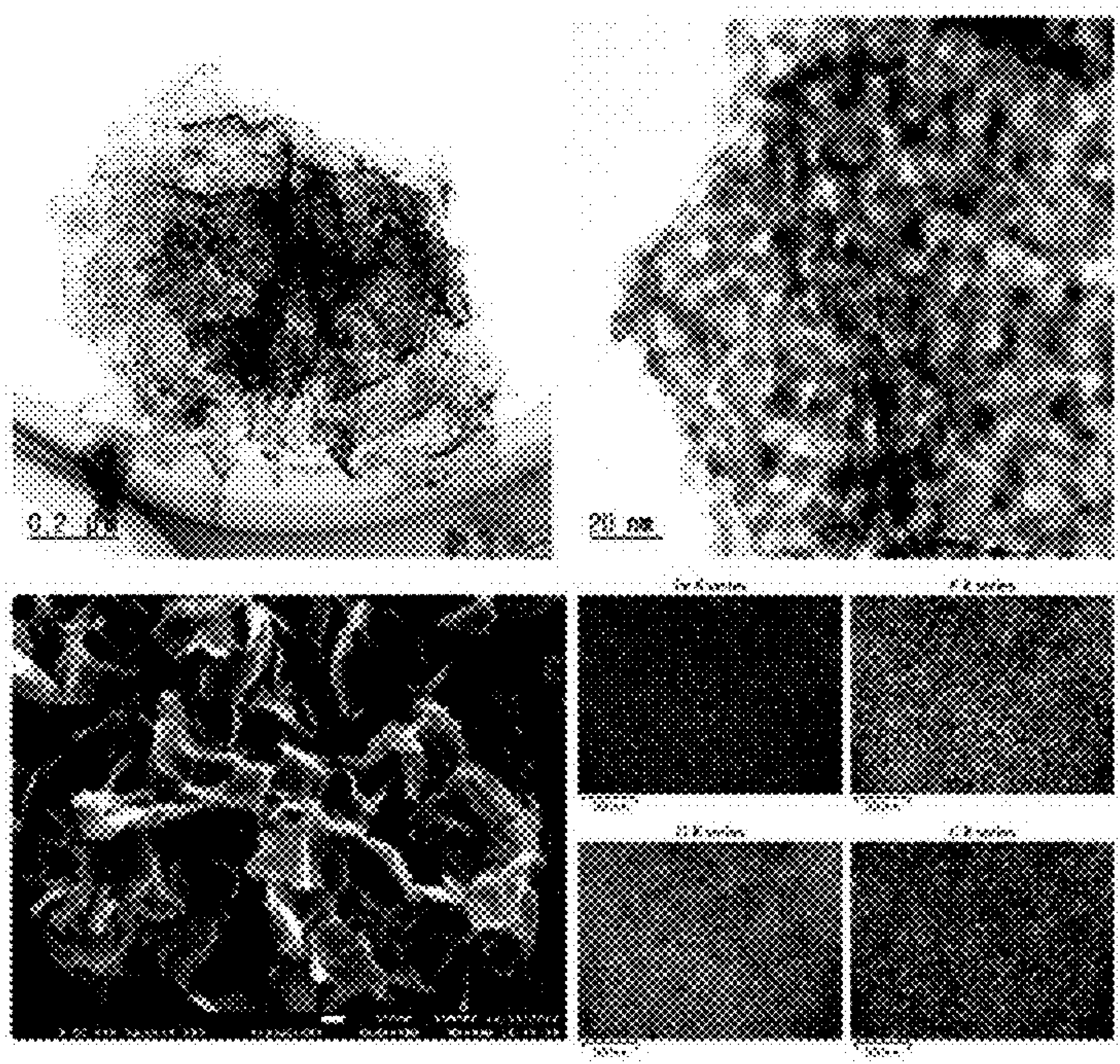


Fig. 3

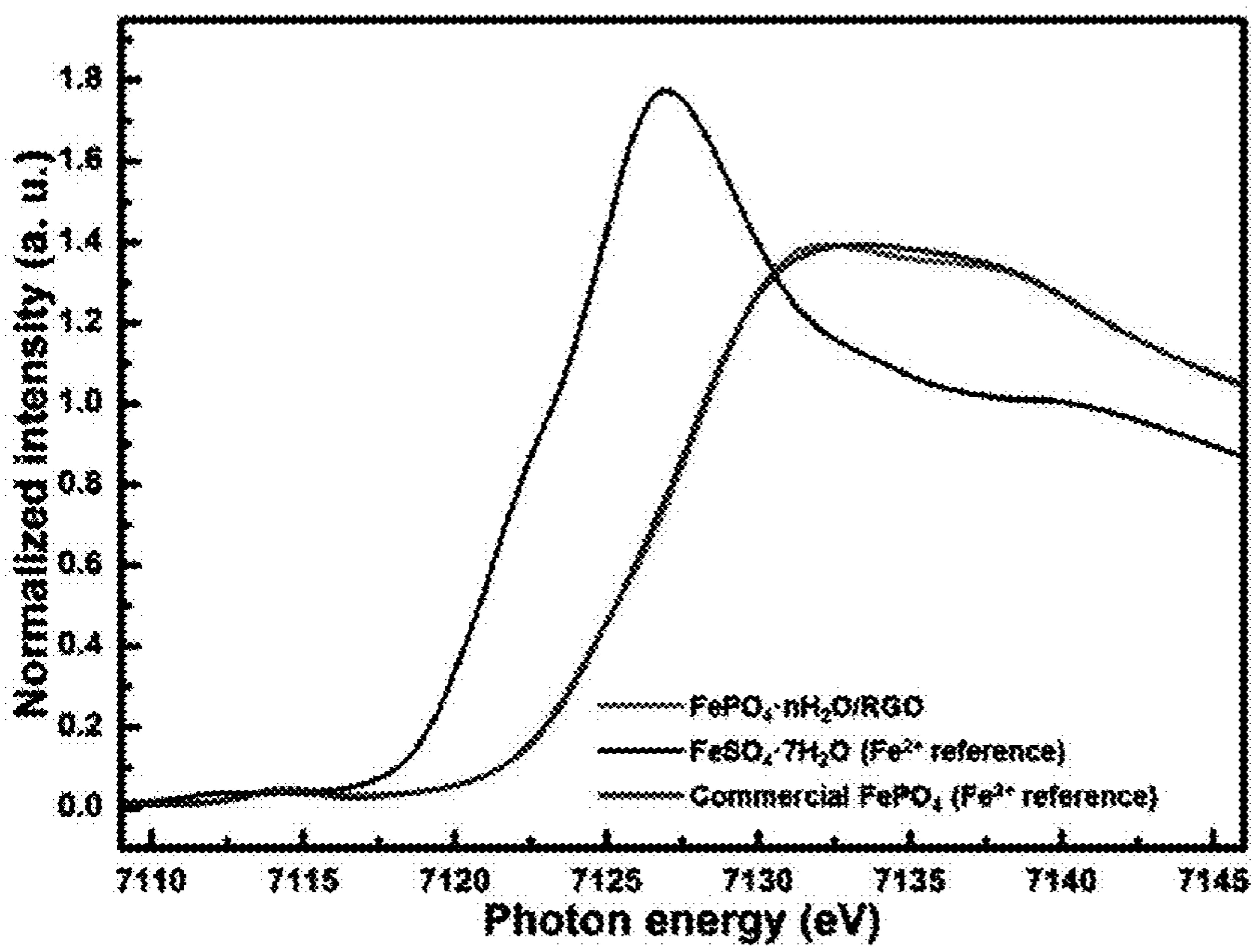

Normalized intensity (a. u.)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
7110
7115
7120
7125
7130
7135
7140
7145
Photon energy (eV)
$FePO_4 \cdot nH_2O$/RGO
$FeSO_4 \cdot 7H_2O$ (Fe^{2+} reference)
Commercial $FePO_4$ (Fe^{2+} reference)

Fig. 4a

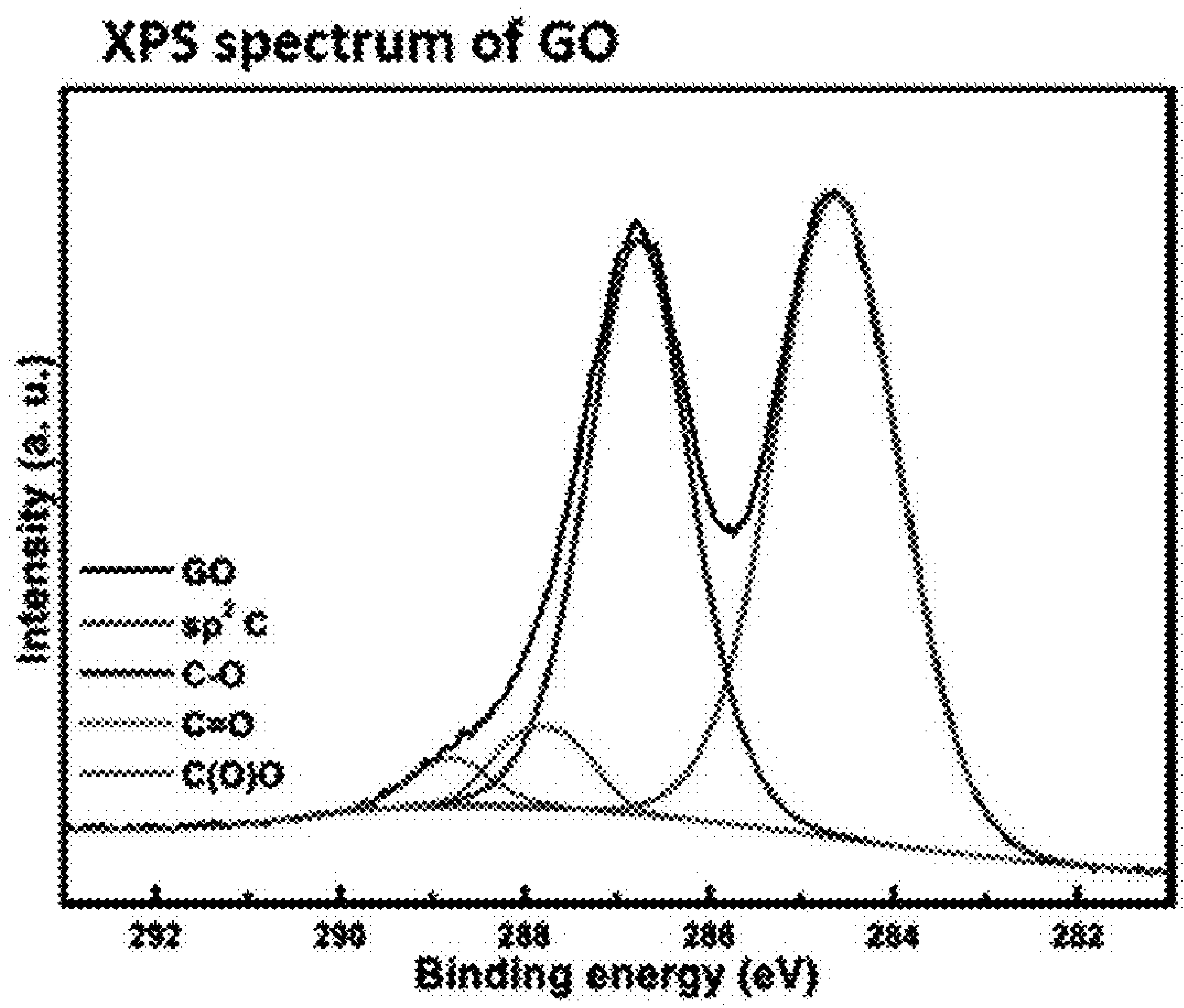

XPS spectrum of GO
Intensity (a. u.)
GO
sp² C
C-O
C=O
C(O)O
292
290
288
286
284
282
Binding energy (eV)

Fig. 4b

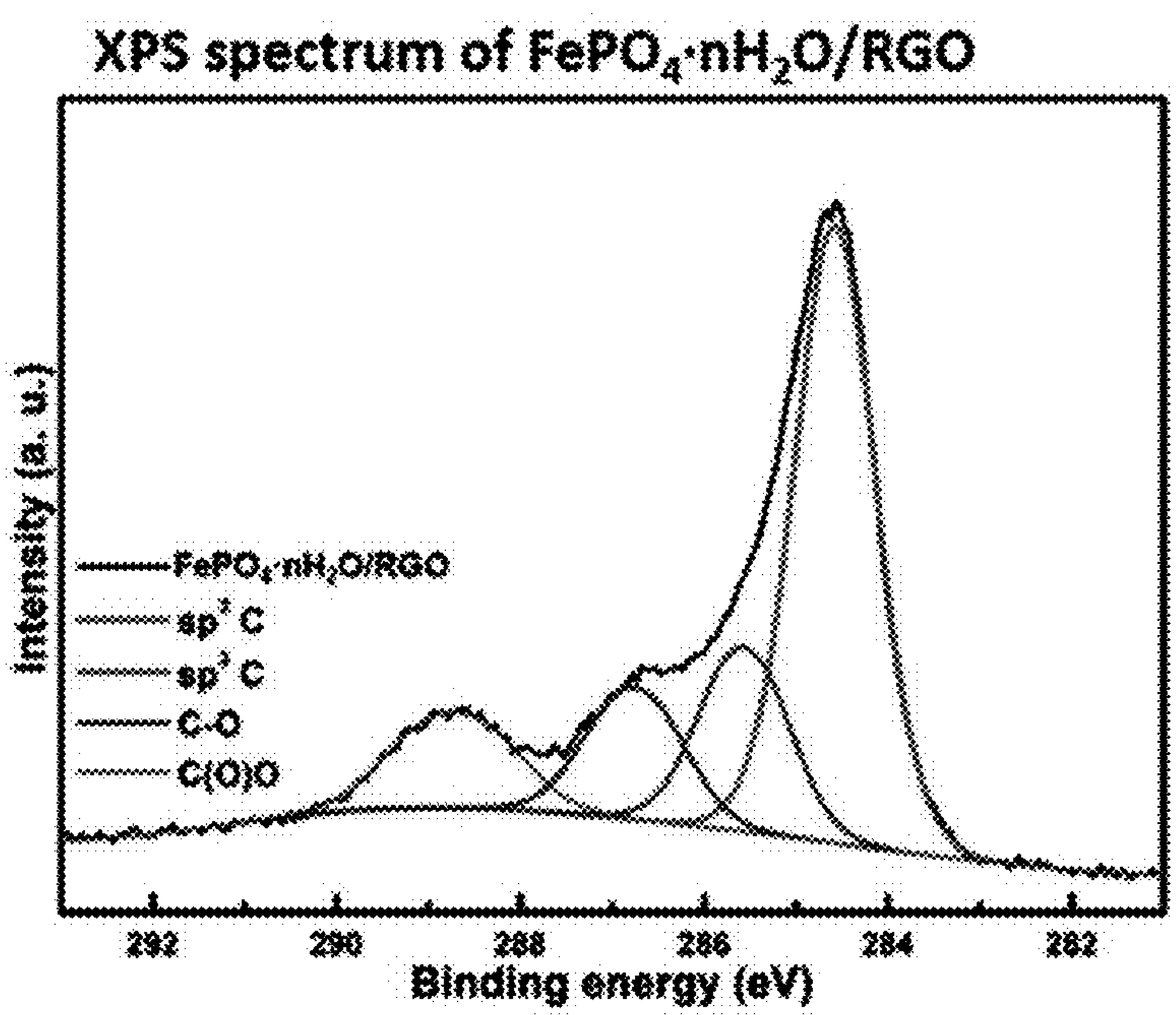
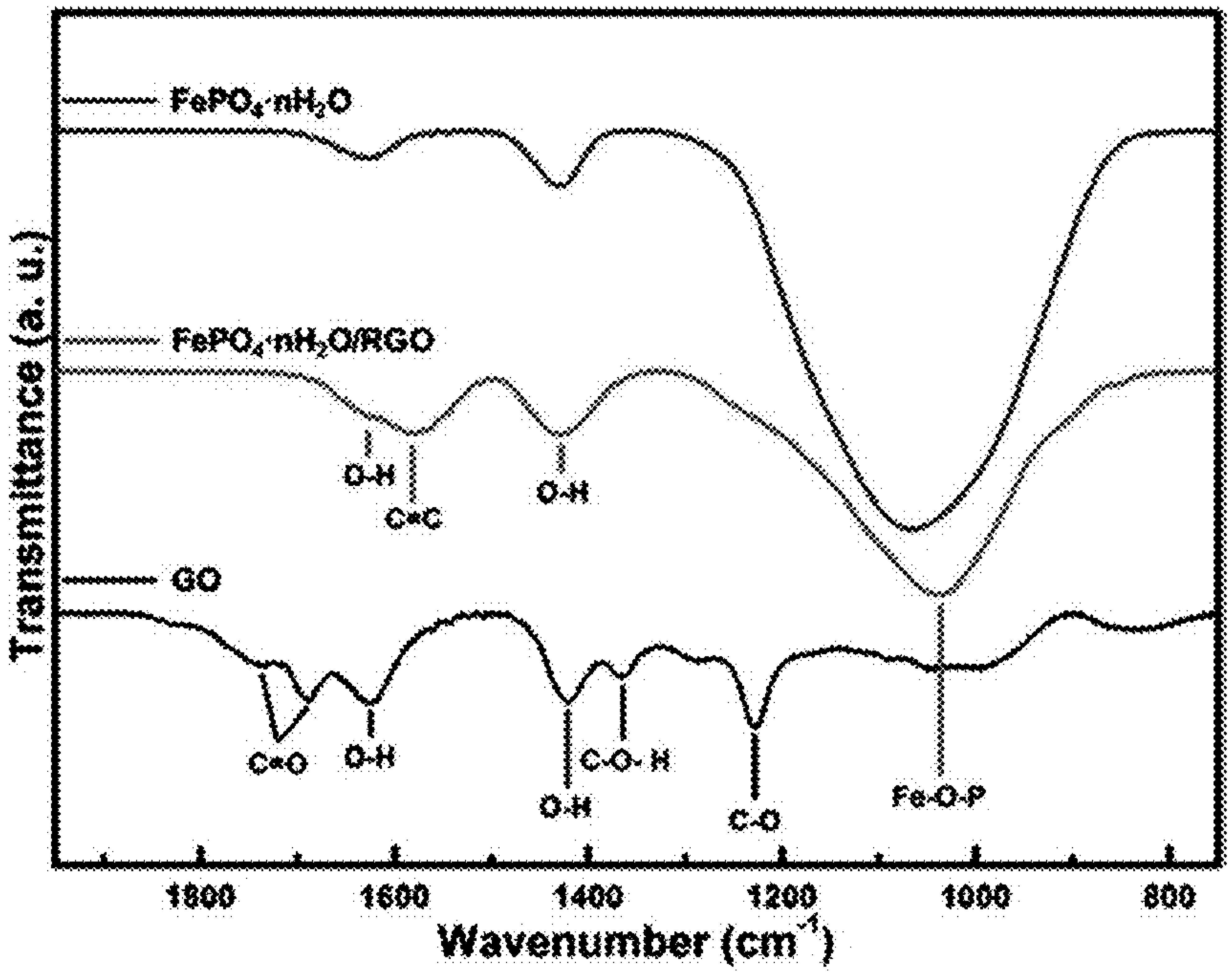
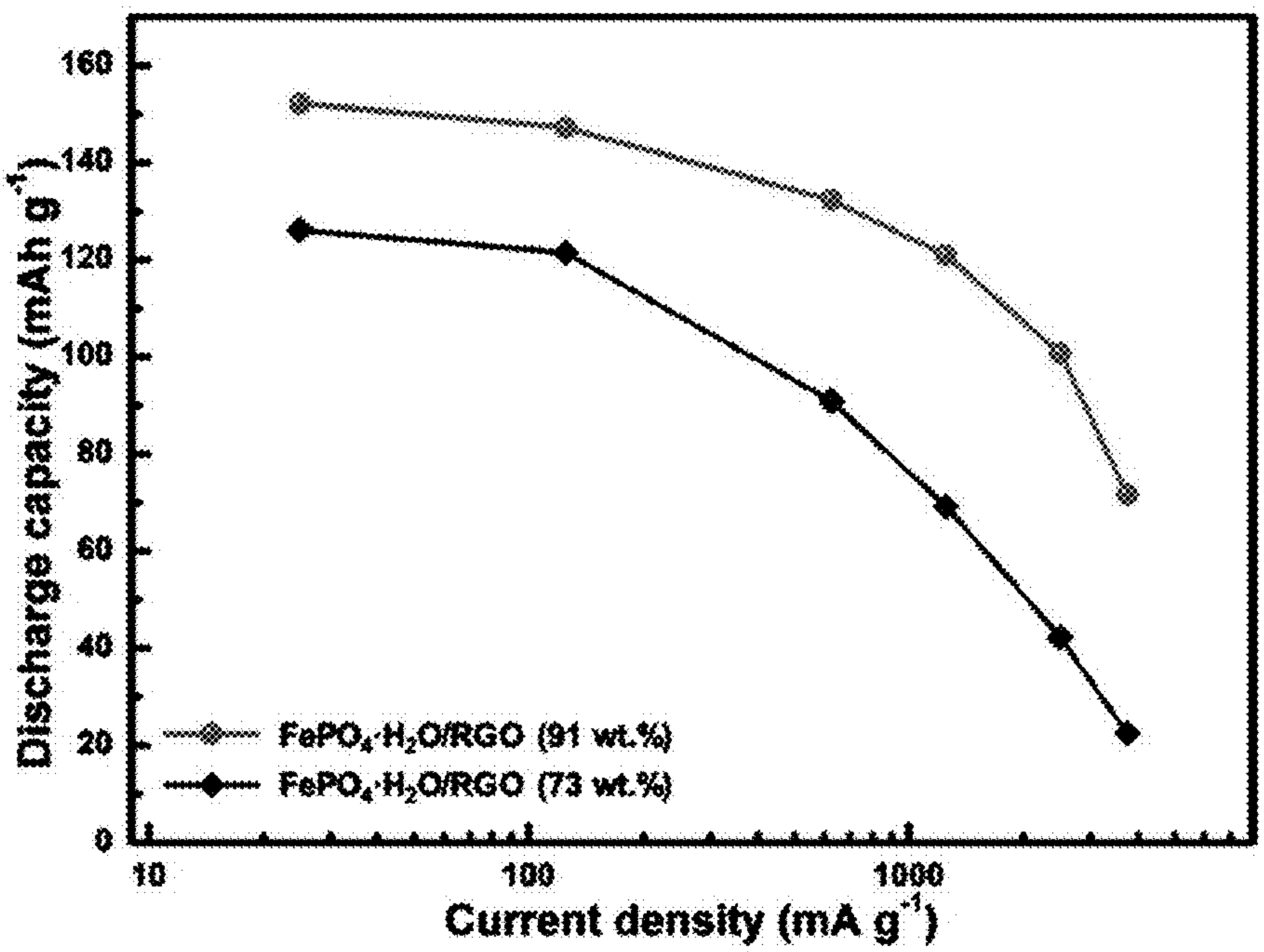

XPS spectrum of FePO₄·nH₂O/RGO
Intensity (a. u.)
FePO₄·nH₂O/RGO
sp² C
sp³ C
C-O
C(O)O
292
290
288
286
284
282
Binding energy (eV)

Fig. 5



FePO4·nH2O
FePO4·nH2O/RGO
GO
O-H
C=C
O-H
C=O
O-H
O-H
C-O-H
C-O
Fe-O-P
Transmittance (a. u.)
1800
1600
1400
1200
1000
800
Wavenumber (cm-1)

Fig. 6



160
140
120
100
80
60
40
20
0
Discharge capacity (mAh g-1)
FePO4·H2O/RGO (91 wt.%)
FePO4·H2O/RGO (73 wt.%)
10
100
1000
Current density (mA g-1)

Fig. 7a

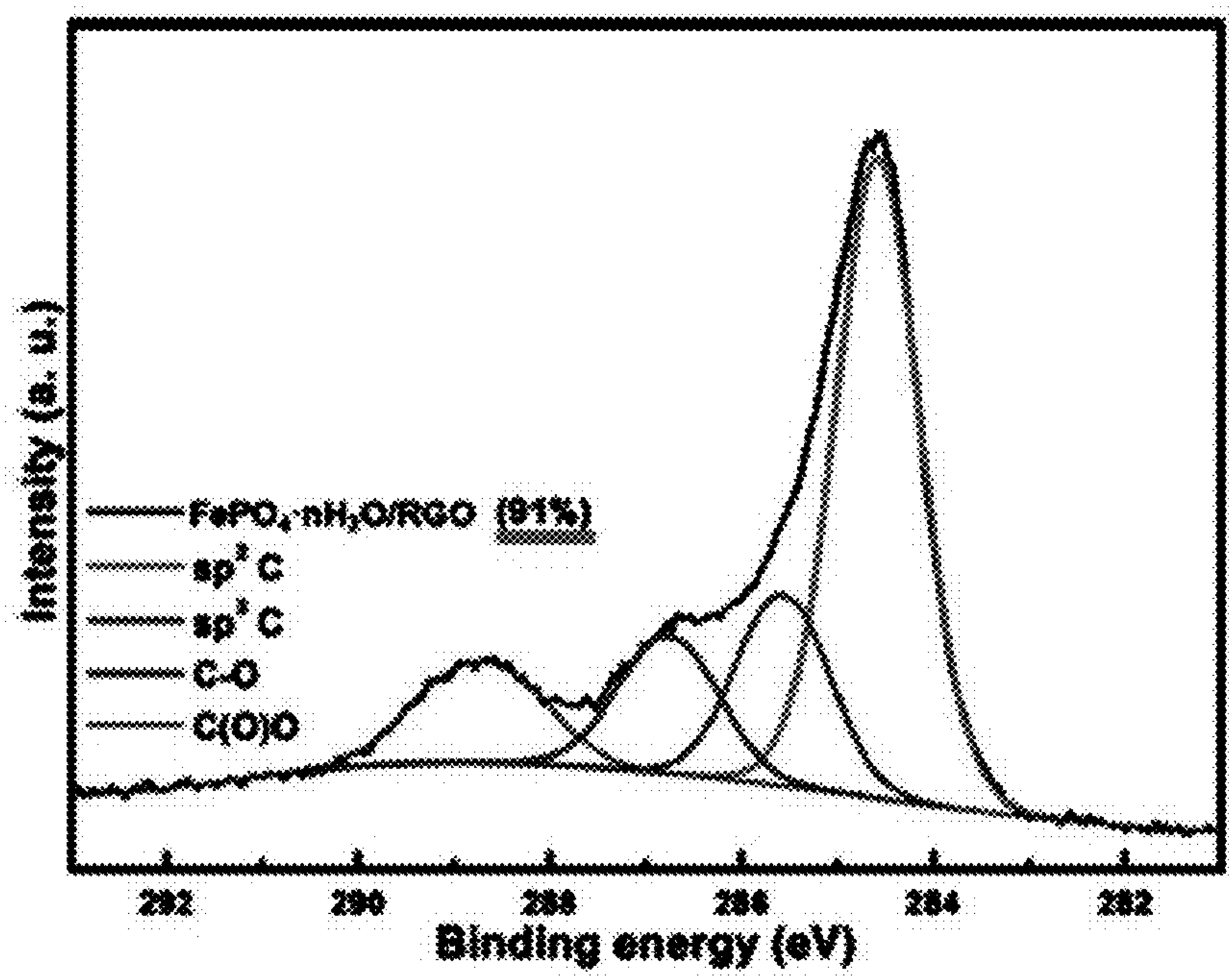

Intensity (a. u.)
FePO4·nH2O/RGO (81%)
sp2 C
sp3 C
C-O
C(O)O
292
290
288
286
284
282
Binding energy (eV)

Fig. 7b

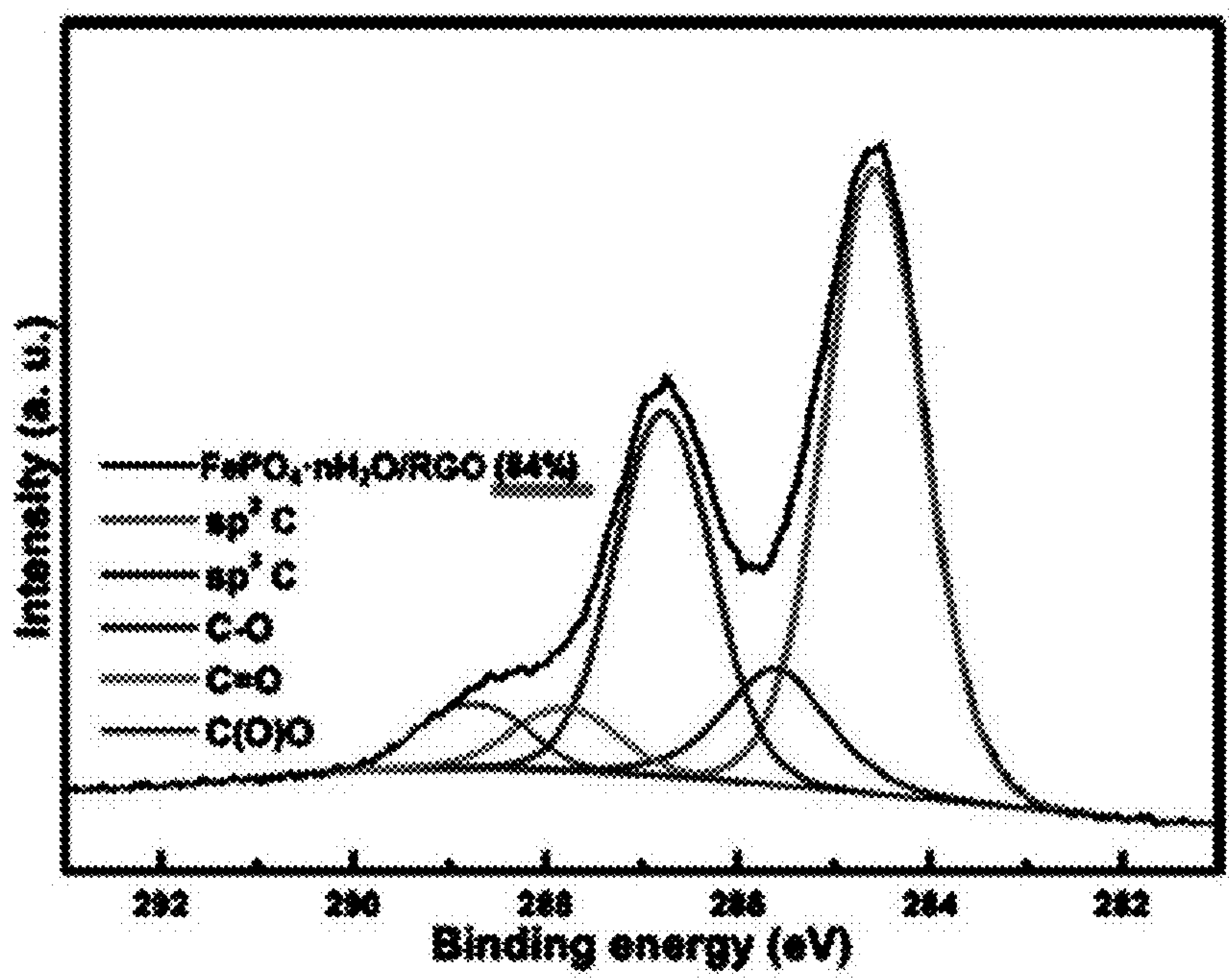

Intensity (a. u.)
FePO4·nH2O/RGO (84%)
sp2 C
sp3 C
C-O
C=O
C(O)O
292
290
288
286
284
282
Binding energy (eV)

Fig. 7c

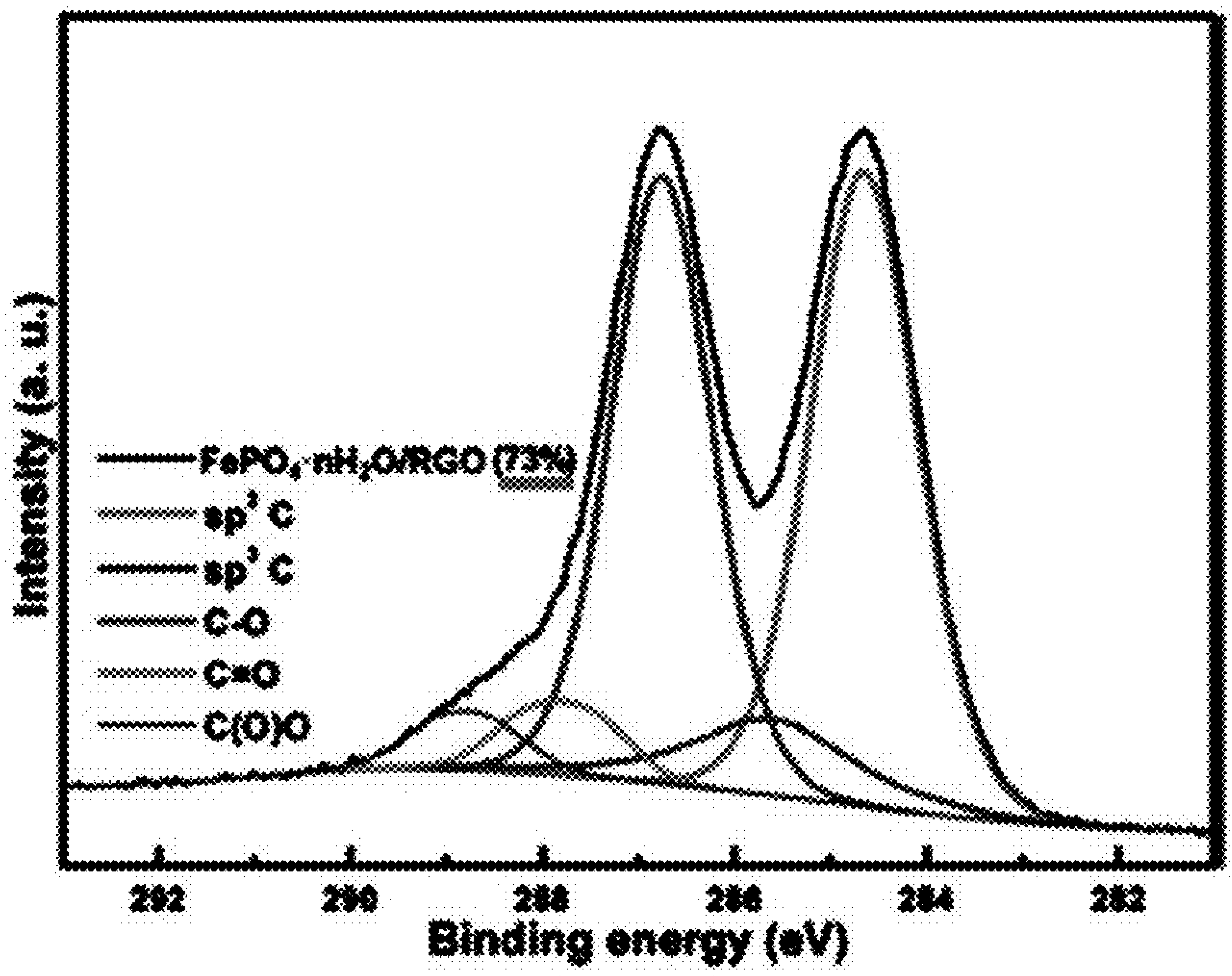

Intensity (a. u.)
FePO4·nH2O/RGO (73%)
sp2 C
sp3 C
C-O
C=O
C(O)O
292
290
288
286
284
282
Binding energy (eV)

Fig. 8a

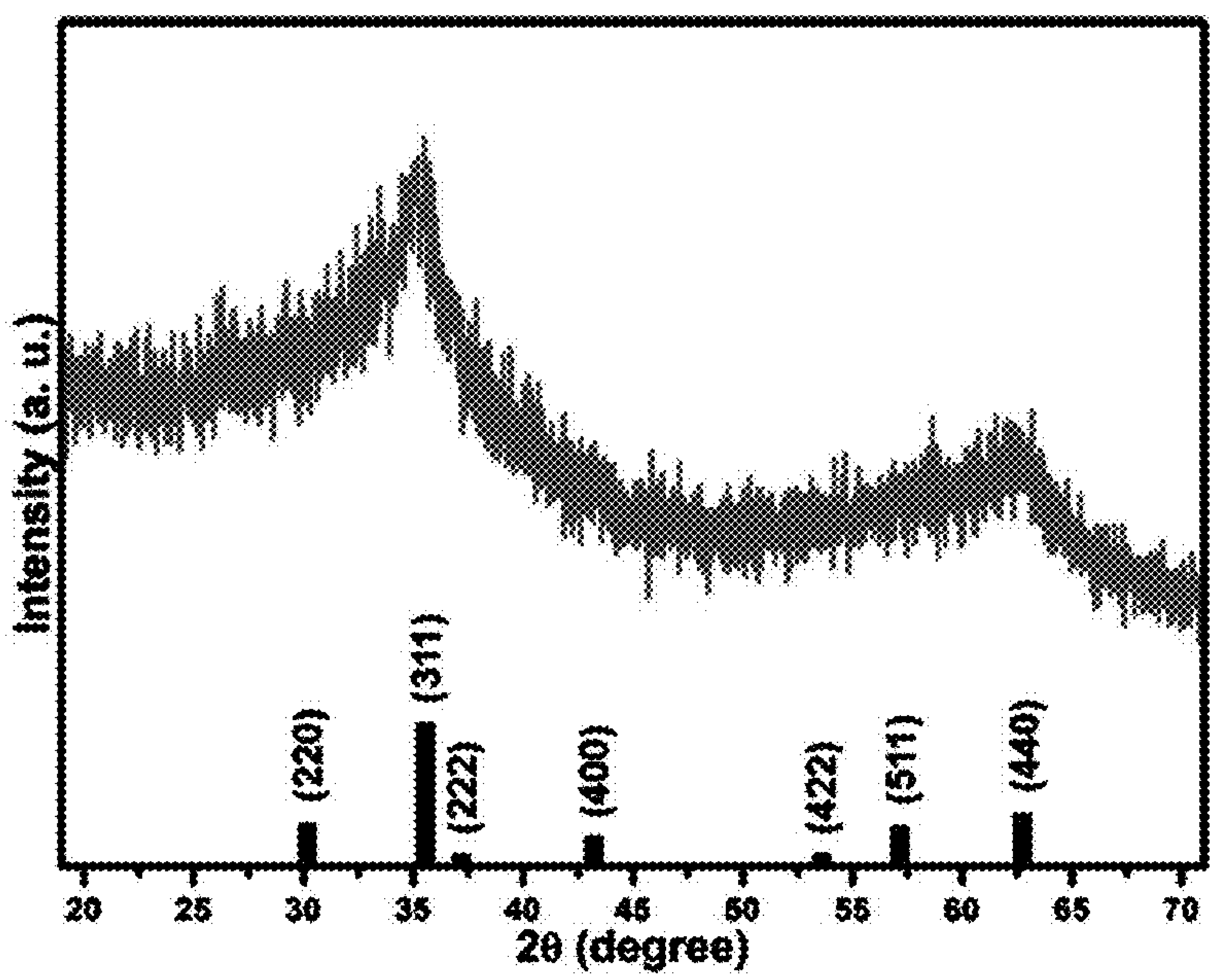

Intensity (a. u.)
(220)
(311)
(222)
(400)
(422)
(511)
(440)
20
25
30
35
40
45
50
55
60
65
70
2θ (degree)

Fig. 8b

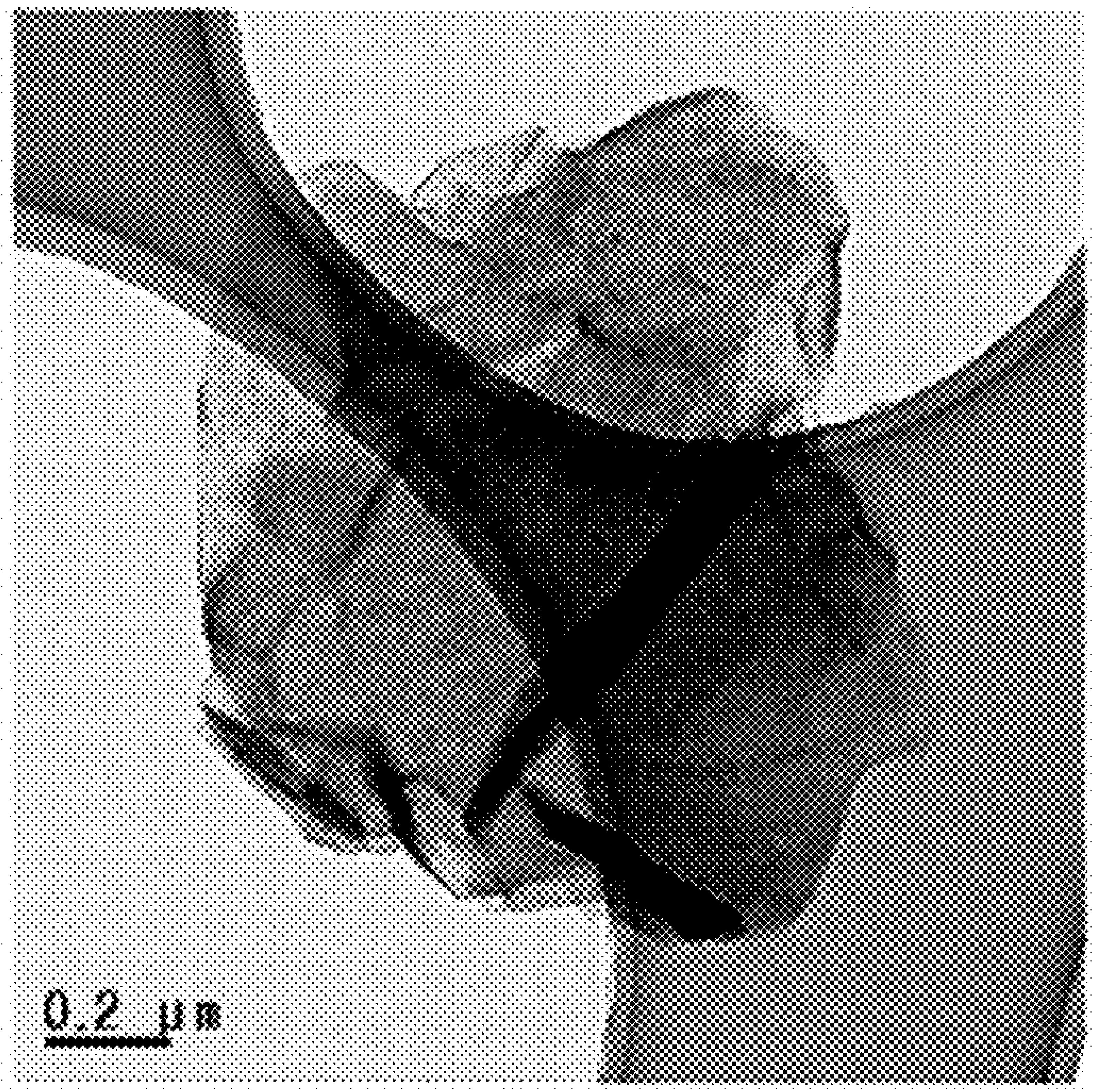


Fig. 8c

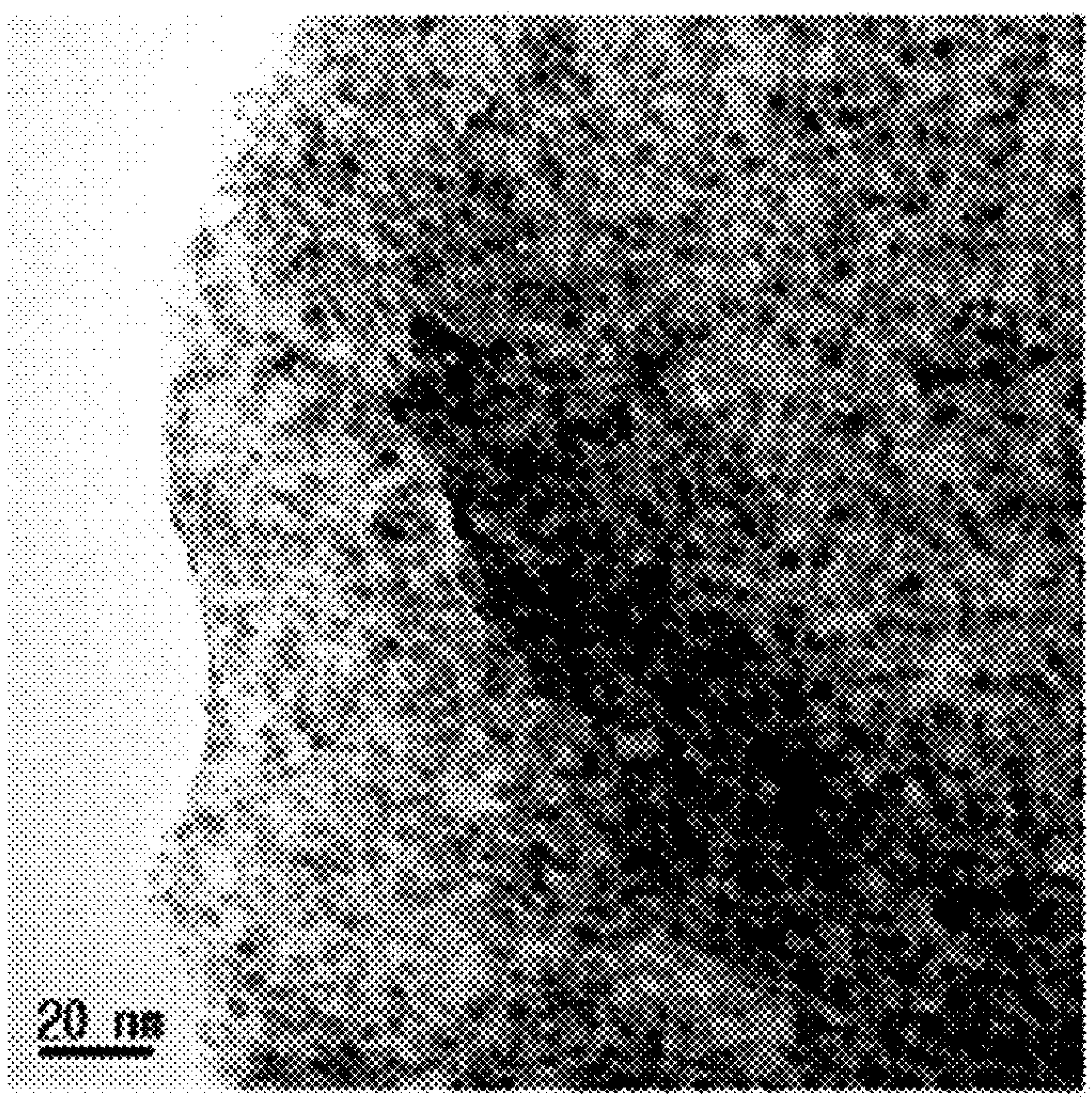


Fig. 9a

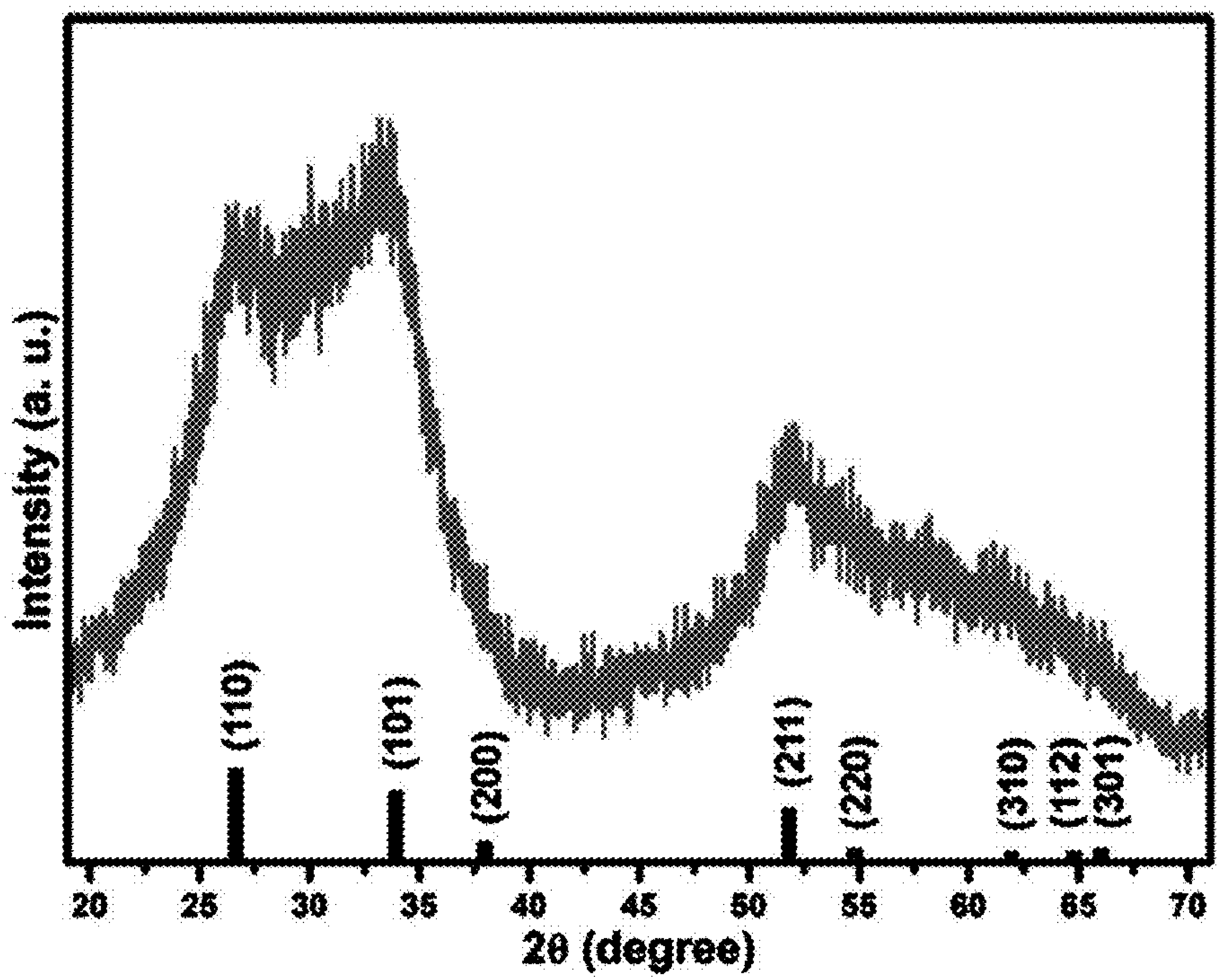

Intensity (a. u.)
(110)
(101)
(200)
(211)
(220)
(310)
(112)
(301)
20
25
30
35
40
45
50
55
60
65
70
2θ (degree)

Fig. 9b

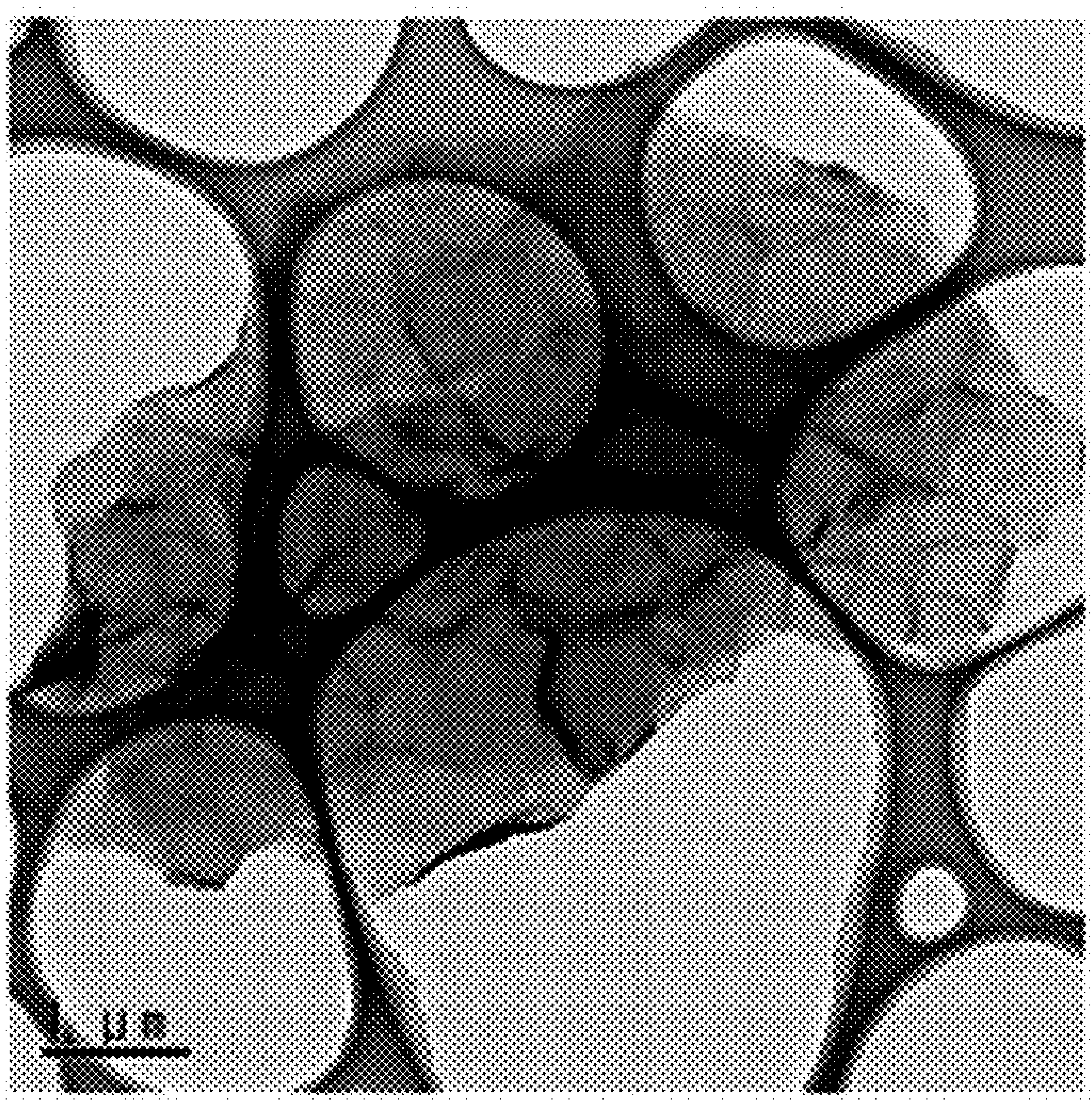
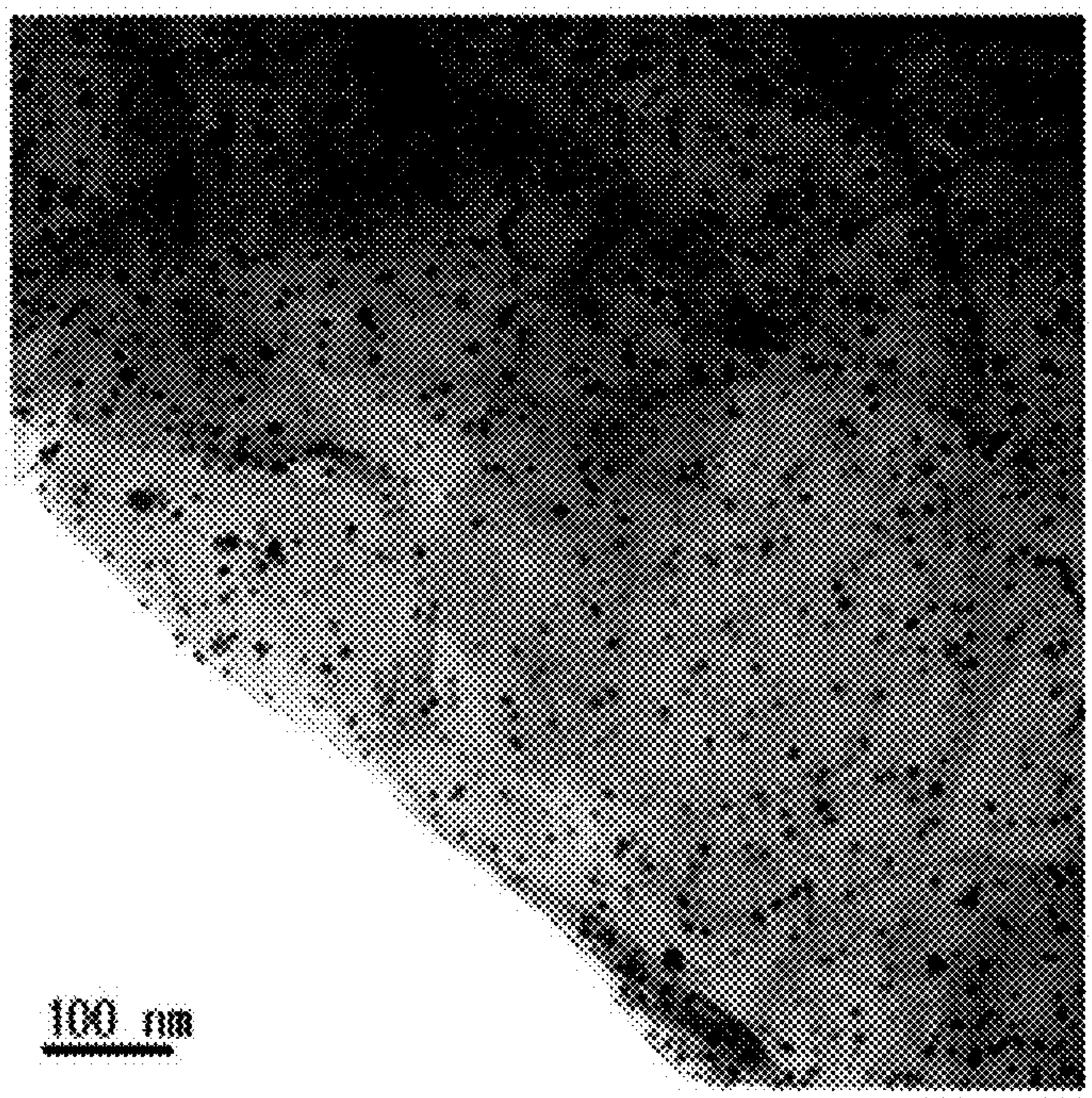

1 μm

Fig. 9c



METHOD FOR SYNTHESIZING GRAPHENE-BASED NANOCOMPOSITE AND GRAPHENE-BASED NANOCOMPOSITE SYSTNESIZED USING THE METHOD

CROSS REFERENCE TO RELATED APPLICATION

[0001] The present application claims priority from Korean Patent Application Number 10-2013-102981 filed on Aug. 28, 2013, the entire contents of which are incorporated herein for all purposes by this reference.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to a method of fabricating a graphene-based nanocomposite, and more particularly, to a method of rapidly fabricating a graphene-based nanocomposite using oxidation-reduction and a graphene-based nanocomposite fabricated by the same method.

[0004] 2. Description of Related Art

[0005] Graphene is gaining attention from both academic and industrial fields as a material that will become a basis for future industries due to its unique properties, such as a high electrical conductivity of about 10^6 Scm^{-1} and a wide specific surface area 2630 m^2g^{-1}, which are superior to those of existing carbon materials. Graphene-based nanocomposites are also in the spotlight as future materials that will substitute for existing materials in a variety of fields, such as catalysts, electronic materials, energy materials and biomedical materials, since their characteristics are superior to those of existing materials graphene. Therefore, many research groups in the world are actively attempting to obtain technologies for synthesizing graphene-based nanocomposites that have superior characteristics.

[0006] Uniform distribution between graphene and an active material is important in order to use superior properties of graphene in nanocomposites. For this, a method that introduced heterogeneous nucleation of an active material on the surface of graphene has been regarded as the most reliable, and many studies have been done on this method. According to the reported studies, applied processes include the use of toxic additives, are complicated due to a multiplicity of steps, require a long synthesizing time ranging from several days to several months, or consume a large amount of energy.

[0007] Therefore, although graphene-based nanocomposites have superior characteristics, it is difficult to commercially distribute graphene-based nanocomposites because of high processing costs and the environmental burden. Accordingly, it is required to develop technology for synthesizing graphene-based nanocomposites having superior characteristics in an environmental friendly process at a low cost.

[0008] The information disclosed in the Background of the Invention section is provided only for better understanding of the background of the invention and should not be taken as an acknowledgment or any form of suggestion that this information forms a prior art that would already be known to a person skilled in the art.

BRIEF SUMMARY OF THE INVENTION

[0009] The present invention has been made to solve the foregoing problems with the related-art method of synthesizing a graphene-based nanocomposite which is complicated, consumes a large amount of energy, or requires a long amount of time, and an object of the present invention is to provide a method and apparatus for fabricating a graphene-based nanocomposite from a variety of metal oxides, such as a metal phosphorus oxide, and graphene at room temperature for a short time without introducing additional energy for the synthesis of the graphene-based nanocomposite.

[0010] Another object of the present invention is to provide a method and apparatus for simply forming a nanocomposite from a metal oxide and a graphene material for a short time.

[0011] In an aspect of the present invention, provided is a method of fabricating a graphene-based nanocomposite. The method includes the following steps of: preparing a solution in which a graphene oxide is dispersed; adding a source material for a metal oxide into the solution in which the graphene oxide is dispersed; and forming a nanocomposite by forming the metal oxide on at least one surface of graphene that is reduced using oxidation-reduction between the graphene oxide and the source material for the metal oxide. The reduction voltage of the source material for the metal oxide is 1.0 V or less.

[0012] The reduction voltage of the source material for the metal oxide may be 0.8 V or less.

[0013] The metal oxide may be one selected from the group consisting of a metal phosphorus oxide, an iron oxide and a tin oxide.

[0014] The metal oxide may be one selected from the group consisting of $FePO_4$, Fe_3O_4 and SnO_2.

[0015] The graphene-based nanocomposite may have a diameter of 10 μm or less.

[0016] In another aspect of the present invention, provided is a graphene-based nanocomposite comprising graphene and a metal oxide formed on one surface of the graphene. The graphene-based nanocomposite is fabricated by a process that includes the following steps of: preparing a solution in which a graphene oxide is dispersed; adding a source material for a metal oxide into the solution in which the graphene oxide is dispersed; and forming a nanocomposite by forming the metal oxide on at least one surface of graphene that is reduced using oxidation-reduction between the graphene oxide and the source material for the metal oxide. The reduction voltage of the source material for the metal oxide is 1.0 V or less.

[0017] The reduction voltage of the source material for the metal oxide may be 0.8 V or less.

[0018] The metal oxide may be one selected from the group consisting of a metal phosphorus oxide, an iron oxide and a tin oxide.

[0019] The metal oxide may be one selected from the group consisting of $FePO_4$, Fe_3O_4 and SnO_2.

[0020] According to the method of fabricating a graphene-based nanocomposite as set forth above, it is possible to simply fabricate a metal oxide/graphene nanocomposite for a short time.

[0021] The methods and apparatuses of the present invention have other features and advantages which will be apparent from, or are set forth in greater detail in the accompanying drawings, which are incorporated herein, and in the following Detailed Description of the Invention, which together serve to explain certain principles of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] FIG. **1** is a view schematically showing process steps of fabricating a graphene-based nanocomposite according to an exemplary embodiment of the present invention;

[0023] FIG. **2** shows TEM pictures of a $FePO_4.nH_2O$/graphene nanocomposite fabricated according to an exemplary embodiment of the present invention;

[0024] FIG. **3** is a graph showing the XANES of the $FePO_4.nH_2O$/graphene nanocomposite fabricated according to an exemplary embodiment of the present invention;

[0025] FIG. **4**A and FIG. **4**B are graphs showing the XPS data of a graphene oxide and the $FePO_4.nH_2O$/graphene nanocomposite;

[0026] FIG. **5** is a graph showing FT-IR data of the graphene oxide and the $FePO_4.nH_2O$/graphene nanocomposite;

[0027] FIG. **6** is a graph showing variations in capacity according to the current density of the $FePO_4.nH_2O$/graphene nanocomposite;

[0028] FIG. **7**A, FIG. **7**B and FIG. **7**C are graphs showing the XPS data of the $FePO_4.nH_2O$/graphene nanocomposite according to the content of $FePO_4.nH_2O$;

[0029] FIG. **8**A is a graph showing the XRD data of a Fe_3O_4/graphene nanocomposite synthesized using the oxidation-reduction according to an exemplary embodiment of the present invention;

[0030] FIG. **8**B and FIG. **8**C show TEM pictures of the Fe_3O_4/graphene nanocomposite synthesized using the oxidation-reduction according to an exemplary embodiment of the present invention;

[0031] FIG. **9**A is a graph showing the XRD data of a SnO_2/graphene nanocomposite synthesizedusing the oxidation-reduction according to an exemplary embodiment of the present invention; and

[0032] FIG. **9**B and FIG. **9**C are TEM pictures of the SnO_2/graphene nanocomposite synthesized using the oxidation-reduction according to an exemplary embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0033] Reference will now be made in detail to a graphene-based nanocomposite that includes graphene and a metal oxide formed on one surface of the graphene and a method of fabricating the same according to the present invention, embodiments of which are illustrated in the accompanying drawings and described below.

[0034] FIG. **1** is a view schematically showing process steps of fabricating a graphene-based nanocomposite according to an exemplary embodiment of the present invention.

[0035] As shown in FIG. **1**, a solution having a graphene oxide dispersed therein is prepared by dispersing graphene oxide pieces in a solvent. It is preferred that the graphene oxide pieces be provided at a size that corresponds to the size of graphene nanocomposite pieces that are to be formed. Although the size of a graphene-based nanocomposite is not specifically limited, it is determined by the size of graphene, which is typically several micrometers.

[0036] Subsequently, an oxide to be formed on graphene is inputted into the solution in which the graphene oxide is dispersed. According to an exemplary embodiment of the present invention, a phosphoric acid (PO_4^{3-}) solution and a solution containing iron ions (Fe^{2+}) were inputted into the graphene oxide-dispersed solution in order to form a metal phosphorus oxide on the graphene surface.

[0037] Then, the graphene oxide in the graphene oxide-dispersed solution forms reduced graphene thin films through reduction and the metal ions Fe^{2+} are oxidized into Fe^{3+} ions, thereby forming $FePO_4.nH_2O$, which is subsequently deposited on at least one surface of the reduced graphene thin films. The application of the method according to an exemplary embodiment of the present invention directly forms a metal oxide/graphene nanocomposite without any heating or aging step.

[0038] Since the source material for a metal oxide and the graphene oxide must undergo oxidation-reduction according to the present invention, the reducing potential of the source material for the metal oxide must be 1.0 V or less. It is preferred that the reduction voltage of the source material for the metal oxide be 0.8 V or less for a smooth and rapid reaction.

[0039] Since the applicability increases with the size of metal oxide particles decreasing, the size of the metal oxide particles according to an exemplary embodiment of the present invention is preferably 10 nm, and more preferably, 5 nm or less.

[0040] FIG. **2** shows transmission electron microscopy (TEM) pictures of a $FePO_4.nH_2O$/graphene nanocomposite fabricated according to an exemplary embodiment of the present invention. Referring to the top pictures of FIG. **2**, it is appreciated that $FePO_4.nH_2O$ nanoparticles are uniformly distributed on the graphene surface. According to this embodiment, the size of precipitated $FePO_4.nH_2O$ particles is about 5 nm. In addition, referring to the bottom left picture of FIG. **2**, it is appreciated that the nanocomposite was uniformly synthesized in a long range. Furthermore, referring to bottom right pictures of FIG. **2**, it is appreciated that Fe, P, O and C are uniformly distributed in the nanocomposite.

[0041] FIG. **3** is a graph showing the X-ray absorption near edge structure (XANES) of the $FePO_4.nH_2O$/graphene nanocomposite fabricated according to an exemplary embodiment of the present invention. The XANES is an analysis method that can identify the oxidation state of a material. The XANES can qualitatively analyze the oxidation value since the peak position changes depending on the oxidation value of the material. As shown in FIG. **3**, $FePO_4.nH_2O$ was synthesized from $FeSO_4.7H_2O$, the oxidation of which is 2+. It is appreciated that the oxidation value of synthesized $FePO_4.nH_2O$ is 3+ like $FePO_4$ that is commercially available. This indicates that Fe ions were oxidized through the oxidation-reduction according to an exemplary embodiment of the present invention.

[0042] FIG. **4**A is a graph showing the X-ray photoelectron spectroscopy (XPS) data of a graphene oxide. As shown in FIG. **4**A, it is appreciated that a plurality of functional groups such as C—O, C═O and C(O)O is present on the surface by the Hummers method applied for the oxidation of graphene. FIG. **4**B is a graph showing the XPS data of the $FePO_4.nH_2O$/graphene nanocomposite. As shown in FIG. **4**B, it is appreciated that the number of C—O functional groups was significantly reduced after the reduction of the graphene oxide. This indicates that the graphene oxide was reduced into the reduced graphene oxide (RGO) due to the oxidation-reduction between the graphene oxide and the source material for the metal oxide.

[0043] FIG. **5** is a graph showing Fourier transform infrared spectroscopy (FT-IR) data of the graphene oxide and the $FePO_4.nH_2O$/graphene nanocomposite. Comparing the data of the graphene oxide with the data of $FePO_4$-nH_2O/graphene nanocomposite, it is appreciated that the functional groups were removed from the surface of the graphene oxide after the synthesis of the nanocomposite. This indicates that the graphene oxide (GO) was reduced into graphene (RGO) after the oxidation-reduction.

[0044] FIG. **6** is a graph showing variations in capacity according to the current density of the $FePO_4.nH_2O$/graphene nanocomposite. In general, the high-rate discharge characteristic of a nanocomposite decreases when the content of an active material in the nanocomposite increases. However, as shown in FIG. **6**, it is appreciated that the high-rate discharge characteristic of a nanocomposite according to an exemplary embodiment of the present invention does not decrease with the increased content of the active material.

[0045] FIG. **7**A, FIG. **7**B and FIG. **7**C are graphs showing the XPS data of the $FePO_4.nH_2O$/graphene nanocomposite according to the content of $FePO_4.nH_2O$. FIG. **7**A shows the case in which the $FePO_4.nH_2O$ content is 91%, FIG. **7**B shows the case in which the $FePO_4.nH_2O$ content is 84%, and FIG. **7**C shows the case in which the $FePO_4.nH_2O$ content is 73%. As shown in FIG. **7**A to FIG. **7**C, it is appreciated that C—O functional groups decreased with the increased content of the active material. This makes it possible to predict the electrical conductivity of the $FePO_4.nH_2O$/graphene nanocomposite that was synthesized through the oxidation-reduction increases with the increased content of the active material of graphene (RGO). Therefore, it is possible to freely control the electrical conductivity of the $FePO_4.nH_2O$/graphene nanocomposite by adjusting the content of the active material of graphene (RGO).

[0046] FIG. **8**A is a graph showing the XRD data of a Fe_3O_4/graphene nanocomposite synthesized using the oxidation-reduction according to an exemplary embodiment of the present invention, and FIG. **8**B and FIG. **8**C show TEM pictures of the Fe_3O_4/graphene nanocomposite synthesized using the oxidation-reduction according to an exemplary embodiment of the present invention. FIG. **9**A is a graph showing the XRD data of a SnO_2/graphene nanocomposite synthesized using the oxidation-reduction according to an exemplary embodiment of the present invention, and FIG. **9**B and FIG. **9**C are TEM pictures of the SnO_2/graphene nanocomposite synthesized using the oxidation-reduction according to an exemplary embodiment of the present invention. As shown in FIG. **8**A to FIG. **9**C, it is possible to easily fabricate a nanocomposite, such as a Fe_3O_4/graphene nanocomposite or a SnO_2/graphene nanocomposite, by synthesizing another metal oxide, in which the reduction potential of a source material for a metal oxide is 1 V or less, using the method according to an exemplary embodiment of the present invention.

[0047] As set forth above, the exemplary embodiments of the graphene-based nanocomposite including a metal oxide and the method of fabricating the same according to the present invention have been described in detail. However, a person skilled in the art can make various alternatives and modifications of the exemplary embodiments. It should be therefore understood that the scope of the present invention be defined by the Claims appended hereto and their equivalents.

What is claimed is:

1. A method of fabricating a graphene-based nanocomposite, comprising:

preparing a solution in which a graphene oxide is dispersed;

adding a source material for a metal oxide into the solution in which the graphene oxide is dispersed; and

forming a nanocomposite by forming the metal oxide on at least one surface of graphene that is reduced using oxidation-reduction between the graphene oxide and the source material for the metal oxide,

wherein a reduction voltage of the source material for the metal oxide is 1.0 V or less.

2. The method according to claim **1**, wherein the reduction voltage of the source material for the metal oxide is 0.8 V or less.

3. The method according to claim **2**, wherein the metal oxide comprises one selected from the group consisting of a metal phosphorus oxide, an iron oxide and a tin oxide.

4. The method according to claim **3**, wherein the metal oxide comprises one selected from the group consisting of $FePO_4$, Fe_3O_4 and SnO_2.

5. The method according to claim **1**, wherein the graphene-based nanocomposite comprises a nanomaterial having a diameter of 10 μm or less.

6. A graphene-based nanocomposite comprising graphene and a metal oxide formed on one surface of the graphene,

wherein the graphene-based nanocomposite is fabricated by a process that includes:

preparing a solution in which a graphene oxide is dispersed;

adding a source material for a metal oxide into the solution in which the graphene oxide is dispersed; and

forming a nanocomposite by forming the metal oxide on at least one surface of graphene that is reduced using oxidation-reduction between the graphene oxide and the source material for the metal oxide,

wherein a reduction voltage of the source material for the metal oxide is 1.0 V or less.

7. The graphene-based nanocomposite according to claim **6**, wherein the reduction voltage of the source material for the metal oxide is 0.8 V or less.

8. The graphene-based nanocomposite according to claim **7**, wherein the metal oxide comprises one selected from the group consisting of a metal phosphorus oxide, an iron oxide and a tin oxide.

9. The graphene-based nanocomposite according to claim **8**, wherein the metal oxide comprises one selected from the group consisting of $FePO_4$, Fe_3O_4 and SnO_2.

10. The graphene-based nanocomposite according to claim **6**, wherein the graphene-based nanocomposite comprises a nanomaterial having a diameter of 10 μm or less.

* * * * *