



# Bioactive Carbon-PEEK Composites Prepared by Chemical Surface Treatment

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1 **Bioactive Carbon–PEEK Composites Prepared by Chemical Surface Treatment**

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17

1   **Abstract**

2   Polyetheretherketone (PEEK) has attracted much attention as an artificial intervertebral  
3   spacer for spinal reconstruction. Furthermore, PEEK plastic reinforced with carbon fiber  
4   has twice the bending strength of pure PEEK. However, the PEEK-based materials do  
5   not show ability for direct bone bonding, i.e., bioactivity. Although several trials have  
6   been conducted for enabling PEEK with bioactivity, few studies have reported on  
7   bioactive surface modification of carbon-PEEK composites. In the present study, we  
8   attempted the preparation of bioactive carbon-PEEK composites by chemical treatments  
9   with H<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub>. Bioactivity was evaluated by *in vitro* apatite formation in  
10   simulated body fluid (SBF). The apatite formation on the carbon-PEEK composite was  
11   compared with that of pure PEEK. Both pure PEEK and carbon-PEEK composite  
12   formed the apatite in SBF when they were treated with H<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub>; the latter  
13   showed higher apatite-forming ability than the former. It is conjectured that many  
14   functional groups able to induce the apatite nucleation, such as sulfo and carboxyl  
15   groups, are incorporated into the dispersed carbon phase in the carbon-PEEK  
16   composites.

17

18   **Keywords**

19   Polyetheretherketone (PEEK), carbon-PEEK composite, Apatite, Bioactivity, Simulated  
20   body fluid (SBF), Surface modification

21

## 1 **1 Introduction**

2 Spinal diseases such as disk herniation, spinal stenosis and compression fracture  
3 cause neuropathic pain [1,2]. In severe cases, implantation of artificial intervertebral  
4 spacers is needed. Titanium and its alloys, carbon and polyetheretherketone (PEEK) are  
5 used for this purpose. In particular, PEEK has attracted much attention, as it reduces  
6 stress shielding by having a lower elastic modulus than metallic biomaterials [3]. PEEK  
7 plastic reinforced with carbon fiber has a bending strength twice as high as pure PEEK  
8 [4] and is expected to become a novel biomaterial for spinal reconstruction. Although  
9 elastic modulus of carbon-PEEK is higher than that of pure PEEK, it is analogous to  
10 that of human cortical bone with carbon content less than 30%. Nonetheless, neither  
11 PEEK nor PEEK reinforced with carbon fiber show ability for direct bone bonding.  
12 Thus, autograft implantation around the spinal devices is needed for bone fixation in  
13 bone tissue. Additional surgery is needed to extract the autograft, which subjects the  
14 patient to severe physical strain. Therefore, tight bone integration of PEEK medical  
15 devices is necessary for long-term stability *in vivo* and improvement of patients' quality  
16 of life.

1           It is reported that an essential requirement for artificial materials to exhibit  
2 bioactivity is the formation of bone-like apatite on their surfaces in the body  
3 environment through chemical reaction with body fluid [5]. The apatite formation can  
4 be reproduced in simulated body fluid (SBF) with inorganic ion concentrations similar  
5 to human extracellular fluid [6]. The development of bioactive PEEK has been  
6 attempted by several techniques [7]. For example, sulfuric acid treatment [8], sol-gel  
7 titania coating [9], PEEK–hydroxyapatite composite [10-12] and composite of PEEK  
8 and sol-gel-derived CaO-SiO<sub>2</sub> powder [13] have been proposed. Main technique of  
9 bioactive PEEK preparation is mixing PEEK with bioactive ceramic particles. However,  
10 only a part of the added ceramics is exposed to body fluid to contribute to their  
11 bioactivity. So large amount of the ceramic addition is needed for achieving bone  
12 bonding. The composite with high ceramic content is liable to be brittle. Ha *et al.* also  
13 prepared a bioactive carbon–PEEK composite by Ti coating via vacuum plasma  
14 spraying and subsequent NaOH treatment [14]. In this case, a sodium titanate layer  
15 formed by the NaOH treatment contributed to the apatite formation. However, no other  
16 studies have been proposed on the bioactivity of the carbon–PEEK composite. In

1 particular, using a surface modification to provide the composite itself with  
2 apatite-forming ability has not been suggested.

3 In the present study, we carried out chemical treatments of the carbon-PEEK  
4 composite with sulfuric acid and calcium salt solution. Subsequently, *in vitro*  
5 apatite-forming ability was evaluated in SBF. The effect of carbon incorporation into  
6 PEEK plastics on the apatite formation is discussed. It is assumed that functional group  
7 able to induce the apatite formation well incorporated on the composites, since carbon  
8 has higher reactivity than PEEK. Actually, surface modification of the carbon by  
9 carboxyl group [15] and sulfo group [16] has been reported.

10

## 11 **2 Materials and Methods**

12 Disks of the pure PEEK (Victrex plc, UK) and carbon-PEEK composite  
13 containing 30% by mass of carbon fiber (diameter of 10  $\mu$ m, thickness of 1.2 mm;  
14 Sumitomo Chemical Co., Japan), and rectangular pure carbon substrates (10  $\times$  10  $\times$  1  
15 mm; Nilaco Co., Japan) were soaked in 5 mL of concentrated sulfuric acid (97 wt%) at  
16 20 °C for 10 min, and then soaked in ultrapure water for 10 min and dried at 60 °C for

1 30 min. After the treatment, they were soaked in 30 mL of 1 M-CaCl<sub>2</sub> solution at  
2 36.5 °C for 24 hr. SBF (Na<sup>+</sup> 142.0, K<sup>+</sup> 5.0, Mg<sup>2+</sup> 1.5, Ca<sup>2+</sup> 2.5, Cl<sup>-</sup> 147.8, HCO<sub>3</sub><sup>-</sup> 4.2,  
3 HPO<sub>4</sub><sup>2-</sup> 1.0, SO<sub>4</sub><sup>2-</sup> 0.5 mM) was prepared by the sequential addition of NaCl, NaHCO<sub>3</sub>,  
4 KCl, K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O, MgCl<sub>2</sub>·6H<sub>2</sub>O, CaCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> (Nacalai Tesque Inc., Kyoto,  
5 Japan) to ultra-pure water according to the previous literature [6]. The pH of the  
6 resulting solution was adjusted to 7.4 by the addition of  
7 tris(hydroxymethyl)aminomethane (Nacalai Tesque Inc.) and the appropriate volume of  
8 a 1 M-HCl solution. The samples were then soaked in 30 mL of SBF at 36.5 °C for 14  
9 days.

10 The chemical structures of the samples were analyzed by Fourier transform  
11 infrared spectroscopy (FT-IR; FT/IR-6100, JASCO Co., Tokyo, Japan) using an  
12 attenuated total reflectance method. The scan range for the FT-IR analysis was set from  
13 400 to 4000 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>. The surface morphology and elemental  
14 composition were characterized by energy dispersive X-ray (EDX) analysis using an  
15 EMAX Energy system (Horiba Ltd., Japan) equipped with a scanning electron  
16 microscope (SEM; S-3500N; Hitachi Co., Japan).

1           The crystalline structure of the samples was characterized by thin-film X-ray  
2   diffraction (TF-XRD; MXP3V, Mac Science, Co., Yokohama, Japan). Monochromated  
3   Cu-K $\alpha$  radiation was used for the TF-XRD analysis, which was fixed at 1° against the  
4   surface of each specimen with a scan rate of 0.02°·sec<sup>-1</sup>. The coverage ratio of the  
5   apatite precipitate formed on the substrates in SBF was determined from SEM  
6   photographs using ImageJ software. The amount of Ca<sup>2+</sup> incorporated into the  
7   substrates by CaCl<sub>2</sub> treatment was determined by soaking in ultrapure water at room  
8   temperature for 24 hr and measuring the Ca<sup>2+</sup> concentration of the water by ion/pH  
9   meter (F-23IIC, Horiba Ltd.). Contact angle of the specimens before and after H<sub>2</sub>SO<sub>4</sub>  
10   treatment was measured by a contact angle meter (DMe-200, Kyowa Interface Science  
11   Co., Ltd., Saitama, Japan). One sample was used for one condition except measurement  
12   of contact angle and coverage ratio of the apatite.

13

### 14   **3 Results and Discussion**

15           Figure 1 shows water contact angle of the substrates before and after H<sub>2</sub>SO<sub>4</sub>  
16   treatment. The contact angle was significantly decreased for all the substrates after the



1 treatment. This means that H<sub>2</sub>SO<sub>4</sub> treatment is quite effective for making PEEK and  
2 carbon more hydrophilic.

3 Figure 2 shows EDX spectra of the surfaces of pure PEEK and carbon-PEEK  
4 composites subjected to H<sub>2</sub>SO<sub>4</sub> treatment. Peaks of S are observed for both specimens.  
5 This suggests that the sulfo group is incorporated into both the substrates.

6 Figure 3 shows SEM photographs of the surfaces of pure PEEK and  
7 carbon-PEEK composites subjected to H<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub> treatments. Needle-like  
8 particles were partially observed on the treated surfaces. The present results indicate  
9 that calcium sulfate may be precipitated on the treated specimens, since the typical  
10 calcium sulfate crystal takes needle-like structure.

11 The coverage ratios of the apatite particle on pure PEEK and carbon-PEEK  
12 calculated from SEM photographs were 6.59±7.33% and 64.6±14.0%, respectively  
13 (N=10). The amount of Ca<sup>2+</sup> incorporated into pure PEEK and carbon-PEEK by CaCl<sub>2</sub>  
14 treatment was 2.1±0.9 and 3.6±0.3 μmol/substrate, respectively. This means that  
15 carbon-PEEK has significantly higher ability of the apatite formation in SBF than pure  
16 PEEK even after the same chemical treatments.

1           Figure 4 shows TF-XRD patterns of the surfaces of pure PEEK and carbon-PEEK  
2 composites subjected to H<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub> treatments. Peaks assigned to CaSO<sub>4</sub>·2H<sub>2</sub>O  
3 (JCPDS#33-0311) were observed for both substrates after the treatment. The peaks at  
4 20.7, 23.4, 29.1, 31.1, 33.3° were due to  $\bar{1}\bar{2}1$ , 040,  $\bar{1}\bar{4}1$ , 121 and 051 diffraction of  
5 CaSO<sub>4</sub>·2H<sub>2</sub>O, respectively [17]. This indicates that the deposited needle-like particles  
6 are CaSO<sub>4</sub>·2H<sub>2</sub>O.

7           Figure 5 shows SEM photographs of the surfaces of pure PEEK and  
8 carbon-PEEK composites subjected to H<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub> treatments, which were soaked  
9 in SBF for 14 days. Spherical particles were partially observed on pure PEEK, while the  
10 surface of carbon-PEEK substrates were almost covered with fine particles. Ca/P molar  
11 ratio of the deposits was 1.42 for both the specimens. This result coincides with  
12 characteristic of bone mineral and bone-like apatite with Ca deficiency.

13           Figure 6 shows TF-XRD patterns of the surfaces of pure PEEK and carbon-PEEK  
14 composites subjected to H<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub> treatments, which were soaked in SBF for 14  
15 days. Peaks assigned to low-crystalline apatite (JCPDS #09-0432) were observed at 26  
16 and 32°. The peak at 26° is due to 002 diffraction of apatite while a broader peak at

1 about  $32^\circ$  is an envelope of 211, 112 and 300 diffractions of apatite [16]. Peak intensity  
2 of the carbon-PEEK composite was higher than that of pure PEEK. These results also  
3 support higher apatite-forming ability of the carbon-PEEK composites.

4 Figure 7 shows FT-IR ATR spectra of the surfaces of pure carbon substrates  
5 subjected to  $\text{H}_2\text{SO}_4$  treatment. Peaks assigned to  $\text{O}=\text{S}=\text{O}$  were observed at 1050 and  
6  $1200\text{ cm}^{-1}$ , while that assigned to  $\text{C}=\text{O}$  was observed at  $1650\text{ cm}^{-1}$  [16]. This means that  
7 sulfo group can be incorporated even on pure carbon by  $\text{H}_2\text{SO}_4$  treatment.

8 Figure 8 shows SEM photographs of the surfaces of pure carbon substrates  
9 subjected to  $\text{H}_2\text{SO}_4$  and  $\text{CaCl}_2$  treatment, which were soaked in SBF for 14 days.  
10 Deposits were observed on the specimens after soaking in SBF. They were confirmed to  
11 contain Ca and P by EDX. This indicates that  $\text{H}_2\text{SO}_4$ -treated pure carbon has ability to  
12 form a calcium phosphate in SBF, although it was not confirmed with the apatite.

13 The hydrophilic sulfo group was incorporated into both the pure PEEK and  
14 carbon-PEEK composites by  $\text{H}_2\text{SO}_4$  treatment. This is supported by the significant  
15 improvement of hydrophilicity shown in Fig. 1. Judging from the result that the  
16 incorporated sulfo group was converted to calcium sulfate dihydrate by the subsequent

1 CaCl<sub>2</sub> treatment, it was eliminated from the PEEK chain. The sulfonation reaction of the  
2 aromatic ring is represented as follows [18]:

3



5

6 On the other hand, desulfonation occurs as a reverse reaction in aqueous conditions. The  
7 eliminated sulfo group may react with Ca<sup>2+</sup> to form the calcium sulfate dihydrate, which  
8 has the lowest solubility in water among various calcium sulfates [19]. The release of  
9 the calcium sulfate would induce the apatite formation by increasing the supersaturation  
10 degree of the surrounding SBF with respect to the apatite.

11 The present results indicate that both pure PEEK and carbon-PEEK composites can  
12 form the apatite in SBF when they are treated with H<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub> solutions. The  
13 carbon-PEEK composites showed significantly higher ability for apatite formation than  
14 pure PEEK (Figs. 5 and 6). It is assumed that many functional groups able to induce  
15 apatite nucleation are incorporated into the dispersed carbon phase in the carbon-PEEK  
16 composites. This assumption is supported by the results that even pure carbon can be

1 incorporated into the sulfo group and carboxyl group by H<sub>2</sub>SO<sub>4</sub> treatment (Fig. 6), and  
 2 that the treated carbon forms calcium phosphate in SBF (Figs. 7 and 8). Both the sulfo  
 3 group and the carboxyl group have the ability for apatite formation in the body  
 4 environment [20–22]. Furthermore, carbon–PEEK composites contained larger amounts  
 5 of Ca<sup>2+</sup> than the pure PEEK by CaCl<sub>2</sub> treatment. Actually, Ca concentration of SBF was  
 6 2.7 and 3.7 mM after soaking of pure PEEK and carbon-PEEK, respectively, for 7 days  
 7 (Original SBF: 2.5 mM). The ionic activity product (*IP*) of the hydroxyapatite was  
 8 estimated according to equation (2) and using Ca<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup> concentrations, and pH of  
 9 SBF.

$$10 \quad IP = (g_{Ca^{2+}})^{10} (g_{PO_4^{3-}})^6 (g_{OH^-})^2 [Ca^{2+}]^{10} [PO_4^{3-}]^6 [OH^-]^2 \quad (2)$$

11 The ionic activity coefficient value of  $\gamma_{Ca^{2+}}$ ,  $\gamma_{PO_4^{3-}}$  and  $g_{OH^-}$  are supposed to be  
 12 0.36, 0.06 and 0.72 at physiological ionic strength ( $\mu=0.16$ ) [23]. The pH of SBF after  
 13 soaking of both the specimens for 7 days was almost the same (7.58). Judging from the  
 14 result that the carbon-PEEK released larger amount of Ca<sup>2+</sup> than pure PEEK, the  
 15 composite would provide higher degree of supersaturation with respect to the

1 hydroxyapatite. Overall, these factors would contribute to superior apatite formation on  
2 the carbon-PEEK composites.

3         Zhao *et al.* reported that apatite covered almost the entire surface of the specimen  
4 after soaking in SBF for 28 days [8]. On the other hand, most of the surface treated with  
5 carbon-PEEK composite was covered with the apatite within 14 days. This suggests  
6 that surface modification in the present study is effective for acceleration of the apatite  
7 formation. However, most of clinically used bioactive materials form the apatite within  
8 1 week [24]. Therefore further acceleration in the apatite formation is needed for  
9 medical application in future work. Moreover, adhesion of the apatite layer on the  
10 substrates was not so high. This would be attributed to desulfonation from PEEK.  
11 Therefore improvement of this point is also needed to proceed to further assessment of  
12 biological compatibility such as cell culture.

13

#### 14 **4 Conclusions**

1 Carbon-PEEK composites were found to show bioactivity by surface chemical  
2 modification using H<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub> solutions. Their bioactivity was significantly  
3 higher than that of pure PEEK. It was assumed that many functional groups able to  
4 induce apatite nucleation are incorporated into the dispersed carbon phase in the  
5 composites. These composites are expected to become novel biomaterials for spinal  
6 reconstruction for their bioactivity and high mechanical strength. Furthermore, the  
7 present modification process would be effective for the development of bioactive  
8 carbon-based materials such as graphene.

9

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- 24

1 **Figure captions**

2

3 **Fig. 1.** Water contact angle of the substrates before and after H<sub>2</sub>SO<sub>4</sub> treatment (N=3).

4 **Fig. 2.** EDX spectra of the surfaces of pure PEEK and carbon-PEEK composites  
5 subjected to H<sub>2</sub>SO<sub>4</sub> treatment.

6 **Fig. 3.** SEM photographs of the surfaces of pure PEEK and carbon-PEEK composites  
7 subjected to H<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub> treatments.

8 **Fig. 4.** TF-XRD patterns on the surfaces of pure PEEK and carbon-PEEK composites  
9 subjected to H<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub> treatments.

10 **Fig. 5.** SEM photographs of the surfaces of pure PEEK and carbon-PEEK composites  
11 subjected to H<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub> treatments, which were soaked in SBF for 14 days.

12 **Fig. 6.** TF-XRD patterns of the surfaces of pure PEEK and carbon-PEEK composites  
13 subjected to H<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub> treatments, which were soaked in SBF for 14 days.

14 **Fig. 7.** FT-IR ATR spectra of the surfaces of pure carbon substrates subjected to  
15 H<sub>2</sub>SO<sub>4</sub> treatment.

16 **Fig. 8.** SEM photograph of the surfaces of pure carbon substrates subjected to H<sub>2</sub>SO<sub>4</sub>  
17 and CaCl<sub>2</sub> treatments, which were soaked in SBF for 14 days.

Figure

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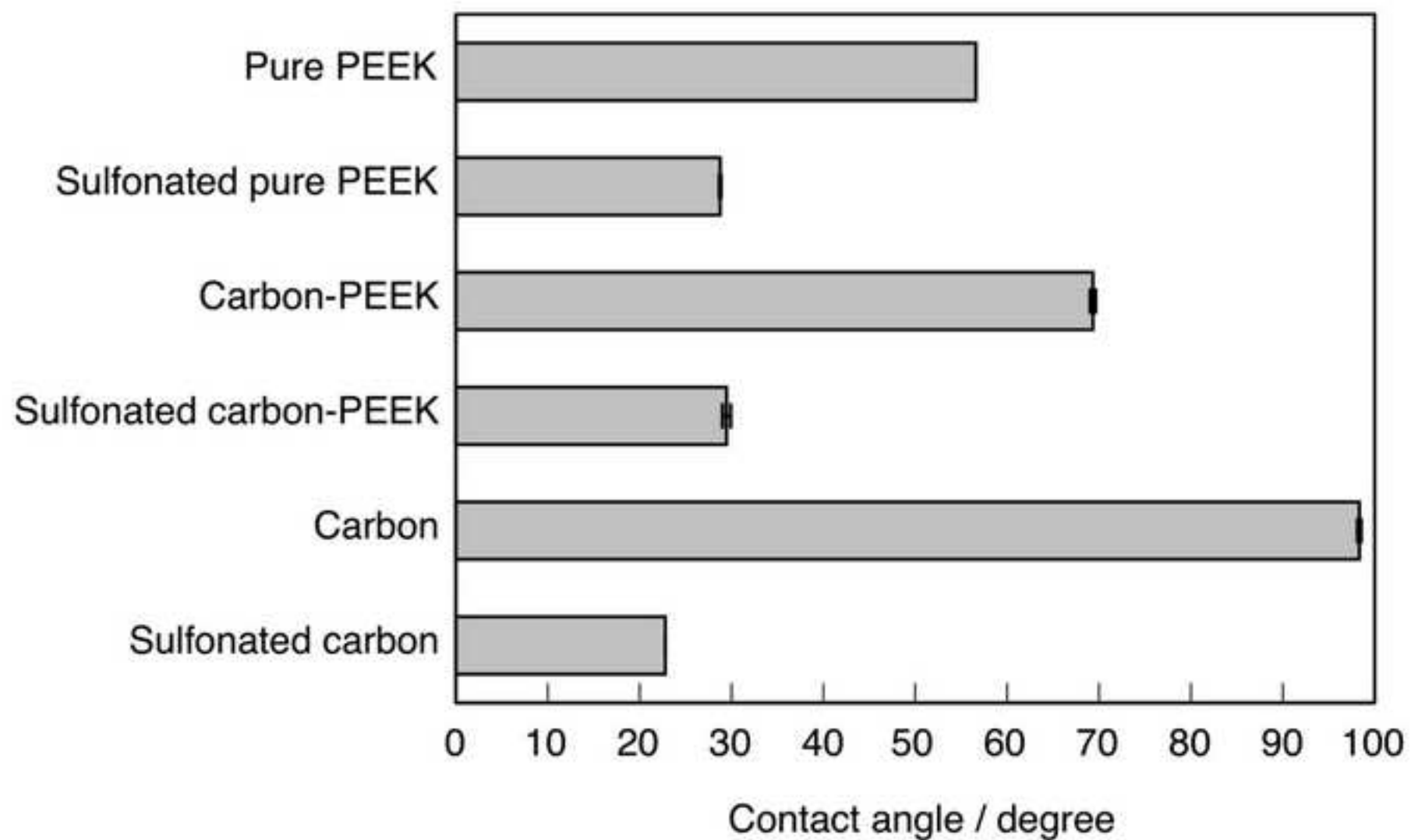


Fig. 1

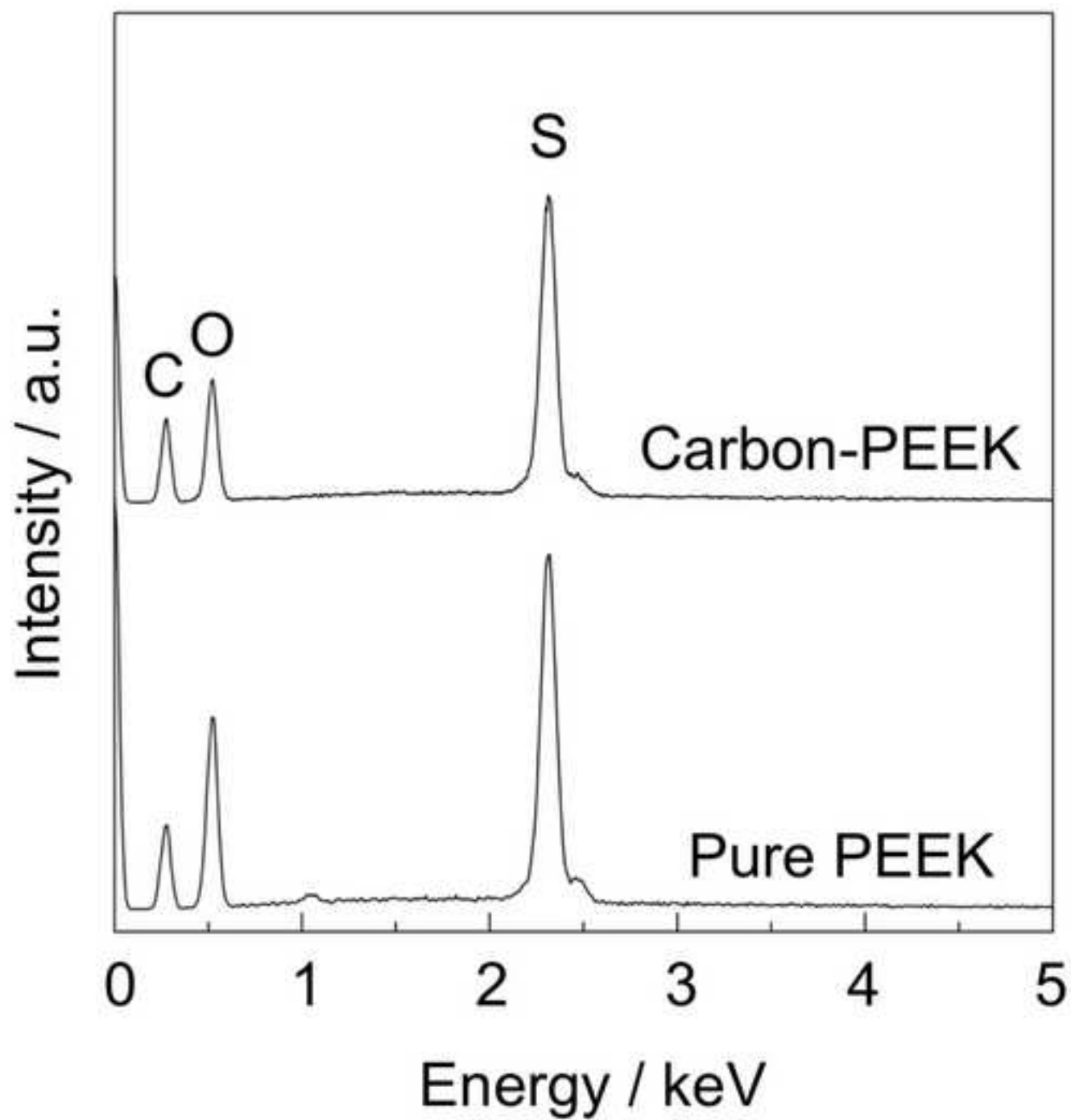


Fig. 2

Figure

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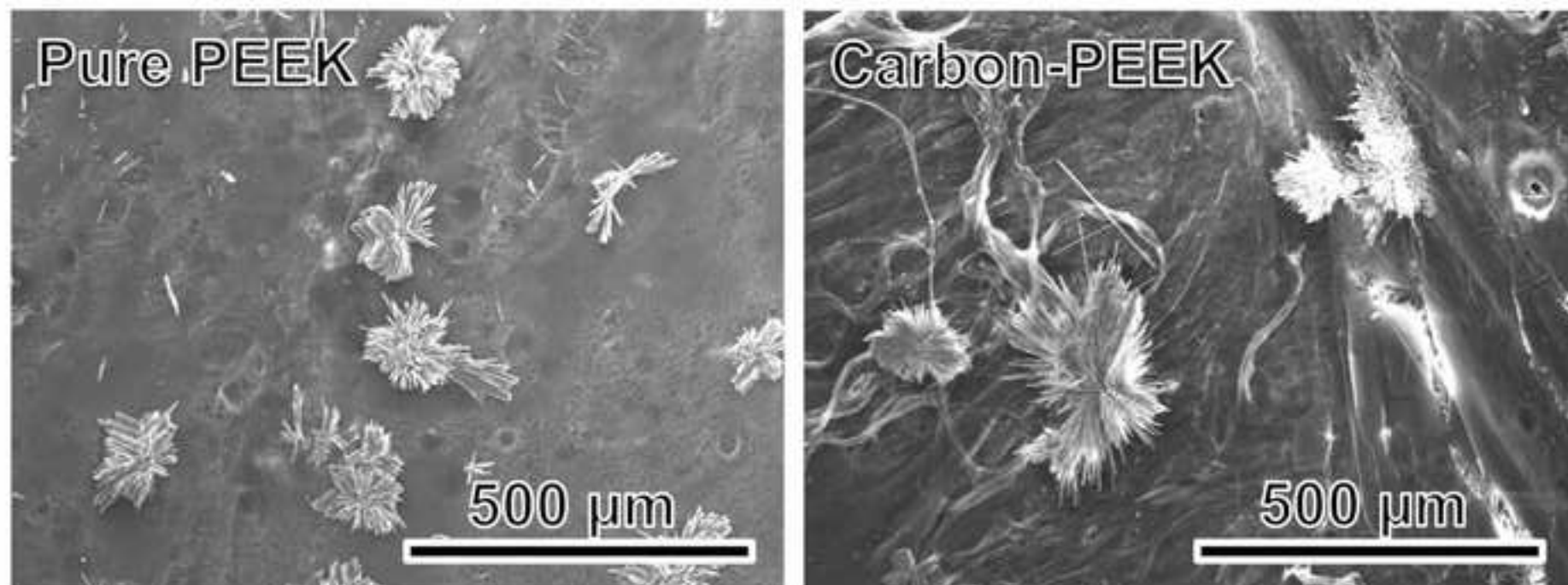


Fig. 3

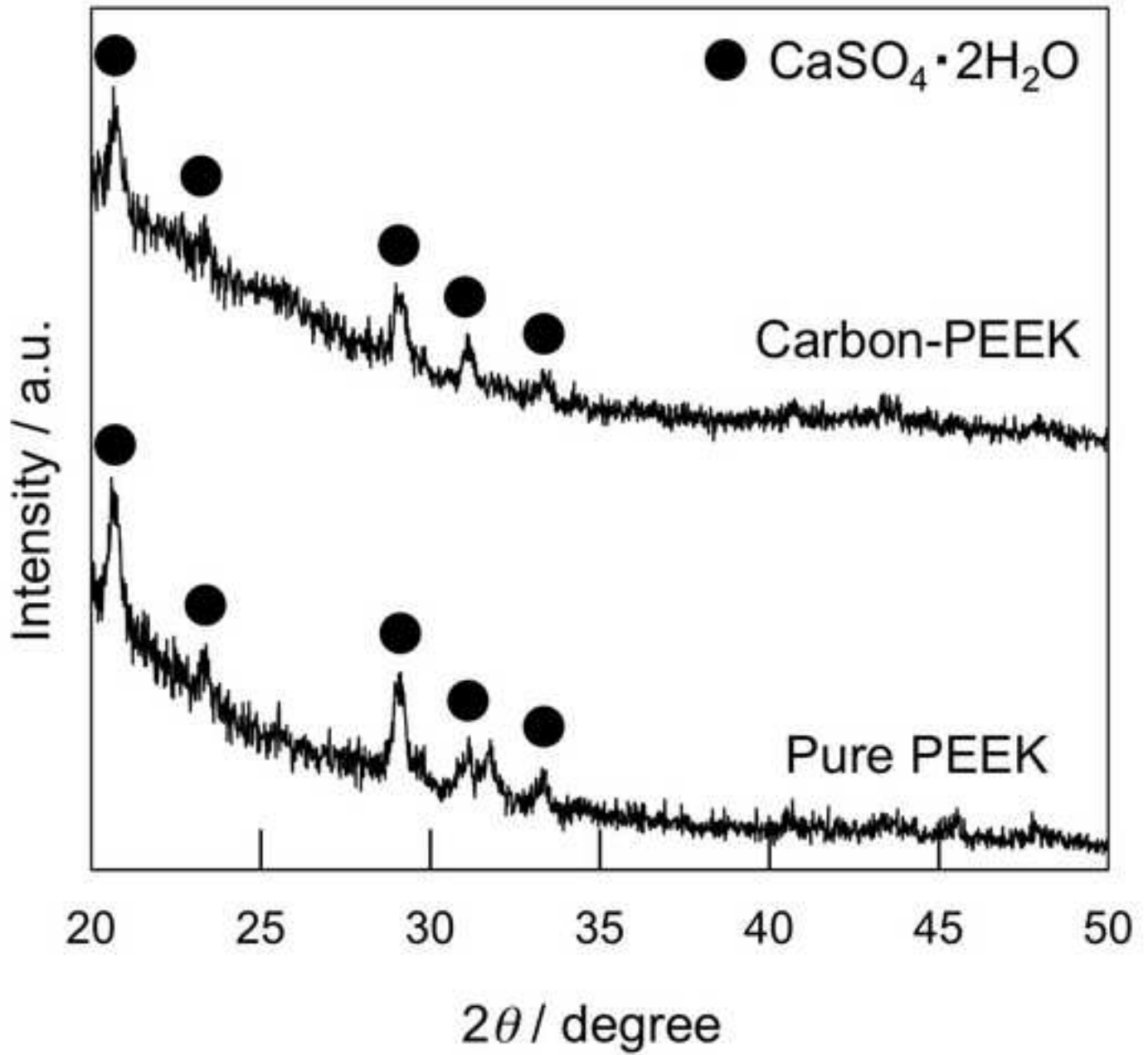


Fig. 4

Figure

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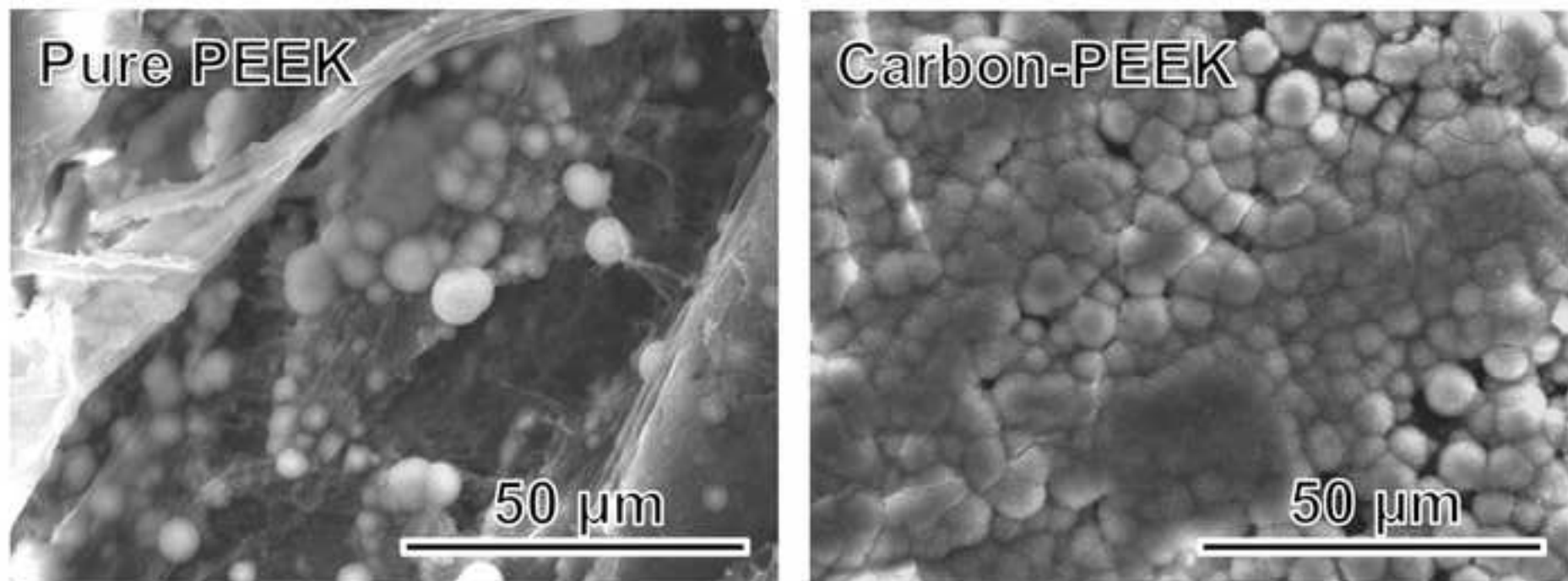


Fig. 5

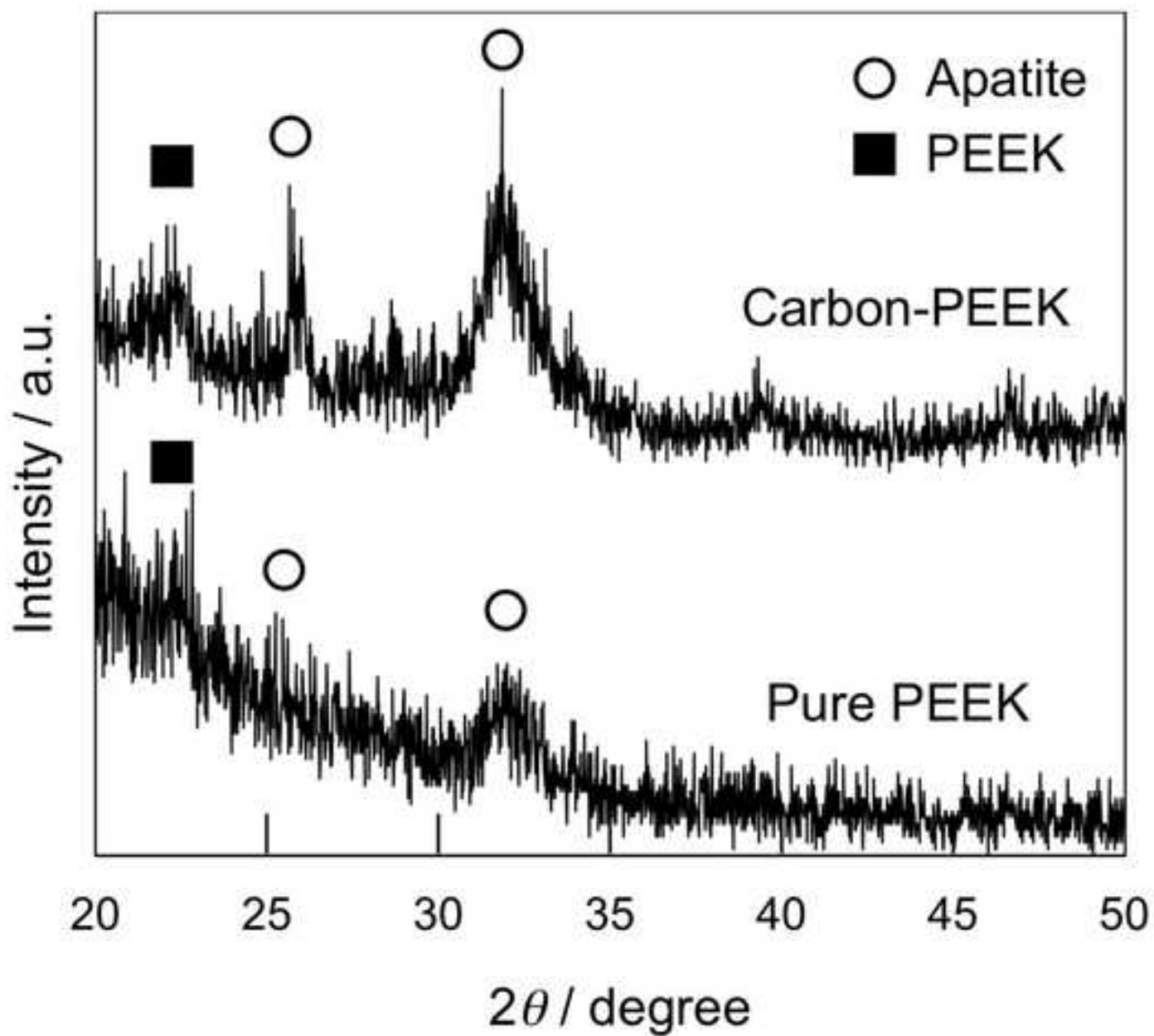


Fig. 6



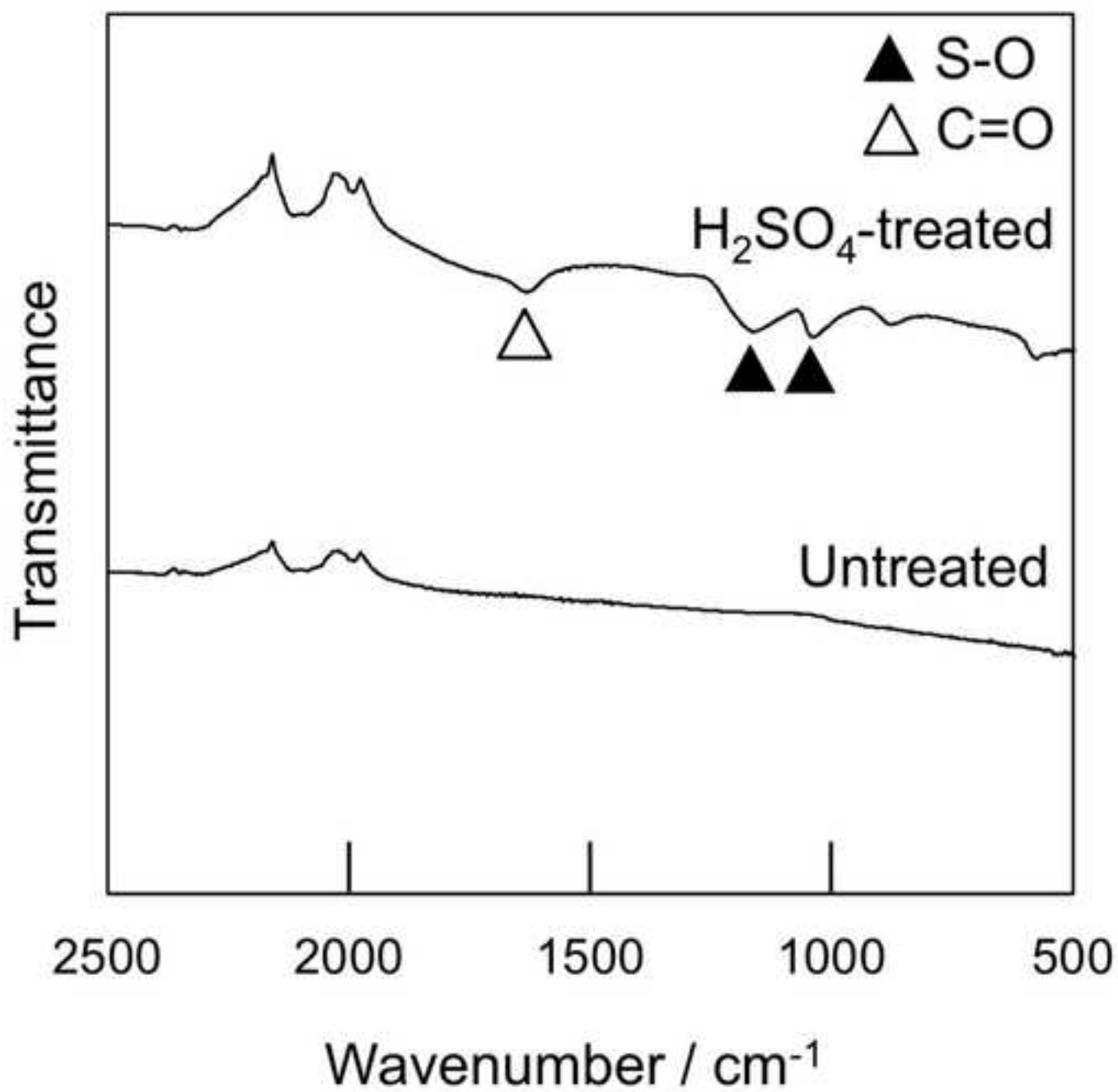


Fig. 7

Figure

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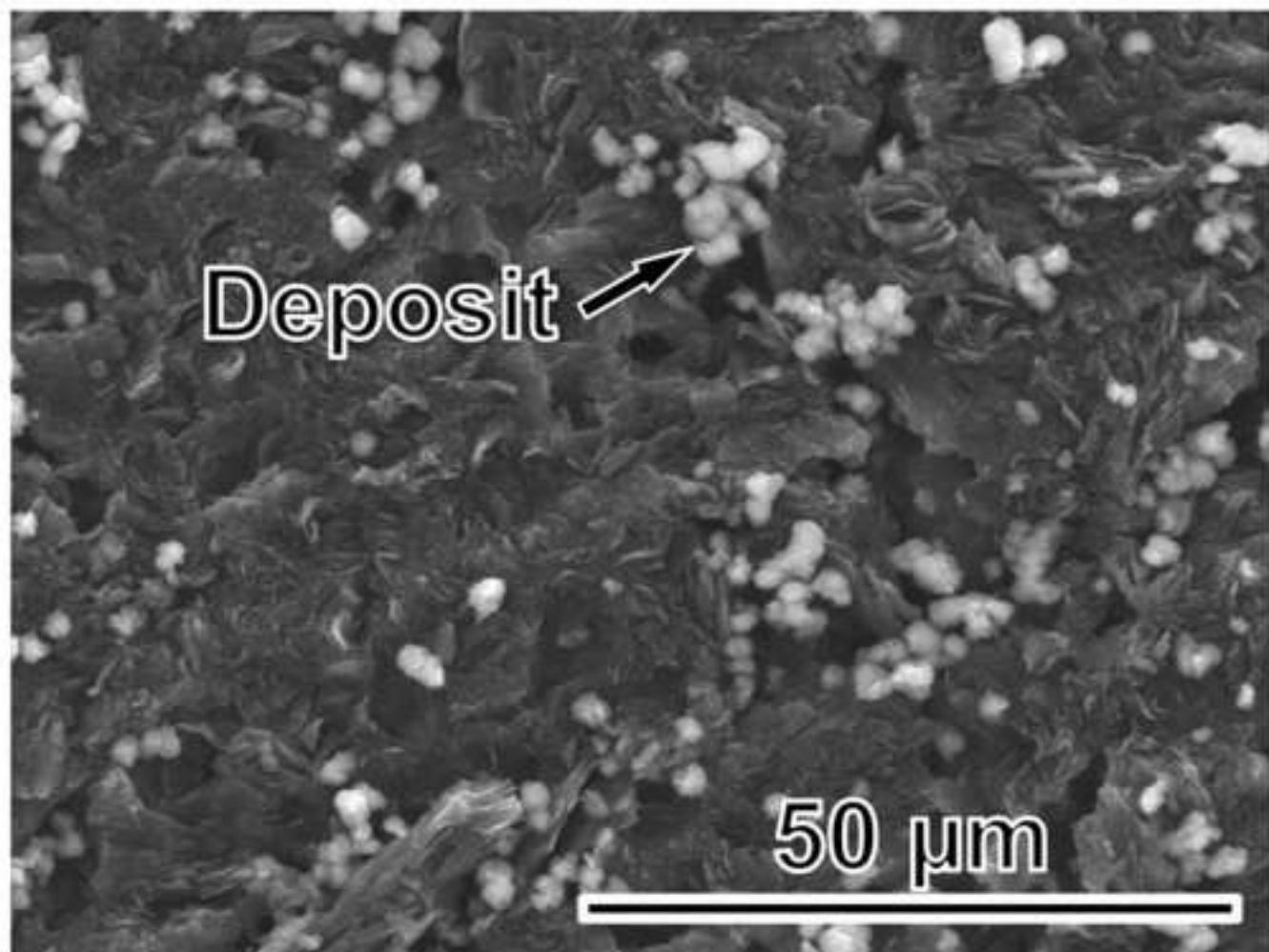


Fig. 8