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Surface graft polymerization acrylic acid onto bamboo charcoal and to improve ammonia adsorption

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ABSTRACT

Bamboo charcoal is a kind of bioinert material with porous structure which provides surface area about 1,500 m^2/g. However, the adsorption ability of polar ammonia gas is still undefined. In this study, the ammonia adsorption ability of bamboo charcoal was significantly enhanced by surface modification. The bamboo charcoal was first silicone oxide modified by hexa-methyldisilazane (HMDSZ) plasma to protect the bulk property and the surface was then oxidized by O_2 plasma. The hydrophilic bamboo charcoal was next titanium oxide treated by sol–gel method and following grafted acrylic acid under UV light to immobilize acid group on the surface and make the treated bamboo charcoal being able to absorb the ammonia. The property of the modified bamboo charcoal was characterized by SEM, weight measurement, wettability, ammonia adsorption test and electron spectroscopy for chemical analysis (ESCA) for surface functionalization, respectively. The ammonia adsorption of bamboo charcoal grafted with 10% acrylic acid, compared with untreated sample, was found improved from 61% to 98%.

Keywords: Plasma; Graft; Surface modification; Film; Bamboo charcoal

1. Introduction

Air pollutants such as ammonia cause various health disorders and have pungent, ruinous odor, followed by the irritation of the eyes and respiratory tract and nausea [1]. To reduce the ammonia in the air and improve the environment, bamboo charcoal with nice ability in ammonia adsorption [2] was investigated. Bamboo charcoal, a kind of bioinert material prepared from bamboo under high temperature and pressure, has been applied to various fields such as environment protections, biomaterials and medicines due to advantages as far infrared rays and being able to limit the electromagnetic wave [3,4]. With porous structure, bamboo charcoal is good in adsorption. In this study, plasma treatment was applied to modify bamboo charcoal due to homogeneity, good adhesion to substrates and high fracture toughness [5–7]. The surface was first deposited by hexamethyldisilazane (HMDSZ) plasma polymerization to induce hardness of the structure and protect the bulk from oxidation. In the next step, O_2 plasma was applied to improve the hydrophilicity of bamboo charcoal. The sample was than treated by sol–gel

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method to prepare TiO_2 on the surface. In order to absorb ammonia, acylic acid was grafted on the surface. Graft polymer (–COOH) can react with ammonia (NH_3) to make it efficient to absorb ammonia.

$$-COOH + NH_3 \rightarrow COONH_4$$

This reaction can turn ammonium molecule becomes the non-toxic nitrogen in the air.

2. Materials and methods

2.1. Preparation of bamboo charcoal

Bamboo charcoal was purchased from Taiwan Takada co. and cut into 2 × 1 × 1cm^3. The sample was washed with distilled water before plasma deposition to remove the surface contamination, and then dried within oven under 45°C overnight.

2.2. Plasma polymerization

In order to maintain the bulk property, the sample was first polymerized by HMDSZ plasma. The experimental power input from RF generator was 30 W and the treating time is 5 min under 150 mtorr. Plasma system was PD-2S (Samco. Japan). Secondly, O_2 plasma was applied with 25 W experimental power input from RF generator for 1 min under 200 mtorr to achieve a hydrophilic surface.

2.3. Surface grafting

In this study, 10 wt% acrylic acid was grafted on the surface of bamboo charcoal under UV exposure for 30 min. After grafting experiment, the grafted bamboo charcoals were washed with distilled water for overnight to remove the homopolymer and residues.

2.4. Characterization

The physical characterization was observed by wettability, weight measurement and surface morphology. Wettability was measured by ratio of water absorption to check the variation in HMDSZ plasma polymerization and O_2 plasma treatment. Surface morphology was monitored by scanning electron microscope (SEM).

2.5. Ammonia adsorption test

Samples treated under different condition were put into a 2,000 ml container and degas by pumping out the air. Ammonia gas was next filled into the degassed container and measured the concentration of ammonia.

Table 1
The ammonia adsorption on bamboo charcoal with different treatment.

Sample no.	Modification	Wt (mg)
Untreated	Untreated	2,290.0
1	HMDSZ→O_2→Ti-org.→TiO	2,328.1
2	HMDSZ→O_2	2,455.4
3	HMDSZ→O_2 →Ti-org.TiO→ 20% AAc graft	2136.9
4	HMDSZ→O_2 →Ti-org.TiO→ AAc+ NIPPAm graft	2,527.9

After 2 h, the ammonia concentration was monitored to compare the ammonia adsorption between different conditions as listed in Table 1. After bamboo charcoal was treated by HMDSZ and O_2 plasma as sample 2, sol–gel method was applied to immobilize a TiO_x film on the surface and marked as sample 1. The sample under No. 1 condition was grafted with 20% acrylic acid as sample 3 and mixture of acrylic acid and *N*-isopropylacrylamide (NIPPAm) as sample 4, respectively.

2.6. Electron spectroscopy for chemical analysis (ESCA) surface chemical composition

The elemental composition of the sample surface was determined by ESCA spectra (Perkin-Elmer PHI 590AM) using Mg Kα exciton radiation. Typical operating conditions were X-ray gun operating at 15 kV, 250 W, and 10^{-10} torr pressure at the sample chamber.

3. Results and discussion

3.1. Morphology

In this study, the SEM was applied to show the surface morphology of bamboo charcoal. The SEM is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern and a convenient way to characterize plasma polymerization films. Fig. 1 showed the SEM of all test groups. After being treated by HMDSZ and O_2 plasma, the surface was modified without changing porous structure. From (d) and (e), some of the pores on the surface modified with sol-gel methods were observed jam. The results can be explained by TiO_x formed in the surface.

3.2, Wettability

The wettability of bamboo charcoal was evaluated by water absorption ratio ΔW (%). Table 2 shows after being

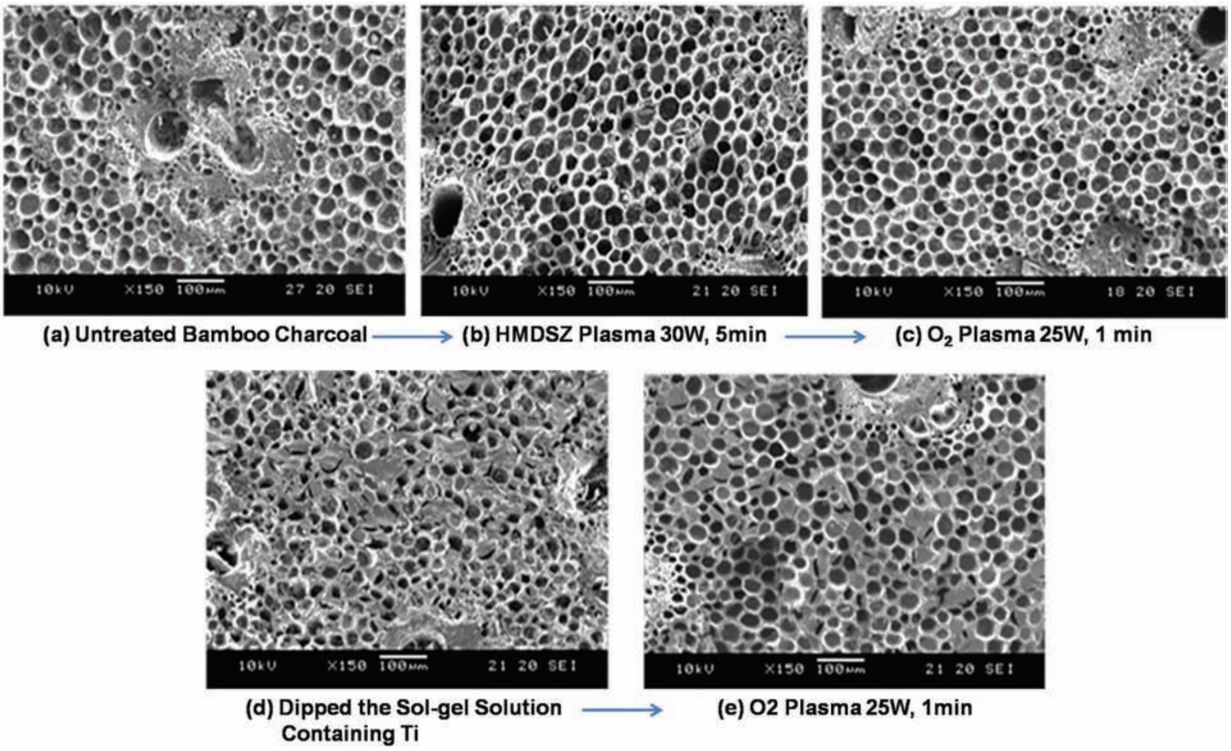

Fig. 1. SEM of modified bamboo charcoal (a) control, (b) HMDSZ, (c) O_2 plasma (d) sol–gel, and (e) O_2 plasma treated on (d).

Table 2
The wettability of bamboo charcoal.

Modified	Water absorption ratio, ΔW (%)*
Untreated	58
PDHMDSZ (30 W, 150 mtorr, 5 min)	18
Oxygen plasma (25 W, 200 mtorr, 1 min)	21
Oxygen plasma (50 W, 200 mtorr, 10 min)	38

*ΔW (%) (water absorption weight/untreated weight).

treated by HMDSZ, the ratio reduced from 58% to 18% and afterward enhanced to 21% due to O_2 plasma treatment. The result showed that surface was hydrophobic after HMDSZ plasma polymerized and turned hydrophilic by O_2 plasma treatment respectively. This can be explained to the success of plasma treatment.

3.3. Weight measurement

The result of weight measurement was shown in Table 3. Bamboo charcoal surface was deposited organic like Si film by HMDSZ plasma polymerization and cause 7% weight losing. The untreated bamboo charcoal adsorption considerable mist and air. When low pressure HMDSZ plasma polymerization, the moist and gas were carried out by the vacuum pump and procured the weight losing. Weight of bamboo charcoal also reduced after being treated by O_2 plasma, which oxidized the surface. Due to the nice absorption ability, bamboo charcoal is able to absorb and gain weight easily while exposed to atmosphere condition.

Table 3
The weight measurement on modified bamboo with different treatment

Modified	ΔW (%)*
PDHMDSZ (30 W, 150 mtorr, 5 min)	−7
Oxygen plasma (25 W, 200 mtorr, 1 min)	−6
Dipped into $Ti(OR)_4$:TTIP	3
Oxygen plasma (25 W, 200 mtorr, 1 min)	−7

*ΔW (%) (treated weight/ untreated weight).

3.4. Ammonia adsorption test

The ammonia adsorption ability of bamboo charcoal with different condition was found in Table 4. The group number represents bamboo charcoal treated

Table 4
The ammonia adsorption ability of surface modified bamboo charcoal

Sample	Untreated	1 TiOx	2 SiOx	3 g-AAc	4 g-AAc +NIPAAm
Ammonia adsorption (ppm)	68	103	70	108	90
Ammonia adsorption ratio (%)	61	93	63	98	81
Ammonia adsorption effect (ppm/g)	30	44	29	51	36

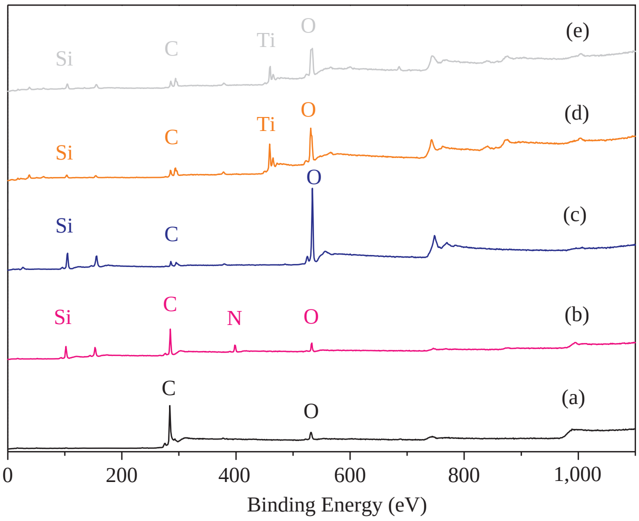

Fig. 2. ESCA wide scan of bamboo charcoal: (a) untreated, (b) HMDSZ plasma deposition film, (c) O_2 plasma modification, (d) dip to the Ti contained organic solution and (e) O_2 plasma post treated.

under different condition as listed in Table 1. Untreated sample can only absorb 68 ppm of 110 ppm ammonia (61%) and relatively group 1 can absorb 93% because TiO_x is able to decompose ammonia after adsorption. Group 3 grafted with acrylic acid showed the best effect.

3.5. ESCA surface chemical composition

The surface chemical composition of the control and the treated bamboo charcoal was evaluated by the ESCA. In all substrate oxygen could be observed (Fig. 2). Fig. 2a shows the untreated bamboo charcoal, (b) shows the bamboo charcoal after HMDSZ plasma treated. After HMDSZ plasma treated, the carbon and silicon pear was increased because the alkyl group and silicon containing in plasma monomer. O_2 plasma was used to activation the bamboo charcoal and showed in Fig. 2c. The oxygen peak increase due to the activation by oxygen plasma and carbon was decrease. Finally the bamboo charcoal immerses in organic Ti solution and use O_2 plasma post-treated showed in Figs. 2d and e,

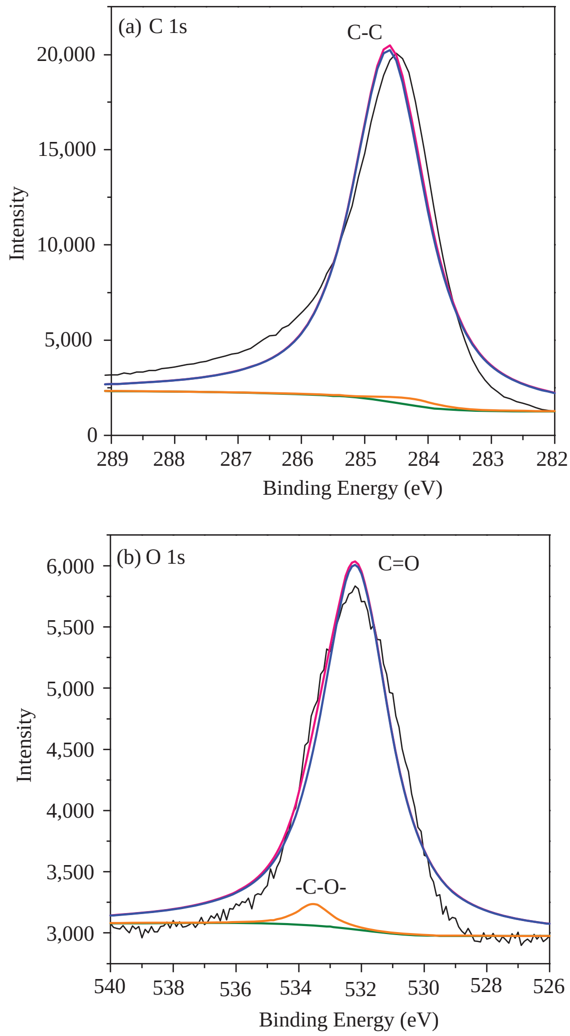

Fig. 3. The untreated bamboo charcoal: (a) C1s spectra and (b) O1s spectra.

the Ti peak could be observed and the Si, O peak was reduced significantly.

The deconvolution analyses of the C1s peak were performed as shown in Fig. 3. The C1s peaks were deconvoluted into one peak corresponding to C–C (284.5 eV). The O1s peaks were deconvoluted into two peaks corresponding to –C=O (531.6 eV) and –C–O– (532.5 eV).

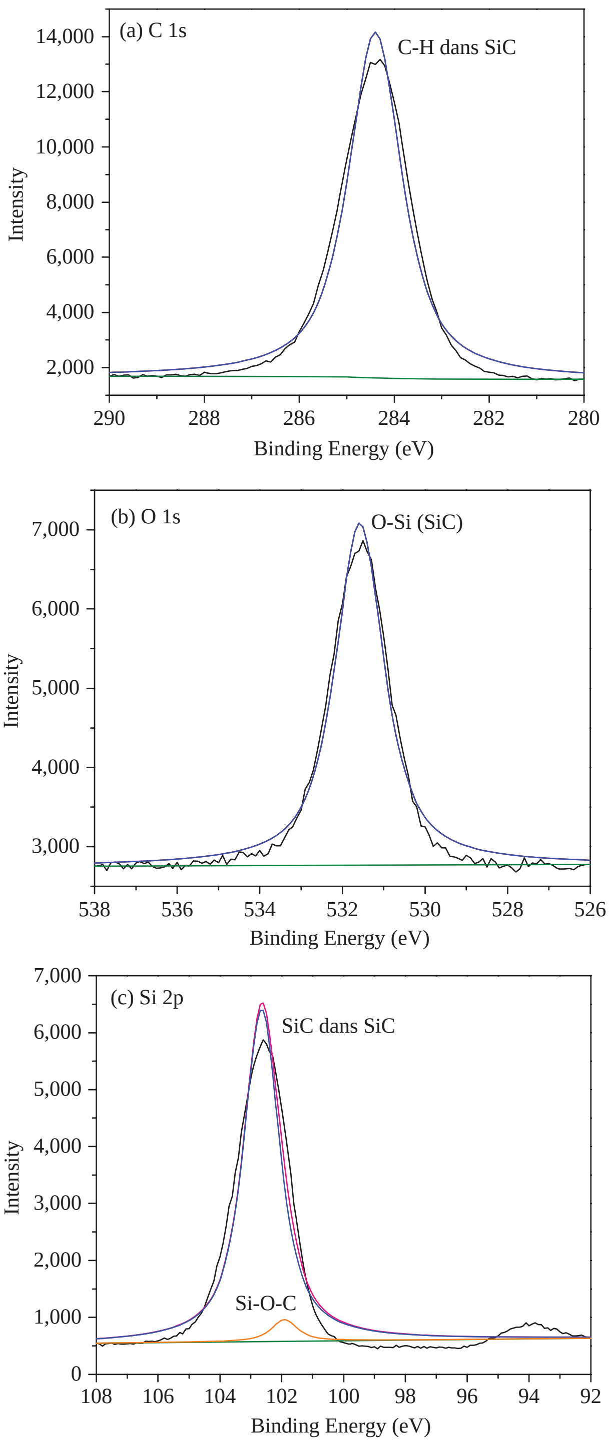

Fig. 4. The bamboo charcoal after HMDSZ plasma deposition film: (a) C1s spectra, (b) O1s spectra and (c) Si2p spectra.

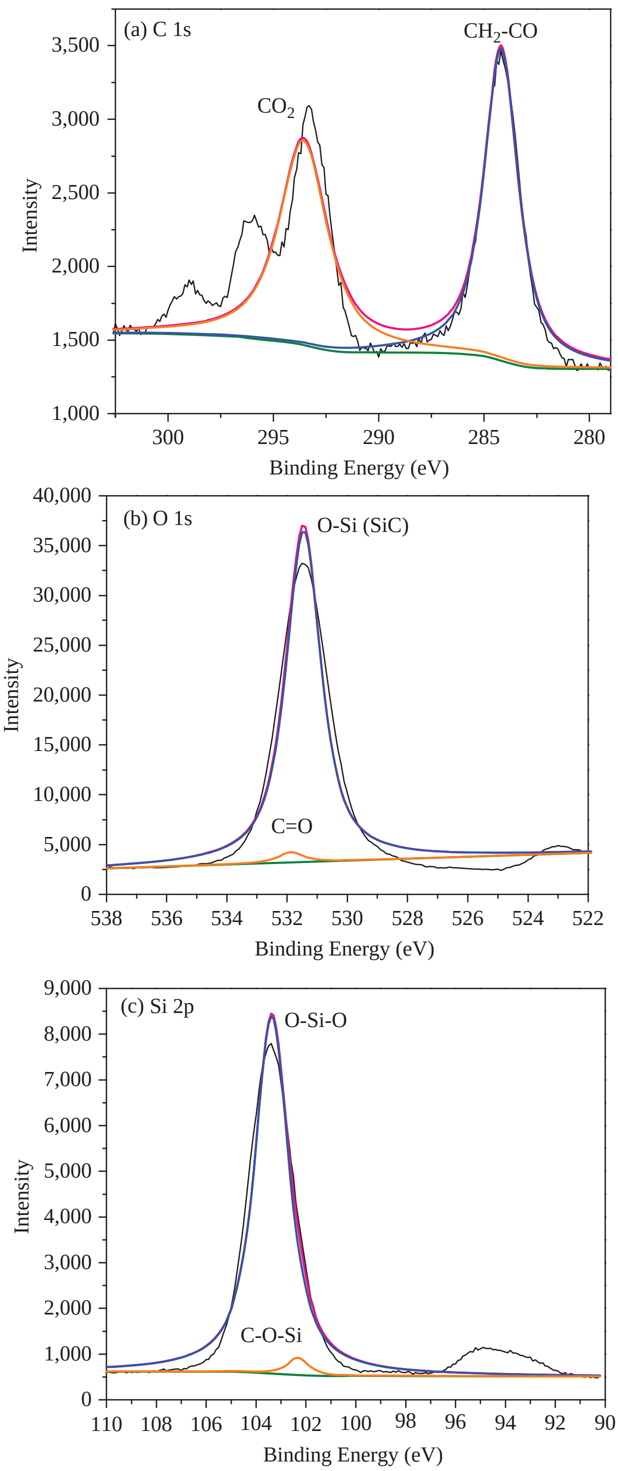

Fig. 5. The activation by O_2 plasma on bamboo charcoal: (a) C1s spectra, (b) O1s spectra and (c) Si2p spectra.

After HMDSZ plasma deposition organic thin film the deconvolution analyses of the C1s, O1s and Si2p peaks were performed as shown in Fig.. 4. The C1s peaks were deconvoluted into one peak corresponding to C–H dans SiC (285.0 eV). The O1s peaks were deconvoluted into one peak corresponding to –O–Si (SiC) (531.9 eV). The Si2p peaks were deconvoluted into two

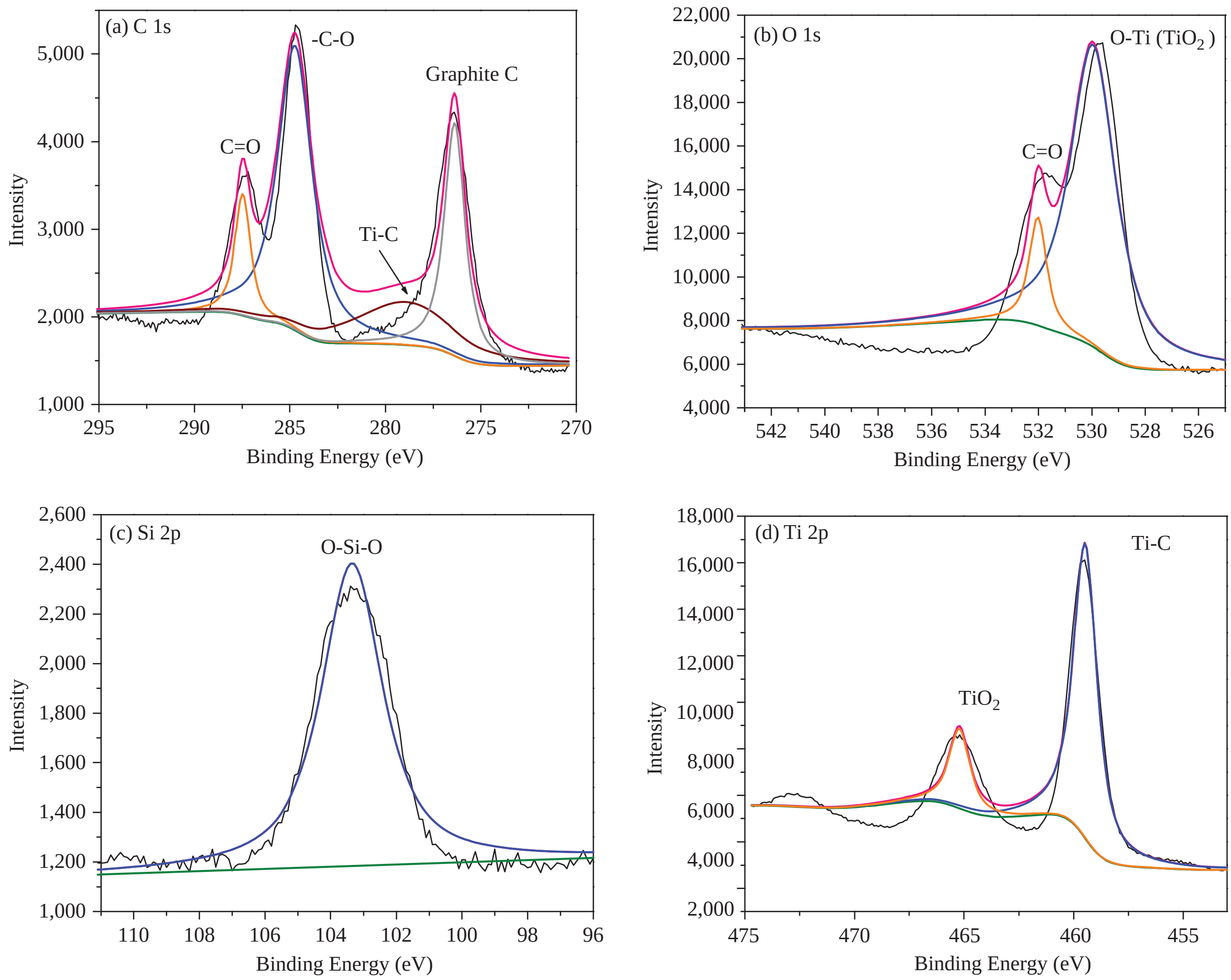

Fig. 6. The bamboo charcoal after dip Ti contain organic solution: (a) C1s spectra, (b) O1s spectra, (c) Si2p spectra and (d) Ti2p spectra.

peaks corresponding to SiC dans SiC (101.9 eV) and Si–O–C (102.1 eV). The result of ESCA could demonstrate the organic film on the bamboo charcoal via HMDSZ plasma deposition.

The nature of the chemical groups produced on the bamboo charcoal deposited organic film with HMDSZ plasma and then activation by O_2 plasma was determined from curve fitting of the C1s, O1s and Si2p core level spectra of the treated bamboo charcoal (Fig. 5). C1s core level spectrum of activation by O_2 plasma treated bamboo charcoal is made up by two peaks at 285.4 eV due to the –CH_2–CO and 292.9 eV due to the CO_2. O1s core level spectrum is made up by two peaks at 531.6 eV due to the –C=O and 531.9 eV due to the –O–Si(SiC). Si2p core level spectrum is made up by two peaks at 102.1 eV due to the Si–O–C and 103.7 eV due to the O–Si–O.

The wettability of bamboo charcoal was increased though the activation by O_2 plasma surface modification and the Ti contain organic solution was easily adhesion on the bamboo charcoal. Fig. 6 shows the nature of the chemical groups produced on the bamboo charcoal dip organic solution contain Ti after deposited organic film with HMDSZ plasma and then activation by O_2 plasma was determined from curve fitting of the C1s, O1s, Si2p and Ti2p core level spectra of the treated bamboo charcoal. C1s core level spectrum of activation by is made up by four peaks at 277.1 eV due to the Graphite C, 281.3 eV due to the Ti–C, 284.83 eV due to the –C–O–, and 287.3 eV due to the –C=O. O1s core level spectrum is made up by two peaks at 529.4 eV due to the O–Ti(TiO2) and 531.6 eV due to the O–Ti(TiO_2) or –C=O. Si2p core level spectrum is made up by one peak at 103.7 eV due to the O–Si–O. Ti2p core level

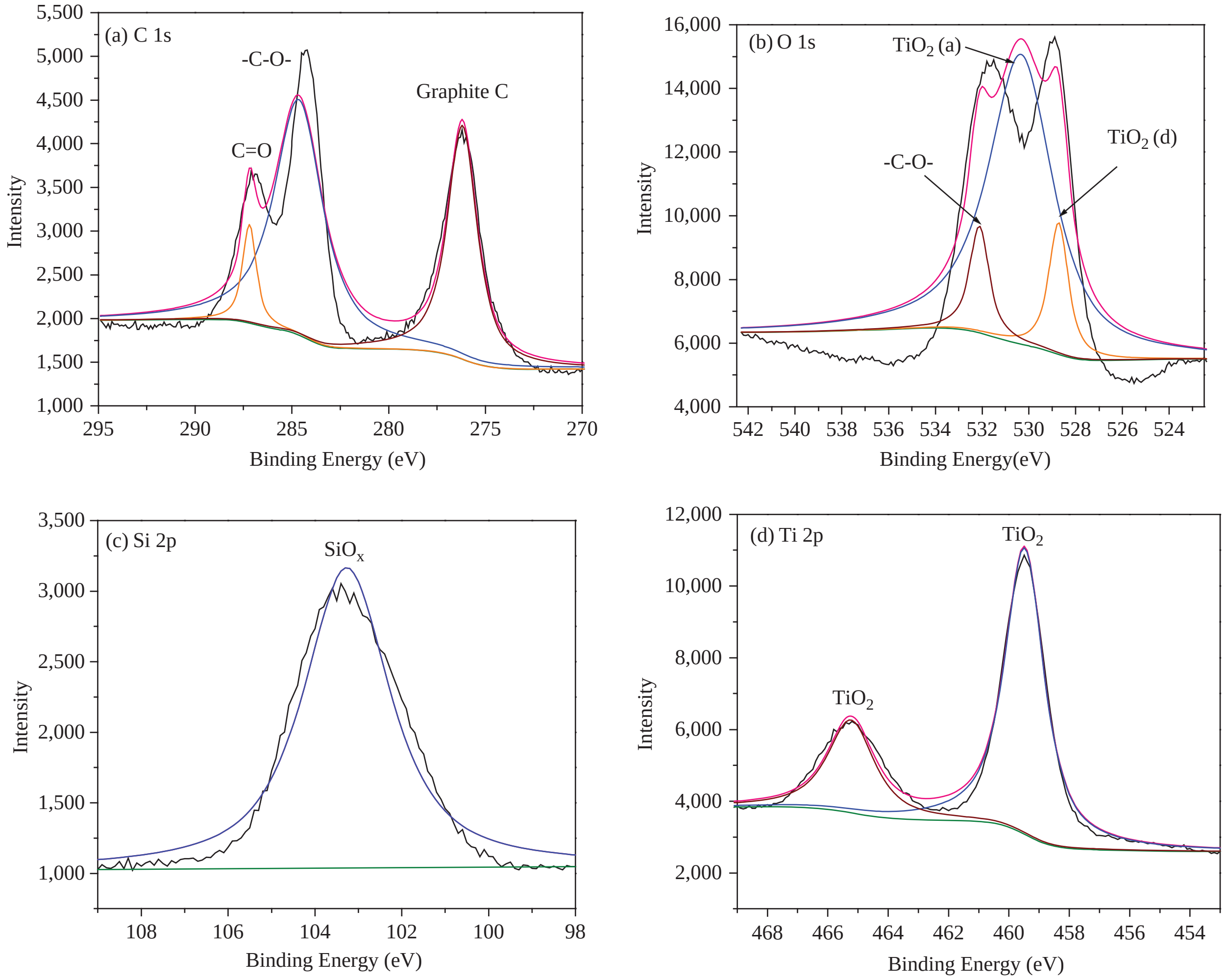

Fig. 7. Bamboo charcoal after O_2 plasma post treatment: (a) C1s spectra, (b) O1s spectra, (c) Si2p spectra and (d) Ti2p spectra.

spectrum is made up by two peaks at 460.0 eV due to the Ti–C and 464.9 eV due to the TiO_2.

O_2 plasma used to oxidize the Ti contains organic solution on bamboo charcoal to form TiO_x. Fig. 7 shows the nature of the chemical groups produced on the bamboo charcoal used O_2 plasma surface modify after dip organic solution contain Ti on bamboo charcoal was determined from curve fitting of the C1s, O1s, Si2p and Ti2p core level spectra of the treated bamboo charcoal. C1s core level spectrum of activation by is made up by three peaks at 277.1 eV due to the Graphite C, 284.83 eV due to the –C–O–, and 287.3 eV due to the –C=O. O1s core level spectrum is made up by three peaks at 529.0 eV due to the TiO_2(d), 530.4 eV due to the TiO_2(a) and 532.5 eV due to the –C–O–. Si2p core level spectrum is made up by one peak at 103.3 eV due to the SiO_x. Ti2p core level spectrum is made up by two peaks at 460.0 and 464.9 eV due to the TiO_2.

4. Conclusion

The HMDSZ plasma polymerization prepared a Si film on the surface of bamboo charcoal to protect the bulk property during O_2 plasma treatment in the second step, which can improve the surface hydrophilicity of bamboo charcoal. Thus, the hydrophilic surface makes bamboo charcoal easily to be treated by sol–gel method and grafting. Surface morphology observed by SEM exhibited the integrity of bamboo charcoal porous structure. Ammonia adsorption ability of bamboo charcoal (increased from 61% to 98%) was improved by plasma/sol–gel method (TiO_x) and surface grafted with acrylic acid.

Acknowledgement

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