



Carbon spheres/activated carbon composite materials with high Cr(VI) adsorption capacity prepared by a hydrothermal method

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ABSTRACT

Glucose and commercial activated carbon (AC) were used as starting materials to hydrothermally synthesize carbon spheres on the surface of AC, producing new carbon sphere–AC hybrid carbon materials. It was found that micrometer-sized carbon spheres, rich in oxygen-containing functional groups, can be effectively anchored to, and well-dispersed on, the surface and at the entrance to the macropores of AC. As the glucose concentration increased, the size and dispersion of carbon spheres changed, the porosity of the AC decreased, the number of oxygen-containing functional groups increased, and C–OH gradually became the dominant functional group. The carbon composites that were obtained exhibited a remarkably enhanced adsorption capacity for Cr(VI) per unit mass and per unit surface area. The highest adsorption capacity per unit mass achieved was $0.4834 \text{ mmol g}^{-1}$, about 4 times that of unmodified AC. The abundant surface oxygen-containing functional groups and relatively well-developed pore structure were the main causes of the high specific adsorption capacity of the carbon sphere/AC composites.

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1. Introduction

Activated carbon materials (ACs) have been extensively used as adsorbents, catalysts and catalyst supports for removal of pollutant species from gases or liquids, and for purification or recovery of chemicals. Their large sorption capacity is linked to their well-developed internal pore structure and the presence of a wide spectrum of surface functional groups. Pore structure is an important factor for physical adsorption [1–3], while surface chemistry plays a key role in specific adsorption and surface reactions [2–6]. Among the surface groups in ACs, surface oxygen-containing groups are of particular importance. The amount and chemical composition of these groups are largely dependent on the origin of the starting materials and the method of preparation. In addition, surface functional groups containing oxygen can be formed when ACs are treated with oxidizing agents by various dry and wet methods [4–8]. The surface chemistry of ACs provides an unlimited, imaginative and simple tool to tackle environmental challenges. Tailoring the surface chemistry of carbon may allow many current industrial challenges to be overcome in many fields including catalysis, water remediation and energy storage.

The adsorption of metal ions from aqueous solution onto AC is generally assumed to be the main role of the functional groups of AC [3–12], although other factors such as coordination with defect sites and van der Waals interactions may also contribute

to the adsorption process. Chromium, which is on the top priority list of toxic pollutants as defined by the Environmental Protection Agency (EPA), can accumulate in the food chain and can cause several ailments. The strict environmental regulations relating to the discharge of heavy metals make it necessary to develop efficient adsorption processes for removal of Cr(VI) from wastewater. Generally, the ion exchange mechanism has been used for adsorption removal of Cr(VI) [4–6,8,10,12]. Ion exchange using AC relies on the presence of surface functional groups such as carboxylic, hydroxy and lactones, which have a high affinity for metal ions and are the main sites of metal ion adsorption [4]. Oxidative treatment in an oxidized gas atmosphere or reaction with a strong acid, such as HNO_3 , can increase the total amount of acidic functional groups on AC, leading to an increased adsorption capacity for Cr(VI) [2,4,6]. Because the limits for pollutants are constantly being revised, industry requires highly effective adsorbents with specific chemical properties. Consequently, the latest research on ACs has focused on their modification and characterization to improve their ability to remove pollutants [4–12]. Considering the adsorption mechanism of Cr(VI) onto carbonaceous materials, developing an novel composite carbonaceous adsorbent with both developed porosity and an abundance of oxygen-containing functional groups should have great significance in both science and technology field.

When a polyhydric sugar, such as glucose or sucrose, is hydrothermally treated in a sealed autoclave, dewatering of the sugar can occur [13]. The partly dewatered sugar (semi-fluid) separates from the solution and disperses as an aqueous emulsion at certain temperatures and pressures (generally larger than 20 atm). Further dewatering of the sugar leads to the formation of nuclei-

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oligomers within the sugar micelles in the form of tiny particles. These nuclei gradually grow into nanoscale spherules by absorbing micelles. Through polymerization of the nuclei with dehydrated sugar dissolved in an aqueous phase, micrometer-size spherules are formed until all of the sugar has been depleted [13–22]. Mi et al. [8] synthesized carbon microspheres using aqueous glucose solution as a starting material in a stainless steel autoclave at 500 °C for 12 h. The carbon microspheres produced in high yield had a regular shape and narrow size distribution with diameters ranging from 1 to 2 μm . Wang et al. [14] prepared amorphous carbon microspheres with a diameter of several micrometers by hydrothermal treatment of a methylcellulose sol at 400 °C. Because of the aromatization of sugar, the carbon spheres produced were rich in OH and C=O groups, which are formed from hydrated or partially dehydrated sugar molecules [15–22]. Through the reductive role of the CHO group generated by glucose hydrothermal treatment, Ag^+ was reduced to Ag and Ag/C hybrids, which included hollow carbon spheres encapsulating silver nanoparticles in their cores [17]. Ag/C cables can be obtained by the hydrothermal treatment of silver nitrate and glucose in the presence of an ionic liquid [17,22].

Carbon-inorganic hybrid materials are a new class of functional materials that have attracted tremendous interest in recent years [5,18,22]. The combination of carbon spheres with AC will create new possibilities for the preparation of novel functional materials.

The purpose of this study was to develop a new composite that combines abundant oxygen-containing functional groups with a highly developed pore structure, and has a high adsorption capacity for Cr(VI) ions. The relative mechanism for the formation of the novel composite was discussed.

2. Experimental

2.1. Sample preparation

Commercial coconut AC ($S_{\text{BET}} = 868.8 \text{ m}^2 \text{ g}^{-1}$, particle size 2–4 mm) prepared by traditional two-step physical activation was used in this work. The AC was designed specifically for water treatment, and was generously supplied by Jianxin Company (Tangshan, China). Prior to use, the carbon sample was washed with distilled

water and oven-dried at 105 °C for 24 h; this sample is referred to as AC_{raw}. The dried AC was then calcined in air at 400 °C for 4 h. The composite carbon materials were synthesized as follows. Calcined AC (0.5 g) was added to each aqueous glucose solution (30 mL) with the concentrations 0.1, 0.3, 0.5, 0.7 and 1.0 mol L⁻¹. The corresponding composite carbon materials obtained are referred to as AC₀₁, AC₀₃, AC₀₅, AC₀₇ and AC₁₀, respectively. The mixtures were sonicated for 10 min and then shaken at 25 °C for 24 h to form homogeneous dispersions. Each dispersion was transferred to a 40 mL Teflon-sealed autoclave vessel and then autoclaved at 180 °C for 4 h. The products were then cooled to room temperature, washed with alcohol and distilled water, and oven-dried for 10 h at 105 °C.

2.2. Characterization

The BET surface area (S_{BET}), total pore volume and pore size distribution (PSD) of the samples were obtained from N₂ adsorption-desorption isotherms measured at 77 K using a constant-volume adsorption apparatus (Autosorb-1, Quanta Chrome). Prior to measurement, the samples were out-gassed at 100 °C under a N₂ flow for 2 h to a pressure in the range of 10⁻⁶ to 10⁻⁵ Torr. The S_{BET} values of the samples were calculated by the Brunauer, Emmett, and Teller (BET) method using adsorption isotherms in the range of 0.05 \leq relative pressure (p/p_0) \leq 0.30. The total pore volume of the samples was calculated from the volume of adsorbed N₂ at $p/p_0 = 0.99$. The PSDs of the samples were calculated by the Barrett, Joyner, and Halenda (BJH) method. The t -plot method was used to calculate the micropore volume and external surface area. The particle size and morphology of the resulting composites were characterized using an environmental scanning electron microscope (QUANTA200). The surface composition and bonding of the carbon composites were detected by X-ray photoelectron spectroscopy (XPS) using a PHI5700 spectrometer and Al K α radiation ($h\nu = 1486.6 \text{ eV}$). Binding energies were referenced to the C_{1s} line at 284.6 eV. Quantitative analysis of C and O was obtained from the peak intensities of the C_{1s} and O_{1s} signals, respectively. FTIR analysis was conducted using a Nicolet Magna 560 spectrophotometer, in KBr pellets.

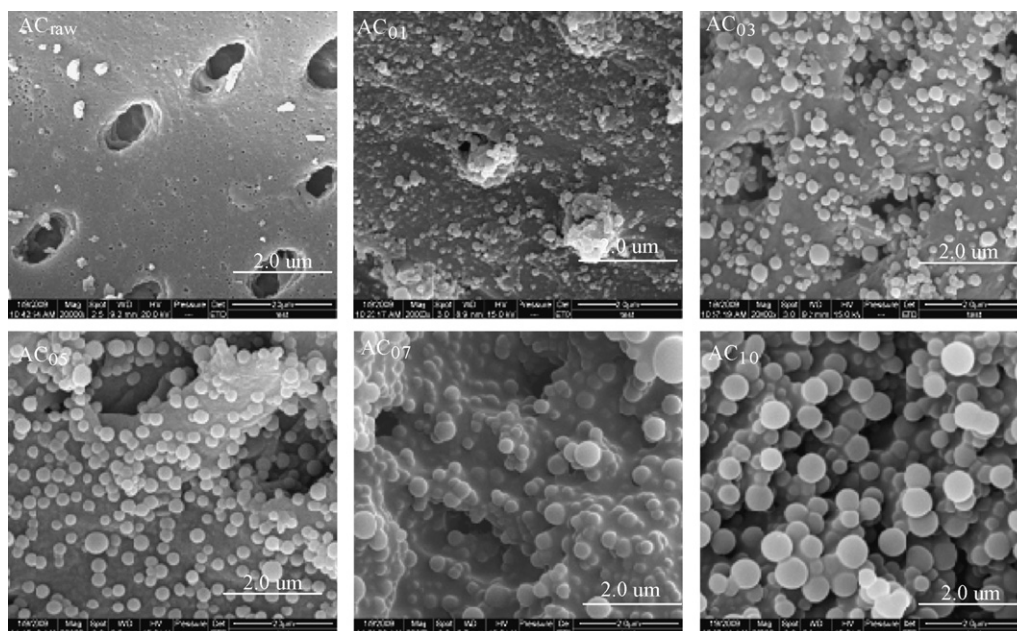


Fig. 1. SEM images of the carbon sphere/AC composites.

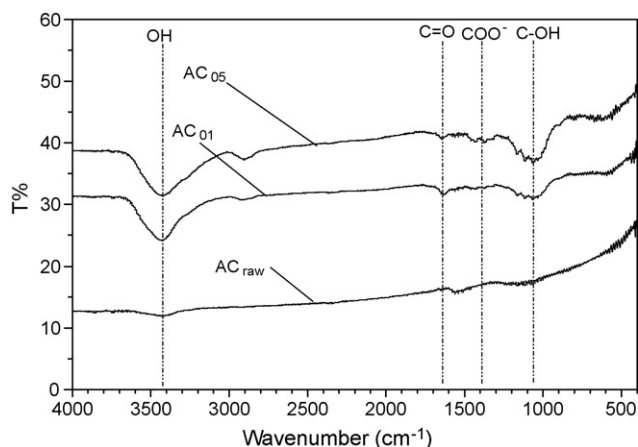


Fig. 2. FTIR spectra of the carbon sphere/AC composites.

2.3. Equilibrium adsorption

Measurement of the equilibrium adsorption of Cr(VI) from an aqueous solution was carried out as follows. 0.2 g of the prepared composite sample was added to each of a series of Cr(VI) solutions (30 mL) with concentrations ranging from 0.1 to 3.0 mM. The bottles were sealed with paraffin film and then shaken for 36 h at 30 °C, at a frequency of 150 strokes min^{-1} . The amount of Cr(VI) adsorbed was evaluated from the change in Cr(VI) concentration determined using a TAS-900 atomic adsorption spectrometer at 365 nm.

3. Results and discussion

3.1. Scanning electron microscopy (SEM) results

Fig. 1 shows typical SEM images of the carbon sphere-anchored AC composites prepared hydrothermally at 180 °C for 4 h. It is apparent that a large number of carbon microspheres, with perfect spherical morphology and very smooth surfaces, were generated on the surface and near the edges of the macropores of the AC. This material was unlike the sample prepared using only an aqueous glucose solution, which contained uniform carbon spheres [13]. The size distribution of the carbon spheres synthesized on AC was influenced significantly by the concentration of the sugar solution. When the glucose concentration was $<0.5 \text{ mol L}^{-1}$, the AC surface was covered with a monolayer of carbon spheres with sizes in the range 50–200 nm. Increasing the sugar concentration increased the diameter and reduced the size distribution of the carbon spheres. When the glucose concentration was 0.7 mol L^{-1} , the AC surface was completely covered with carbon spheres, and a second layer of 300–500 nm diameter spheres was formed. A further increase of the sugar concentration to 1.0 mol L^{-1} resulted in a multilayer arrangement of carbon spheres, and the AC surface was covered to the extent that very few of the AC macropores were visible.

3.2. FTIR results

Carbon spheres hydrothermally synthesized from glucose are rich in OH and C=O groups because of a lack of, or only partial, dehydration [13–17]. Furthermore, some polymerized glucose which bound strongly to the AC surface also contributed to enrichment in oxygen-containing functional groups. FTIR spectra of the composites are shown in Fig. 2. For all of the samples, bands observed at 3400 and 1060 cm^{-1} were assigned to C–OH groups [10–12,14].

The starting material AC_{raw} did not show bands at 1380 and 1060 cm^{-1} , and the 3400 cm^{-1} band was weaker than in the spectra of AC_{01} and AC_{05} . Thus AC_{raw} contained a smaller

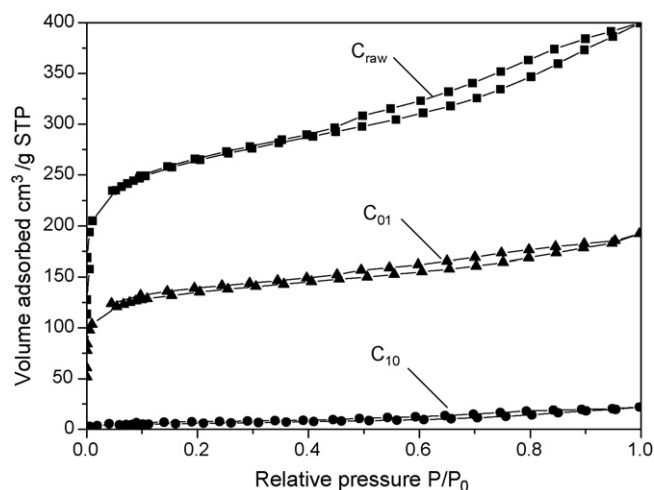


Fig. 3. Nitrogen adsorption–desorption isotherms of the carbon sphere/AC composites.

amount of oxygen-containing functional groups, which were mostly C–OH. For the carbon sphere/AC composites, the intensity of the characteristic C–OH bands increased significantly, indicating the introduction of a large number of hydroxyl groups during the hydrothermal reaction. In addition, a weak vibration was observed at 1380 cm^{-1} which is consistent with the presence of O=C–O groups, and the intensity of this band increased with increasing

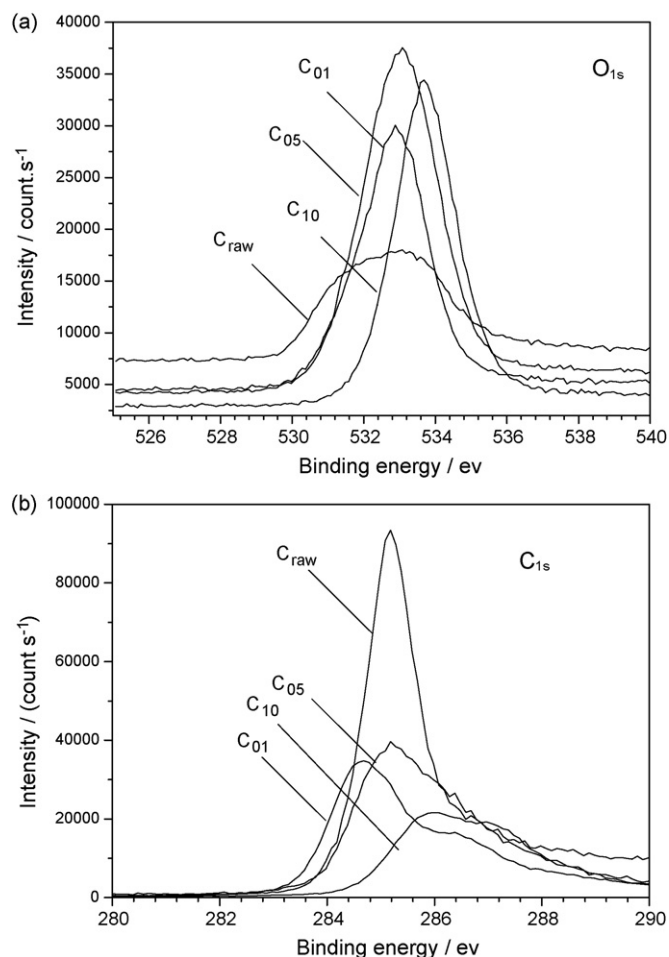


Fig. 4. (a) O_{1s} and (b) C_{1s} XPS spectra of the carbon sphere/AC composites.

Table 1
Physicochemical characterization of carbon sphere/AC composites.

Item	AC _{raw}	AC ₀₁	AC ₀₃	AC ₀₅	AC ₀₇	AC ₁₀
BET surface area (m ² g ⁻¹)	868.8	441.0	35.68	28.80	24.00	21.2
Langmuir surface area (m ² g ⁻¹)	1067	550.7	37.12	29.37	24.89	21.5
t-Method External surface area (m ² g ⁻¹)	780.9	441.0	35.5	28.7	23.8	21.2
t-Method Micropore Area (m ² g ⁻¹)	87.8	0	0	0	0	0
Total Pore Volume (cm ³ g ⁻¹)	0.62	0.30	0.06	0.04	0.03	0.03
t-Method Micropore Volume (cm ³ g ⁻¹)	0.08	0	0.03	0	0.03	0.02
Average pore Diameter (nm)	2.85	2.69	6.31	6.37	6.40	6.43

glucose concentration. The band at 1640 cm⁻¹ was assigned to the C=O stretching of a non-aromatic carboxylic moiety, which might be derived from partial dehydrogenation of glucose during the hydrothermal reaction. The spectra of AC₀₁ and AC₀₅ show marked similarities, suggesting that the microspheres possessed similar functional groups on their surfaces in both samples.

From the FTIR spectra, it was concluded that the amount of oxygen-containing functional groups on the surface of the prepared composites was much higher than that of the raw AC.

3.3. Pore structure analysis

N₂ adsorption–desorption isotherms for AC_{raw}, AC₀₁ and AC₁₀ are illustrated in Fig. 3. According to the IUPAC classification, the adsorption isotherms of AC_{raw} and AC₀₁ have similar type I shapes. Nitrogen uptake was significant only in the low-pressure region (region 1) where $p/p_0 < 0.1$ indicating that the adsorbents AC_{raw}

and AC₀₁ were typically microporous. However, the N₂ adsorption capacity of AC₀₁ was smaller than that of AC_{raw}, suggesting that during the hydrothermal reaction, the pores of AC₀₁ were partially blocked by the carbon spheres. At $0.1 < p/p_0 < 0.9$, the knee of the isotherm of AC_{raw} was more open than for AC₀₁ indicating AC₀₁ contains smaller mesopores. For AC₁₀, almost no adsorption occurred at relative pressure $p/p_0 < 0.1$, indicating that the number of micropores available for N₂ adsorption was very small.

Table 1 presents the microstructural properties of the carbon sphere/AC composites including specific surface area, micropore volume, total pore volume, and pore diameter. It is apparent that the porosity of the composites decreased with increasing glucose concentration. The data indicate that AC₁₀ was almost nonporous. The values of S_{BET} for AC_{raw}, AC₀₁ and AC₁₀ were 868.8, 441.0 and 21.2 m² g⁻¹, respectively, and the total pore volumes were 0.62, 0.30 and 0.03 cm³ g⁻¹, respectively.

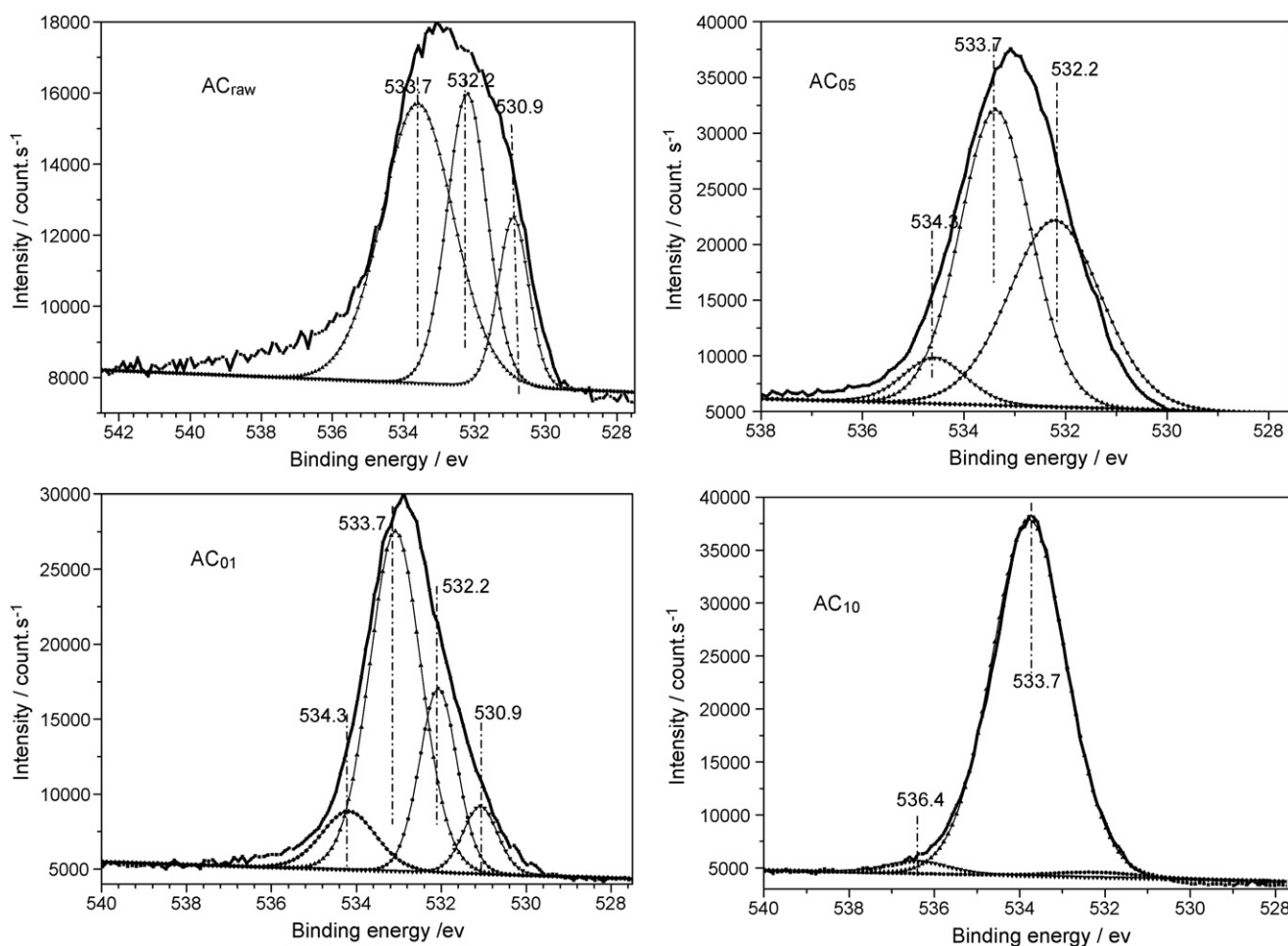


Fig. 5. Deconvolution of the O_{1s} signal for each of the carbon sphere/AC composites.

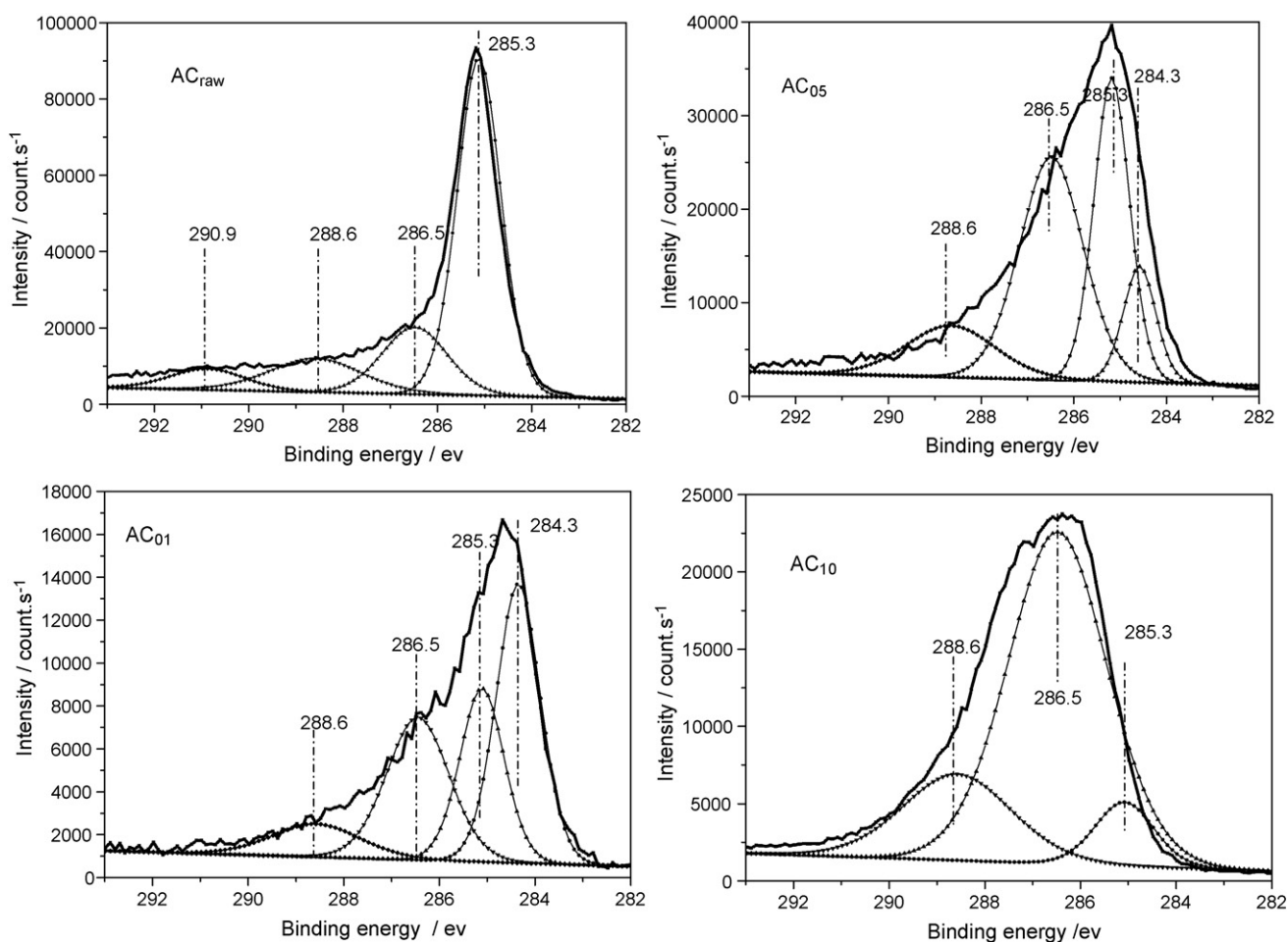


Fig. 6. Deconvolution of the C_{1s} signal for each of the carbon sphere/AC composites.

3.4. XPS results

XPS was used to investigate the elemental composition of the carbon sphere/AC composites, and provide further evidence for the presence of oxygen-containing functional groups. Fig. 4 shows the O_{1s} and C_{1s} XPS spectra of the composites. It is apparent that with increasing glucose concentration, the O_{1s} and C_{1s} signals progressively shifted to higher binding energies. This trend suggests that complex oxidation reactions occurred during hydrothermal treatment.

High-resolution O_{1s} spectra of AC_{raw} and the carbon sphere/AC composites are shown in Fig. 5. The main signals (solid lines) of the composites are narrower than those of AC_{raw} and their centers are shifted from 533.0 to 533.7 eV. The O_{1s} subpeaks (dotted lines) indicate the presence of several different groups [9–12,14,22]: (1) C=O (BE = 530.9 eV); (2) C–O (BE = 532.6 eV); (3) C–OH (BE = 533.7 eV); (4) O=C–O (BE = 534.3 eV). The intensities of the characteristic signals from the C=O and C–O groups decreased gradually and the signals from the C–OH and O=C–O groups showed the reverse tendency as the glucose concentration increased. According to the O_{1s} XPS spectra, C–OH and O=C–O were the most abundant carbon–oxygen functional groups on the surface of the prepared composites; for AC_{10} , C–OH was dominant. Compared with AC_{raw} , the enrichment of oxygen on the surface of the carbon sphere/AC composites suggests that hydrothermal treatment resulted in the formation of oxygen–carbon structures on the surface of the AC.

High-resolution C_{1s} spectra are shown in Fig. 6. Each spectrum was resolved into four individual component peaks, namely

[9–12,14,22]: (1) graphitic, aromatic or aliphatic carbon (C–C, C–H; BE = 284.3 eV); (2) sp^3 hybridized C atoms (BE = 285.3 eV); (3) C–OH groups (BE = 286.5 eV); (4) lactone or ester groups (O=C–O, BE = 288.6 eV); (5) carboxyl groups (COOH, BE = 299.0 eV). According to the C_{1s} spectra, a new C–C or C–H bond was produced on the surface of the AC because of decomposition of glucose during hydrothermal treatment. With increasing glucose concentration, there is a significant increase in the relative content of C–OH and O=C–O, especially C–OH. When the glucose concentration was 1.0 mol L^{-1} , C–OH was dominant as was observed in the O_{1s} spectra.

The surface atomic compositions obtained from XPS analysis of the composites are presented in Table 2. With increasing glucose concentration the oxygen content increased significantly, further demonstrating the increased abundance of oxygen-containing functional groups in the composites.

Table 2

Quantitative XPS results for the presence of surface oxygen in the carbon sphere–AC composites. All values in at%.

Sample	O	C
AC_{raw}	10.2	89.80
AC_{01}	23.08	76.92
AC_{05}	24.62	75.38
AC_{10}	30.42	69.58

3.5. Equilibrium adsorption of Cr(VI)

The uptake of metal ions from aqueous solution by AC is mostly through coordination to the surface oxygen-containing functional groups, although other factors such as coordination with defection sites or van der Waals interactions may also contribute to the adsorption process. Cr(VI) adsorption isotherms for the carbon sphere/AC composites and AC_{raw} are presented in Fig. 7.

It can be seen that the three AC samples prepared using different glucose concentrations presented different adsorption isotherms.

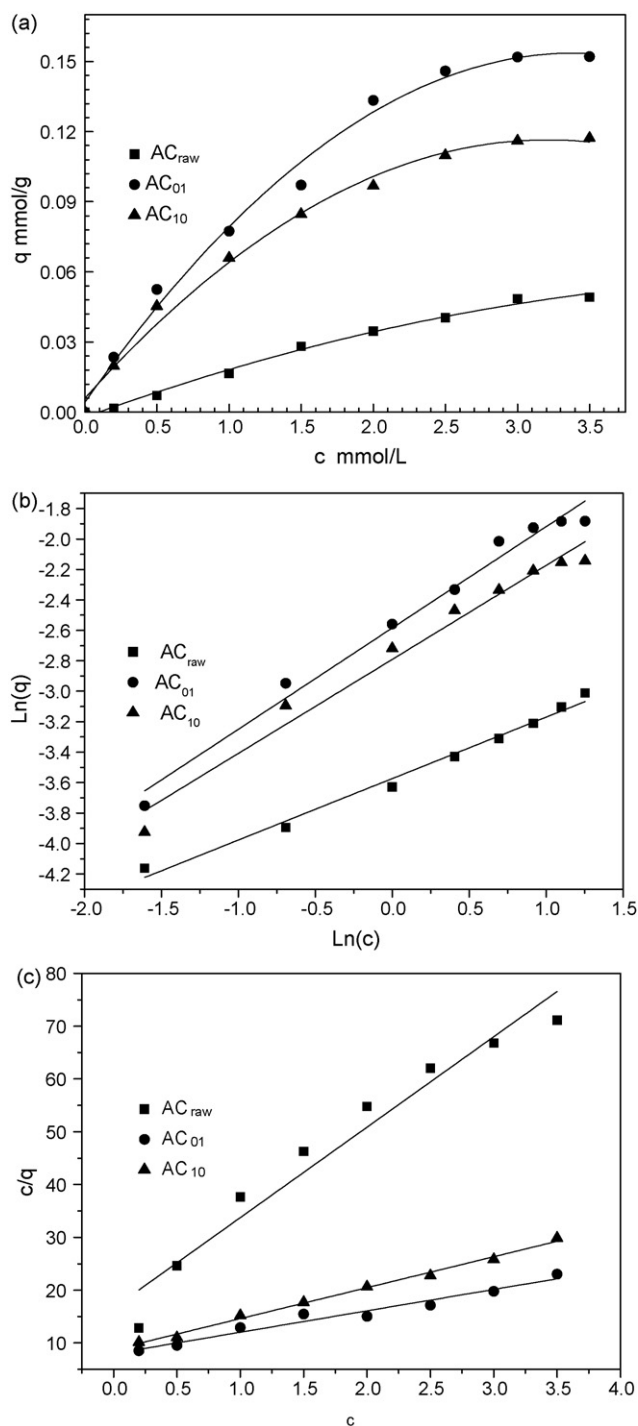


Fig. 7. Adsorption isotherms (a), Freundlich plots (b) and Langmuir plots (c) of CrO_4^{2-} on the carbon sphere/AC composites.

Table 3

Parameters obtained from curve-fitting of the Freundlich and Langmuir equations to the experimental data for the carbon sphere/AC composites.

Adsorbent	Freundlich			Langmuir		
	k	n	r^2	q_m	k	r^2
AC _{raw}	0.02807	0.40383	0.9863	0.1660	1.0302	0.9473
AC ₀₁	0.07547	0.66533	0.9800	0.4834	0.508	0.9581
AC ₁₀	0.0614	0.61733	0.9717	0.3410	0.671	0.9937

The adsorption isotherms of AC₀₁ and AC₁₀ were of typical L2 type; the equilibrium adsorption capacity increased with increasing Cr(VI) concentration and reached a maximum at 3.0 mmol L⁻¹. The adsorption isotherm of AC_{raw} was of L1 type, different to AC₀₁ and AC₁₀. With further increases in the Cr(VI) concentration, the adsorption capacity of AC₀₁ and AC₁₀ remained almost constant. The plateau behavior revealed that Cr(VI) was chemically adsorbed as a monolayer on AC₀₁ and AC₁₀.

To provide a quantitative comparison of the isotherms, the equilibrium adsorption data were fitted to the most frequently used models (Freundlich and Langmuir). The Freundlich model states $q = kc^n$, where k and n are empirical parameters depending on the nature of the adsorbent and adsorbate [1]. The constant k is an approximate indicator of adsorption capacity, while n is a function of the strength of adsorption. The values obtained for k and n are presented in Table 3. The correlation coefficients (r^2) demonstrate that the Freundlich equation described the AC_{raw} system very well. The values of k decreased in the order AC₀₁ > AC₁₀ > AC_{raw}, thus AC₀₁ exhibited the highest adsorption capacity for Cr(VI).

The Langmuir model, which is expressed as

$$\frac{c}{q} = \frac{c}{q_m} + \frac{1}{q_m k_L}$$

assumes an asymptotic approach to a maximum monolayer adsorption capacity, q_m . The factor k determines the affinity of the surface for the solute and corresponds to the strength of adsorption [1]. The Langmuir constants were obtained using nonlinear regression to fit the data to the above equation. The values of the parameters from the Langmuir equation are also summarized in Table 3. The correlation coefficients show that the Langmuir model is more suitable than the Freundlich model to describe the adsorption isotherms of AC₀₁ and AC₁₀. The adsorption capacities of the adsorbents decreased in the order AC₀₁ > AC₁₀ > AC_{raw} over the whole concentration range. The adsorption capacity of AC₀₁ was the highest (0.4834 mmol g⁻¹) and was about 4 times of that of AC_{raw}. Compared with our previous result of 0.2572 mmol g⁻¹ for modified AC prepared under optimum conditions [4], the enhancement in the adsorption capacity for Cr(VI) of AC₀₁ was remarkably high. The adsorption capacity decreased with increasing glucose concentration, possibly because of the significant decrease in porosity at higher glucose concentrations. It follows that both the abundant surface oxygen-containing functional groups and relatively well-developed pore structure of AC₀₁ were the main causes for it having the highest adsorption capacity of the samples. A carbon material good at adsorbing metal ions should have a high adsorption capacity both per unit mass and per unit surface area. As listed in Table 4, the calculated adsorption capacity per unit surface area of AC_{raw}, AC₀₁ and AC₁₀ was 1.4227×10^{-4} , 1.001×10^{-3} and 1.3523×10^{-2} mmol m⁻², respectively. AC₁₀ has the largest adsorption capacity because it has the smallest surface area.

Compared with conventional methods for the surface modification of AC, hydrothermal treatment of AC in an aqueous glucose solution is effective, facile and green because the method did not require use of any strong acid, base, organic ligand, oxygen, ozone or other additive. In addition to facilitating metal ion adsorption,

Table 4

Adsorption capacity for CrO_4^{2-} on the prepared carbon sphere/AC composites per unit mass and per unit surface area.

Sample	CrO_4^{2-} adsorption capacity (mmol g^{-1})	CrO_4^{2-} adsorption capacity (mmol m^{-2})
AC _{raw}	0.1236	1.4227×10^{-4}
AC ₀₁	0.4834	1.0961×10^{-3}
AC ₀₃	0.3585	1.0070×10^{-2}
AC ₀₅	0.3462	1.2020×10^{-2}
AC ₀₇	0.2554	1.0641×10^{-2}
AC ₁₀	0.2867	1.3523×10^{-2}

the increase in the number of surface oxygen-containing functional groups can change the affinity of the surface for metal ions and alter the distribution of metal ions on AC [4,12]. The increase of surface oxygen-containing functional groups can also be beneficial for applications in catalytic reactions, as the redox potential of AC is intimately related to the number of oxygen-containing surface groups [4,11,12]. Consequently, the carbon sphere/AC composites should have great potential in the preparation of noble metal-loaded catalysts.

4. Conclusion

A novel carbon-sphere/AC composite carbon material rich in oxygen-containing functional groups was successfully prepared by hydrothermal treatment of commercial AC in aqueous glucose solution. The carbon composites exhibited a remarkably enhanced adsorption capacity for Cr(VI) per unit mass or per unit surface area. The homogeneity of the size of the carbon spheres synthesized on AC was influenced significantly by the concentration of the glucose solution. When the glucose concentration was less than 0.5 mol L^{-1} , a monolayer of carbon spheres with a size range of 50–200 nm covered the surface of AC. With increasing glucose concentration, the diameter of the carbon spheres increased and their size distribution became narrower. The porosity decreased, the number of oxygen-containing functional groups increased and C–OH became the dominant surface functional group with increasing glucose concentration.

Acknowledgments

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