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ABSTRACT

The high moisture content of sub-bituminous coal is associated with the interactions between coal and water. Because of complex composition and structure, the graphite surface modified by hydroxyl, carboxyl and carbonyl groups was used to represent the surface model of sub-bituminous coal according to XPS results. Density profiles for oxygen atoms and hydrogen atoms indicate that the coal surface properties affect the structural and dynamic characteristics of the interfacial water molecules. The interfacial water exhibits much more ordering than bulk water. The results of radial distribution functions, mean square displacement and local self-diffusion coefficient for water molecule related to three oxygen moieties confirmed that the water molecules prefer to absorb with carboxylic groups, and adsorption of water molecules at the hydroxy and carbonyl is similar.

1. Introduction

Low-rank coal is composed of lignite and sub-bituminous coal, which account for nearly half of the world's coal reserves [1]. However, the low-rank coal is abundant with moisture content. The high inherent moisture degrades the energy quality of the coal, which restricts its large-scale utilisation [2]. The high moisture further leads to high stack flue gas flow rate, high power consumption, high fuel consumption and high risk of spontaneous combustion during the utilisation processes of low rank coal [3]. It has been found that the high content of oxygen-containing functional group at the coal surface plays a critical role in determining its high moisture content [4]. Oxygen moieties in low-rank coal can be mainly categorised into hydroxyl, carboxyl and carbonyl, generally exhibit strong hydrophilicity [5]. Due to the structural complexity and component diversity of low rank coal, a great number of noncovalent intermolecular and intramolecular interactions have been observed, including hydrogen bonding, van der Waals interaction and charge transfer interaction [6–9]. However, the hydrogen bonding between oxygen functional groups and water is the dominant effect [4]. A few techniques including FTIR, DSC, ^{1}H NMR and molecular dynamics (MD) simulation have been used to investigate the coal–water interactions in the past.

Allardice and Evans [10] found that the oxygen functional groups had different hydrogen bonding abilities during the process of water desorption from a raw brown coal. A similar result that the carboxyl groups were the preferential sites of adsorption compared with the other groups was reported by Nishino [11]. Zhang [12] investigated the structure and dynamics of the brown coal–water system with a moisture content ranging from 0 to 60% through MD simulation. Wu et al. [13] obtained a molecular-level description of the interactions between water and sites with both hydrophobicity and hydrophilicity. Vu et al. [14] investigate the interactions between water and lignin as a model system of a brown coal matrix via MD approach.

In present, there have been a few studies which mostly focused on the experiments in the field. However, little research on the low-rank coal–water interaction employs MD simulations. The sub-bituminous coal as an important part of low rank coal provided by Shenhua Shendong Coal Group Corporation Limited in China is modelled based on XPS results, firstly. And then, the effects of oxygen functional groups for structure and dynamics of interfacial water molecules on the sub-bituminous coal model surface were gained. The findings of this investigation could possibly provide insights for theoretical description of interaction between oxygen functional groups and interfacial water at the molecular level. The present work stems from the necessity of better understanding the structure of interfacial water for utilising low-rank coal effectively.

2. Experimental and methods

2.1. Materials

A sub-bituminous coal provided by Shenhua Shendong Coal Group Corporation Limited in China was selected. The proximate analysis of coal samples can be shown as follows: M_{ad} = 10.03%, V_{ad} = 39.17%, FC_{ad} = 60.68% and A_{ad} = 34.21%, where M_{ad} is the

moisture content, V_{ad} the volatilecontent, FC_{ad} the fixed carbon content and A_{ad} is the ash content on a dry basis.

2.2. XPS measurements

To prevent the effect of inorganic ash on the characterisation of the surface oxygen functional groups, the samples are deashed. Firstly, the samples are treated by a solution (the volume ratio of deionised water to 37% HCl and 40% HF is 2:1:1) in a 300-mL beaker for 6 h at 50 °C. Then, it is washed with deionised water until the solution becomes neutral. After that, the sample is dried in a vacuum oven at 105 °C for 24 h.

The XPS experiments are carried out at room temperature in an ultra-high vacuum (UHV) system with the surface analysis system (ESCALAB250 Xi, America). The spectrum of the survey scan is recorded at the pass energy of 100 eV with the step size of 1.00 eV. The high-resolution spectra are recorded at the pass energy of 20 eV with the step of 0.05 eV. Before the data analysis, the binding energies were corrected by setting the C1 s hydrocarbon peak at 284.8 eV. The data processing (peak fitting) is performed with the XPS peak fit software, using a Smart type background subtraction and Gaussian/Lorentzian peak shapes.

2.3. Molecular dynamics simulation methodology

Molecular dynamics simulations were conducted using the Materials Studio 8.0 package. The COMPASS force field was applied for all simulations. The equation of COMPASS force field can be represented as follows:

$$E_{total} = E_{bond} + E_{angle} + E_{oop} + E_{torsion} + E_{cross} + E_{elect} + E_{lj} \quad (1)$$

where E_{bond}, E_{angle}, E_{oop}, $E_{torsion}$ and E_{cross} represent bond stretching energy, angle bending energy, out-of-plane angle coordinates, bond torsion energy and cross-term interacting energy, respectively [15–17].

Since a sub-bituminous coal matrix is very complex in both its physical and chemical structure, the graphite surface modified by oxygen moieties was employed to represent the model coal surface. The graphite is composed of four graphene sheets separated by 3.4 Å from each other. The hydroxyl, carboxyl and carbonyl groups were randomly grafted to the carbon atoms on the first graphene basal plane as shown in Figure 1. The composition ratio of oxygen functional groups was confirmed by results of XPS. The water molecules were simulated using the simple point charge/extended (SPC/E) model [18]. The simulation box was built by placing one slab of the solid substrates at the base and another, specularly symmetric, at a distance $H = 70$ Å along the z axis. The solid substrate is aligned parallel to the x and y plane, and the x and y dimensions are 25.6 and 29.5 Å, respectively. The number of water molecules was 1000, which were placed on the solid substrate. Periodic boundary conditions were applied along the x, y and z axes.

All simulations were performed at NVT ensemble at 298 K using a Nose thermostat, and the time step is set to 1.0 fs. A van der Waals interaction cut-off of 12.5 Å was employed, and the Ewald summation method with an accuracy of 10^{-3} kcal/mol was used to account for the long-range electrostatic interactions. The simulation was performed for 1 ns. The fluctuation curves of energy during the processes of energy minimization and anneal are shown in Figure 2. Potential energy, non-bond energy, kinetic energy and total energy rapidly decrease to a minimum state and keep stable. The final results are calculated based on the production of 500-ps simulation after the equilibration period.
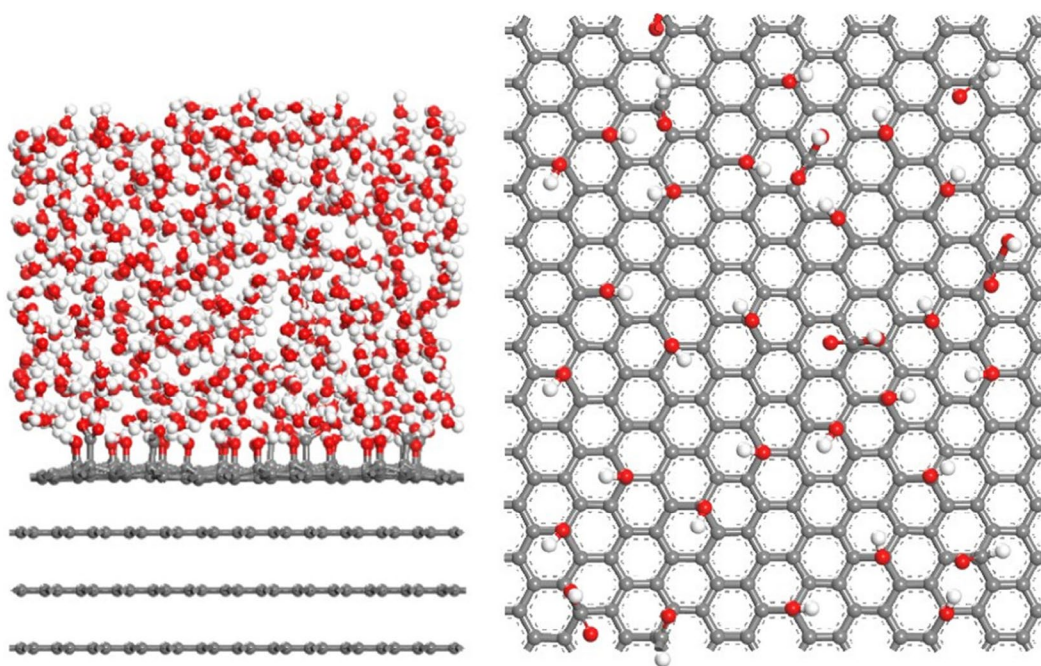

Figure 1. (Colour online) Snapshots of the sub-bituminous coal substrates used in our simulations. (a) Side view of the entire simulation box with water molecules in contact with the coal surface. (b) Top side view of the sub-bituminous coal model. Coloured balls represent O in red, C in gray, H in white.
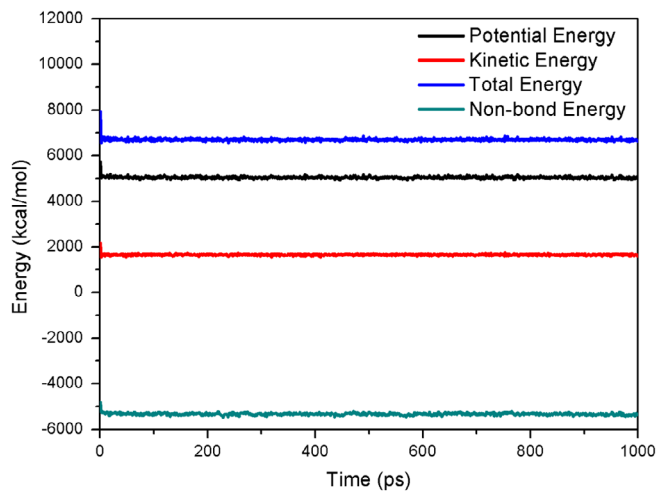
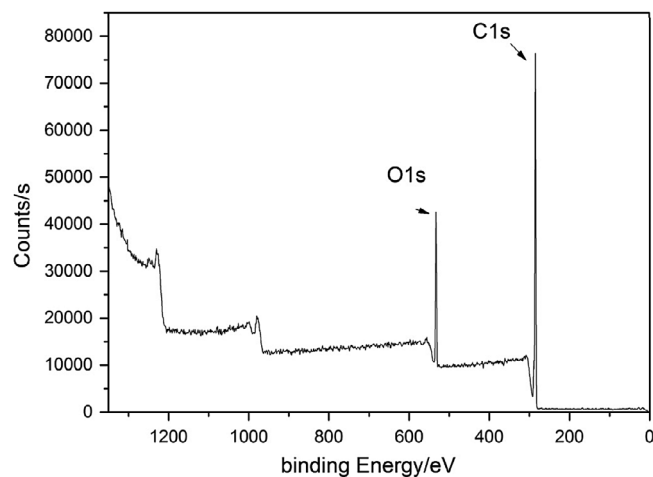**Figure 2.** (Colour online) The fluctuation curves of energy during energy minimization.

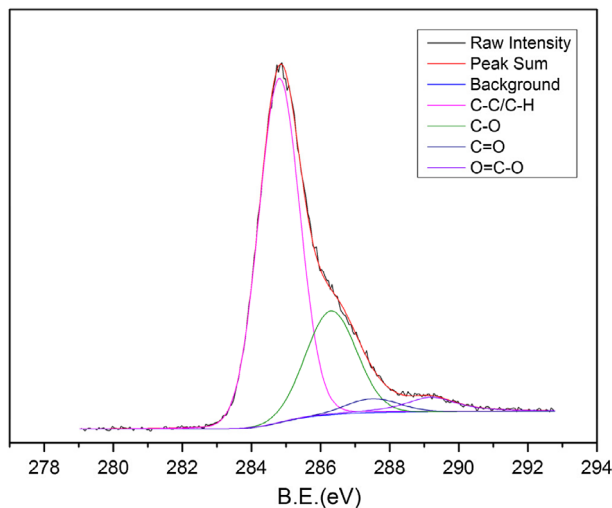**Figure 3.** XPS wide energy spectrums of coal surface.

Figure 4. (Colour online) C 1s peaks for coal surface.

MSD is the statistical average of particle trajectories that means a measurement for average distance of particles around a given particle. The MSD can characterise the diffusion behaviour of water molecules. The MSD can be expressed as [19]:

$$MSD = N^{-1} \left\langle \sum_i |r_i(t) - r_i(0)|^2 \right\rangle \qquad (2)$$

where N is the atom number, $r_i(0)$ represents the position vector at initial time and $r_i(t)$ represents the position vector after time t and the angular brackets signify the ensemble average.

The self-diffusion coefficient can reflect the intensity of atomic mobility. The self-diffusion coefficient can be expressed as follows according to Einstein equation [20]:

$$D = \frac{1}{6N} \lim_{t \to \infty} \frac{d}{dt} \sum_{i \to j} N \left\langle |r_i(t) - r_i(0)|^2 \right\rangle \qquad (3)$$

The MSD and self-diffusion coefficient have close relation as follows:

$$D = \lim \left(\frac{MSD}{6t} \right) = \frac{1}{6} K_{MSD} \qquad (4)$$

3. Results and discussion

3.1. XPS Analysis

Wide-scan spectrum in binding energy range 0~1400 eV was obtained to identify the surface elements present and carry out a quantitative analysis. A typical XPS wide-scan spectrum of demineralised lignite coal is presented in Figure 3. It was obtained that the contents of C 1s and O 1s are 82.47 and 15.87% on coal surface. Other elements are relatively low because of deashing.

A typical curve fitting of the C 1s peak region of coal surface is shown in Figure 4. It is observed that the fitting curve is close to the original curve. The contents of C–C/C–H, C–O, C=O and O=C–O groups could be calculated by the analysis of C 1s peak. The C–C/C–H, C–O (hydroxy or ether), C=O (carbonyl) and O=C–O (carboxyl) are the four forms of carbon present on the surface of the samples, and their binding energies are 284.80, 286.30, 287.50 and 289.20 eV, respectively. C–C/C–H is the main form of carbon element present on the surface of the samples. The content of C–C/C–H is 67.41% on the coal surface. Among coal oxygen moieties, the contents of C–O, C=O and O=C–O groups are 24.51, 3.37 and 4.71%, respectively.

Limited from XPS, C–O could not be clearly divided into hydroxyl and ether. To simplify the model, C–O is considered to be hydroxyl. According to the XPS results, the graphite matrix is modified by three types of oxygen functional groups (hydroxy, carbonyl and carboxyl). The composing proportion for hydroxy, carbonyl and carboxyl is 25:3:5 as shown in Figure 1. The fraction of coverage for oxygen functional groups is about 10%.

3.2. MD simulations: structural properties

In Figure 5, the atomic density profiles of water oxygen and water hydrogen atoms as a function of z perpendicular to the surfaces. The reference point ($z = 0$) for the density profile is the centre of carbon atom in the outermost graphene sheet. The oxygen atomic density profile indicates one pronounced peak at 13.41
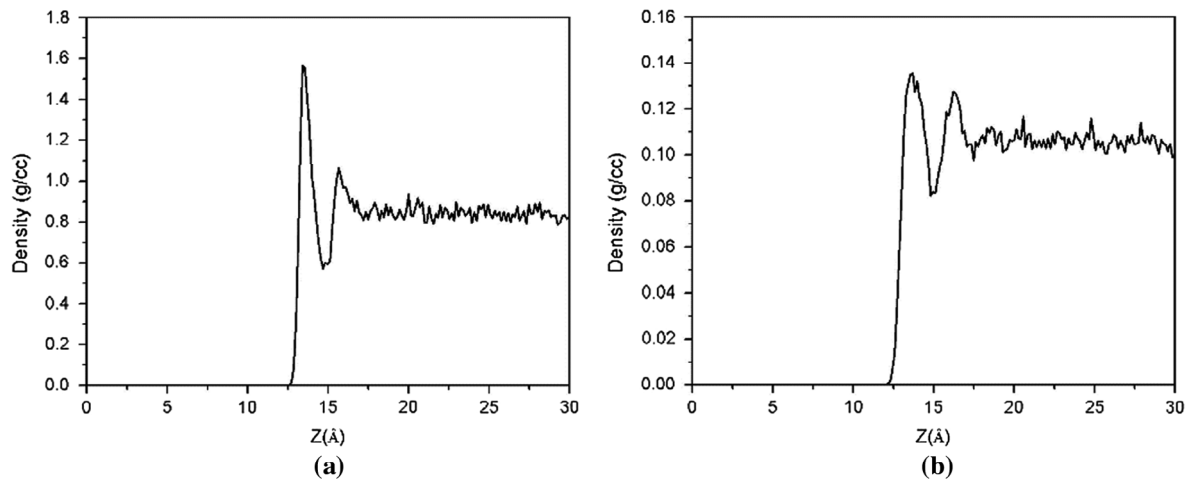
Figure 5. Oxygen (a) and hydrogen (b) atom density profiles as a function of distance z.
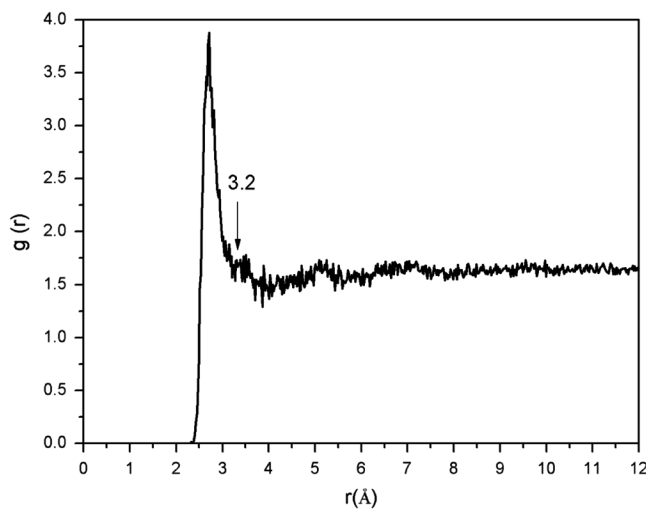

Figure 6. Radial distribution function g (r) for oxygen atom on coal surface with oxygen atom of water.

Å that clearly signifies the formation of one hydration layer of water molecules. In the same plot a second, less pronounced peak can be detected at 15.65 Å. For hydrogen atomic density profile, a distinct peak is located at 13.69 Å and a second, less pronounced peak appears at approximately 16.22 Å. As the distance approaches 17 Å and further, the hydrogen and oxygen density profiles become smooth, suggesting bulk-like behaviour. The profiles indicate that the coal surface properties affect the structural and dynamic characteristics of the interfacial water molecules. The water molecules at the coal/water interface represent much more ordering than those far from the coal surface.

The structural organisation of water in the coal matrix can be described by coal–water radial distribution functions (RDF) representing the relative probability of finding any water molecule whose oxygen atom is at a distance r from oxygen atom on sub-bituminous coal model as shown in Figure 6. It is observed that the peak at 2.71 Å in Figure 6 resulting from the strong hydrogen bond interaction between molecules and coal oxygen moieties. The result confirms that the oxygen moieties are responsible for the absorption of water molecules. In addition,

the first hydration shell with a 3.2-Å cut-off can be confirmed according to the RDF of O_{coal}–O_{water}. The location will become useful in the following discussion.

3.3. MD simulations: dynamic properties of water molecules around oxygen moieties

To better understand the dynamic property of water molecules in the vicinity of different oxygen moieties on the coal model surface, the local self-diffusion coefficient of water molecules in the first hydration shell within 3.2 Å were analysed. The calculated water self-diffusion coefficient around carboxyl, carbonyl and hydroxy is 4.69×10^{-5} cm^2/s, 6.34×10^{-5} cm^2/s and 6.40×10^{-5} cm^2/s, respectively. It is found that the mobility appears to be retarded for the water molecules in the proximity of carboxylic group. It can be attributed to the stronger hydrogen bond interactions between water molecules and carboxyl moieties. It is confirmed that the hydration ability of carboxyl is strongest, which is the preferential site of adsorption, comparing with the other functional groups. Adsorption of water molecules at the hydroxy and carbonyl is similar. The results are consistent with prior studies [11].

4. Conclusions

The graphite surface modified by hydroxyl, carboxyl and carbonyl groups was employed to represent the surface model of sub-bituminous coal according to XPS results, and the composing proportion for hydroxy, carbonyl and carboxyl is 25:3:5. In order to study the structural and dynamic characteristics of the interfacial water molecules, atomic density profiles of water oxygen and hydrogen atoms were calculated. The oxygen and hydrogen atomic density data show the formation of two hydration layers. In addition, the atomic density profiles indicate that the coal surface properties affect the structural and dynamic characteristics of the interfacial water molecules. The water molecules at the coal/water interface represent much more ordering than those far from the coal surface. The results of radial distribution functions, mean square displacement and local self-diffusion coefficient for water molecules related to three oxygen moieties

confirmed that the water molecules prefer to absorb with carboxylic groups, and adsorption of water molecules at the hydroxy and carbonyl is similar.

Acknowledgements

Disclosure statement

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