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Structure evolution characterization of Anyang anthracites via H₂O₂ oxidization and HF acidification

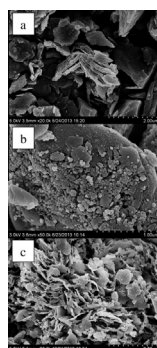
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HIGHLIGHTS

- Aromaticity, crystalline carbon and hydroxyl content increase in derivative coals.
- The particle size of AY–H₂O₂–HF significantly decreases in width.
- Combination of H₂O₂ and HF is effective to reduce the aromatic layer size.
- The superfine crystalline carbon materials like graphite structure were prepared.

GRAPHICAL ABSTRACT

The aromatic layers become much looser and thinner in derivative coals. The thickness of layers is less than 100 nm in AY–H₂O₂–HF. The combination H₂O₂ oxidization and HF acidification is beneficial to reduce the size of the aromatic layers. SEM photographs of the coals: AY (a), AY–H₂O₂ (b) and AY–H₂O₂–HF (c).



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ABSTRACT

The structural characteristics of the raw coal (AY), the H₂O₂ oxidized coals (AY–H₂O₂) and the HF acidified AY–H₂O₂ (AY–H₂O₂–HF) were investigated by SEM, X-ray diffraction, Raman and FTIR spectroscopy. The results indicate that the derivative coals show an obvious increase in the aromaticity, crystalline carbon content and hydroxyl content, especially the AY–H₂O₂–HF. The stacking layer number of crystalline carbon decreases and the aspect ratio (L_a/L_c) remarkably increases for AY–H₂O₂ and AY–H₂O₂–HF. The crystalline layers become much thinner. The particle size of AY–H₂O₂–HF in width significantly decreases from 1 μm to less than 100 nm. The combination of H₂O₂ oxidization and HF acidification is effective to reduce the size of the aromatic layers and to increase the reactivity of derivative coals. The process can help us obtain the superfine crystalline carbon materials like graphite structure.

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Introduction

Coal is a heterogeneous material and the major part of coal consists of a three-dimensional macromolecular network made up of aromatic clusters (mono- and fused aromatic rings with peripheral groups). The aromatic rings are supposed to be linked by aliphatic or hetero aliphatic bridges. The extent of cross-linking in the macromolecular structure influences the decomposition rate and extent of reaction during chemical or thermal depolymerization [1]. Most anthracites represents the highest metamorphic rank in coal [2], virtually all of which is present as aromatic structure contain 30 or more fused aromatic rings [3,4] in large polycyclic sheet [5], resulting in extraordinary properties such as highly ordered carbon and are thus similar to graphite in terms of structure and thermodynamics, yet the substitution of heteroatoms and certain cross-linkages within anthracite make anthracite slightly less stable than graphite [6]. Many attempts have been performed to change the cross-linkage in the macromolecular structure through the oxidation in air, O₂, H₂O₂, alkali, acid medium [7–12]. Fuchs et al. [13] established that acid groupings can be introduced into the coal proper in short time by the use of air at elevated temperature in the presence of small amounts of promoting substances such as vanadates or nitrates. Schwartz et al. [14] studied the macromolecular and chemical changes induced by air-oxidation of a medium volatile bituminous coal. Hayashi et al. [15] proposed that aliphatic C–H bonds are oxidized to form peroxides, which are then cleaved leaving hydroxyl, carboxyl, and carbonyl groups on aromatic clusters. The aromatic rings are oxidized by O₂ with their subsequent decomposition into mono- and di carboxylic acids and carbon dioxide. Coal with high mineral matter content, in particular, certainly requires special beneficiation treatments to remove enough mineral matter for the material to be utilisable. Nyathi et al. [16] considered that the demineralization can endows better graphitization degrees for anthracites. It indicates that the minerals inherent in these anthracites may physically inhibit the ordering of graphene sheets. Hu et al. [17] studied the demineralization of anthracites by chlorination at 2000 °C. After moulding and baking to 850 °C, test specimens produced from the chlorine-demineralized anthracite had lower densities, higher electrical resistivity and lower crushing strength. There are less works to investigate the linkages of cross-linking extent, aromatic carbon, crystalline carbon, hydroxyl groups (OH), ether groups (C–O) and carboxyl groups (COOH) [18] using the combined methods.

Graphite after delaminated can be blended with the polymers to make the functional composites with special performances. Coal crystallites in anthracite are similar to the graphite in structure. But the anthracite is more complicated than the graphite. The structural properties of anthracite have received much attention among coal chemists [1,19–21]. The microstructural changes of the coals have been effectively investigated using the techniques of SEM [22,23], XRD [24–26], Raman [2,25] and FTIR spectroscopy [27,28]. The delaminated structure of coal crystallite can be obtained through destroying the cross-linkages of aliphatic side chains on its edges. Therefore, in this work the combination method of H₂O₂ oxidation and HF acidification were adapted to reduce the linkages within coal crystallites, increase the reactive point on coal particle surface. The derivative coals with high reactivity can be modified by the surfactants to prepare the functional coal-based filler. In order to gain further structural information of the derivative coals, the selected spectra from XRD, FTIR and Raman spectroscopy were fitted using the Peakfit V4.0 software. The aims of the present work are to investigate the influence of H₂O₂ oxidation and HF acidification on the structural of derivative coals and to obtain

a good way to prepare the superfine crystalline carbon materials like graphite structure.

Material and methods

Samples and sample preparation

The anthracite was collected from Anyang in China. The samples were ground into powder (200 mesh) as the experimental materials. The main elemental compositions of the raw coal are as follows: C 81.93%, H, 5.18%, O 10.72%, N 2.17%, S 0.51%. Firstly, 15 g of the Anyang raw (AY) coal was dispersed in 300 mL of concentrated H₂O₂ solution (30.0 wt.%), and the mixture reacted 24 h on magnetic stirrers at 60 °C; therefore, the H₂O₂ oxidized coal (AY–H₂O₂) was obtained after washed by distilled water. Subsequently, 10 g of the AY–H₂O₂ was dispersed in 50 mL of concentrated HF solution (40.0 wt.%), and the mixture stirred for 72 h at ambient temperature; the coal was filtered and washed with distilled water, dried at 80 °C, named as AY–H₂O₂–HF.

X-ray diffraction analysis

The XRD data collection was acquired with a Rigaku D/max-2000 18 kW X-ray diffractometer with Cu K α radiation, 40 kV, 150 mA, and a scanning rate of 2°/min over the range 2.5–65° (2 θ). Peakfit 4.0 software was used for fitting the diffractograms in the 2 θ regions of 16–34° and 39–49°. The broad hump in the region of 16–34° (2 θ) was fitted to two Gaussian peaks around 20° and 26°, representing γ -band and Π -band (d_{002}) respectively. The peak positions, intensities, widths and area were determined.

Theoretically, the areas under the γ and Π -peaks are believed to be equal to the number of aromatic carbon atoms (C_{ar}) and aliphatic carbon atoms (C_{al}), respectively [29]. Therefore, the aromaticity (f_a) of coal i.e. the ratio of carbon atoms in aliphatic chains vs aromatic rings, can be defined as $f_a = C_{ar}/(C_{ar} + C_{al}) = A_{002}/(A_{002} + A_{\gamma})$. The lateral size (L_a) and the stacking height (L_c) of the crystallite were determined using the conventional Scherrer equations [30]: $L_a = 1.84\lambda/(\beta_a \cos \varphi_a)$ and $L_c = 1.84\lambda/(\beta_c \cos \varphi_c)$, where λ is the wavelength of the radiation used, β_a and β_c are the width of the (100) and (002) peaks, respectively, at 50% height, and φ_a and φ_c are the corresponding scattering angles or peak positions. The aspect ratio of stacking aromatic layer is equal to the ratio of L_a vs L_c . The stacking layer number (n) of crystalline carbon can be defined as the ratio of L_c to interlayer spacing (d_{002}) within aromatic layers.

Raman spectroscopy analysis

The Raman spectra were recorded at a resolution of 4 cm⁻¹ using an in Via Laser confocal Raman spectroscopy system, at the conditions of 514.5 nm laser wavelength, 65 μ m slit-width, 20 s data acquisition time and 3 scanning times. The laser power of the incident beam on the sample was kept below 2 mW to prevent irreversible thermal damage to the sample surface. The samples were scanned between 4000 cm⁻¹ and 400 cm⁻¹. For all the spectra, a linear baseline correction was used and the band fitting was performed with Peakfit V4.0 software using Gaussian functions in the region of 1800–1000 cm⁻¹. The band positions, intensities, widths and area were determined. The defect degree (A_{D1}/A_G) of microcrystalline carbon was equal to ratio of the integrated intensities of the D_1 (1350 cm⁻¹) and G bands (1580 cm⁻¹). The content of crystalline carbon (C_{cr}) was calculated from the ratio of the intensity of D_1 and G peaks (I_{D1+G}) to the total intensity (I_{Total}) of D_1 , D_3 (1530 cm⁻¹), D_4 (1200 cm⁻¹) and G peaks [2,31,32]. The content of amorphous carbon (C_{am}) in the coals was the peaks D_3

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