



## Full Length Article

## Coal macromolecular structural characteristic and its influence on coalbed methane adsorption



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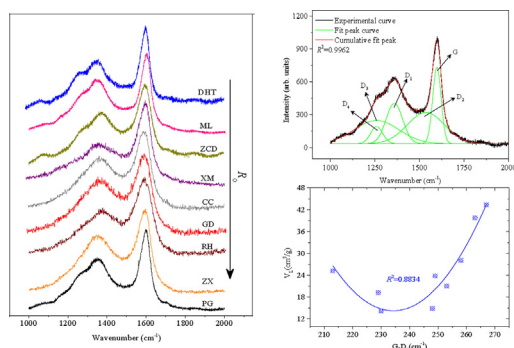
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## GRAPHICAL ABSTRACT



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## ABSTRACT

In order to investigate the effect of coalification on coal macromolecular structure, the combination of Raman spectroscopy and low-pressure  $N_2$  gas adsorption (LP- $N_2$ GA) was adopted to explore the chemical and physical characteristics of selected samples ranging from bituminous C to anthracite. Raman structural parameters, including band position, band area ratio ( $A_{D1}/A_G$ ) and band position difference ( $G-D_1$ ) of G band and  $D_1$  band were derived from curve-fitting analysis. Methane adsorption properties of these samples were measured, and correlations between these Raman parameters and coalbed methane adsorption capacity ( $V_1$ ) were also established. The results indicate that  $D_1$  band generally shifts to the lower wavenumbers decreasing from  $1365\text{ cm}^{-1}$  to  $1339\text{ cm}^{-1}$ , while G band shifts to higher wavenumbers ranging from  $1578\text{ cm}^{-1}$  to  $1609\text{ cm}^{-1}$  with increasing coal rank. The values of  $G-D_1$  increase, but the band area ratio ( $A_{D1}/A_G$ ) declines with the increase of  $R_o$ . Pore parameters, including the BET SSA and pore volume, show a polynomial relationship with  $G-D_1$ , but a reduction for  $A_{D1}/A_G$ . The increase of graphitization and the order degree of aromatic structures in coal can enhance the porosity in coal. The evolution of coal macromolecular has significant impact on methane adsorption, which displays a U-shape correlation with Raman parameters. Coalbed methane adsorption is not only related to the physical structures, but also to the chemical characteristics, which should be taken into account in practice.

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## 1. Introduction

Coal is an organic, porous and heterogeneous sedimentary rock, containing complex physical and chemical structures [1–4]. The organic structural characteristic of coal and its influence on coalbed methane adsorption behavior are one of the key elements in coal science and technology [5,6]. However, the resulting heterogeneity complicates the characterization of coal structure, and thus the fundamental understanding of the physical, chemical and structural properties of coal remains paramount and challenging to coal scientists and engineers [7–10].

Fortunately, the recent advances in technical innovation and soft improvement has promoted a wide variety of analytical techniques, such as Fourier transform infrared spectroscopy (FTIR) [11–14], X-ray diffraction (XRD) [15,16], Raman spectroscopy [17,18], solid state  $^{13}\text{C}$  nuclear magnetic resonance (NMR) [19–22], etc. These techniques have been employed for quantitative evaluation of macromolecular structures of coal with varying degrees of success [23–26]. Compared with other instrumental techniques for exploring the internal microstructure of carbonaceous materials including coal, Raman spectroscopy, which was discovered by C. V. Raman [27], exhibits prominent advantages. Raman spectroscopy can not only explore the functional groups but also the carbon skeleton in coals since its broad determination range. It can also offer higher resolution for coal macromolecular structure, and is more sensitive to the change of coal structure than other analytical techniques [28,29]. This enables a better understanding of coal macromolecular structure.

Typically, it is generally accepted that the organic matrix of coal is composed of three-dimensional macromolecular networks [30,31]. These networks contain a large number of stacked aromatic clusters and amorphous carbonaceous matter, which are linked by aliphatic and hetero-aliphatic bridges [32]. Recently, Raman spectroscopy used for the characterization of coal structure has attracted much attention all over the world, especially for coal scientists. A detailed comprehensive review on Raman spectroscopy for the analysis of coal has been reported by Potgieter-Vermaak et al. [33]. Since the two broad bands in the regions of 1575–1620 and 1355–1380  $\text{cm}^{-1}$ , called the G (graphitic) and D (disordered) bands, were first discovered by Tuinstra and Friedel etc. [34,35], the correlation between Raman parameters and coal rank has been intensively studied. Schito et al. [36] investigated the diagenetic thermal evolution of organic matter using Raman spectroscopy, and found that the thermal maturity was best correlated with the Raman parameters, D-G band distance, D/G area ratio and etc. Hinrichs and coworkers [37] analyzed the Raman spectra of typical 35 coals within various ranks ranging from peat to anthracite, suggesting that the width of G band and both width and position of D band decreases with increasing vitrinite reflectance. Similar results have also been found by Okolo et al. [38], Guedes et al. [39], Ferralis et al. [40] and Ulyanova et al. [41]. Pan et al. [42] applied Raman spectroscopy in tectonically deformed coal, and concluded that tectonic deformation can increase the order degree of aromatic structure to some degree. Verma and Sirvaiya [43] proposed the intelligent models to predict the Langmuir adsorption constants for Indian coals. Wu et al. [44] showed that the macromolecular structures of coals with different coal ranks are closely related to the Raman band area ratios. Work by Morga et al. [45], Konchits et al. [46], and Quirico et al. [47] also observed a decrease in the G band FWHM (full width at half-maximum) and an increase in the  $I_{\text{D1}}/I_{\text{G}}$  ratio with increasing coal rank ranging from bituminous to anthracites.

Methane adsorption on coal surface results from the interaction between  $\text{CH}_4$  molecules and coal macromolecular structure [48–51]. However, only a few literatures have been found regarding the effect of coal molecular on gas adsorption. Both Mosher et al. [52] and Zhang et al. [53] conducted molecular simulation of methane adsorption in coal and gas shale systems, but only pore characteristics were considered and the surface functionalities were ignored. Zhu et al. [54]

found that methane is preferentially adsorbed the sites directly above the carbon atoms by density functional theory. Hao et al. [55] and Fu et al. [56] confirmed that the oxygen-containing functional groups can decrease the  $\text{CH}_4$  adsorption capacity, which is also supported by Nie et al. [57] and Liu et al. [58]. However, work by Tenney et al. [59] and Liu et al. [60] showed that the oxygen-containing functional groups can generally enhance  $\text{CO}_2$  adsorption.

As mentioned above, much attention has been paid to the molecular simulation of methane adsorption in coal or carbonaceous materials, while the influence of macromolecular structure on methane adsorption is less studied through experimental method. The objective of this paper was to probe the macromolecular structural characteristic and its effects on methane adsorption in coals with the aid of Raman spectroscopy, which will provide guidance for the development of coal molecular models and coalbed methane exploitation.

## 2. Sample preparation and experiments

### 2.1. Sample preparation

In this paper, nine coal samples ranging from bituminous C to anthracite were collected from Pingdingshan coalfield in Henan province, Xishan, Qinshui coalfield in Shanxi province, and Kailuan coalfield in Hebei province. Specifically, samples PG and ZX were taken from Pingdingshan coalfield, and the corresponding coal seams belong to the Upper Carboniferous Taiyuan Formation. The average thickness of coal seam is about 1.08 m. Samples RH, GD, XM, ZCD and ML were obtained in Xishan coalfield, belonging to the Lower Permian Shanxi Formation. The corresponding thickness of coal seam ranges from 5.33 m to 12.17 m. Samples CC and DHT were from Qinshui and Kailuan coalfield, respectively. The fresh samples were vacuum-sealed and immediately sent to laboratory for analysis. After pulverization, 200–250  $\mu\text{m}$  (60–80 mesh) size fractions of samples were selected for proximate analysis, following the international standard ISO 11722:2013 and ISO 1171:2010. The ultimate analysis of samples was performed according to ISO 17247:2013 and ISO 19579:2006. Reflectance measurement was conducted on the polished samples using a standard microspectrometer (QDI 302<sup>TM</sup>, CRAIC), and the vitrinite reflectance ( $R_s/\%$ ) of coal samples was determined in accordance with ISO 7404-5:2009. Table 1 presents the conventional analyses of the selected coal samples. It is noted that the result of proximate analysis can be also found in our previous literature [2].

### 2.2. Characterization experiments of coal samples

The adsorption capacity of methane on samples was measured in an iSorb HP apparatus (Quantachrome Company) using the high-pressure volumetric method, according to ISO 18871:2015. Prior to methane adsorption measurement, the pulverized coal samples of approximate 100 g with 60–80 mesh (0.20–0.25 mm in particle size) were dried in a desiccator under vacuum at 100 °C for 6 h, and then these samples were placed into a coal sample tank. The  $\text{CH}_4$  adsorption experiments were conducted at 25 °C in the equilibrium pressure range of 0–5.5 MPa.

The physical microstructure analysis was carried out on 60–80 mesh samples with a Quantachrome Autosorb-6B/3B instrument using low-pressure  $\text{N}_2$  gas adsorption (LP- $\text{N}_2$ GA). After outgassing, pore structure measurements were conducted at 77 K with the relative pressure ranging from 0.01 to 0.995, following the ISO standard ISO 15901-2:2006.

### 2.3. Raman spectroscopy

It should be noted that the inorganic mineral matter in coal has influence on Raman analysis [43,61]. Thus, samples of < 75  $\mu\text{m}$  (200 mesh) were demineralized to reduce the influence before experiments. This demineralization process was accomplished using the typical three step HCl-HF-HCl procedure, which has been described elsewhere

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