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Breaking the limits of structural and mechanical imaging of the heterogeneous structure of coal macerals

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Abstract

The correlation between local mechanical (elasto-plastic) and structural (composition) properties of coal presents significant fundamental and practical interest for coal processing and for the development of rheological models of coal to coke transformations. Here, we explore the relationship between the local structural, chemical composition, and mechanical properties of coal using a combination of confocal micro-Raman imaging and band excitation atomic force acoustic microscopy for a bituminous coal. This allows high resolution imaging (10s of nm) of mechanical properties of the heterogeneous (banded) architecture of coal and correlating them to the optical gap, average crystallite size, the bond-bending disorder of sp^2 aromatic double bonds, and the defect density. This methodology allows the structural and mechanical properties of coal components (lithotypes, microlithotypes, and macerals) to be understood, and related to local chemical structure, potentially allowing for knowledge-based modeling and optimization of coal utilization processes.

1. Introduction

Continued growth and stability necessitates the search for new energy sources to maintain the ever accelerated pace of technological development. While the contribution of renewable energy continues to grow in the US, carbon-based fossil fuels will remain the primary energy source domestically and internationally for a considerable period. The development of efficient extraction, preparation and combustion/use strategies for reducing emissions, optimization of coal-to-liquids and coal-to-chemicals production all require knowledge of the fundamental properties of coal and its behavior during physio-chemical transformations. In particular, optimization of coal processing during all stages of use requires an understanding of the mechanical properties of coal and coal elements. Similar challenges emerge in coal science, for example in natural processes such as metamorphic graphitization [1, 2]. Transformation of kerogen, which is considered the main precursor of graphite in nature, depends on the molecular orientation of domains, and occurs at temperatures of at least 2000 °C [3–5]. Mechanical stress/strain can facilitate graphitization at much lower temperatures, however, through the alignment of aromatic lamellae, and the collapse and coalescence of pore walls [6, 7]. It was speculated that the main component of the activation energy required for graphitization is provided by strain energy [7]. Whether the carboneaceous material is graphitizing (bituminous coal and some anthracite) or commonly non-graphitizing (lignite) depends on the material structure and composition and whether it softens and becomes mobile between 400 and 500 °C to allow growth of molecular oriented domains larger than 10 μm [8–14]. Overall, the complexity between local mechanical (elasto-plastic) and structural (composition) properties of coal presents a significant challenge and is of fundamental and practical interest for metallurgical coke production.

Most studies are limited by the inhomogeneity of coal structure, due to different precursors and depositional environments producing diversity in the maceral structure, its mixtures, as well as mineral inclusions, and porosity. Macerals, the microscopically recognizable components of coal in part originates from different constituents of the original plant tissue and will have varying properties relating to the compositions of oxygen rich components (vitrinite), more hydrogen rich aliphatic components (liptinite) and more carbon rich aromatic (inertinite) components. These structures differ in chemical and physical properties but their variation on the micron to submicron scale often precludes determination of the mixed maceral contribution to micromechanical studies using conventional techniques. Furthermore, chemical and structural variation and micromechanical inhomogeneity of coal on the scale below ~ 1 micron and down to nanometer scale is unknown.

Previous efforts on imaging coals, mineral matter, and coal ash structures with high resolution were focused on fly ash structure-composition [15], high-pressure studies of metamorphic transformations of coal [16] and on characterization of inorganic components [17, 18]. While the spatial resolution of scanning electron microscopy can be below 10 nm, the low atomic weight of elements composing the coal does not create large contrast for high-resolution imaging of macerals. Alternative approaches for probing coal structure are offered by optical methods. Reflectance indicating surface (RIS) parameter has been used to characterize carbon-materials in coal [19], and graphite [20], on the micron scale [21] using optical microscopy. The Kilby method modified by Duber extended the technique to heterogeneous systems like coal [22]. Recently the method was successfully applied to study the microstructure of coal during heating and correlating local changes in RIS parameters to coal ranks [23]. The resolution of Kilby–Duber method can approach diffraction limit (confocal mode) for the detection of macerals with

significantly different values of RIS parameter, but will show poor resolution for the heterogeneous structures composed of materials with similar values of RIS parameter.

Spatially resolved confocal micro Raman spectroscopy could map coal with regard to rank, disorder level, average 'graphite' domain dimension, near infrared (NIR) emission of coal with submicron resolution [3, 24–26]. Significant advances have been reported in obtaining spatially resolved structure of coal using confocal micro Raman for identification of inorganic [5] and ordered and disordered carbon components [3, 7–9], to study changes in the collotelinite, fusinite, macrinite macerals signatures as a function of coal rank [10, 11, 27, 28], chars [15, 16, 29], and coke [17]. Raman spectroscopy and cathodoluminescence allowed correlation of spatially-resolved coal maturity index with the presence of polycyclic aromatic hydrocarbons (PAH) [30]. However, the complexity of coal structure leads to the second order effects including but not limited to quenching and self-quenching of the excited state of asphaltenes and pyridines, thus complicating interpretation of the photoluminescence results [31, 32]. The interpretation of cathodoluminescence or photoluminescence response of coal is further complicated by broad range of luminescent constituents like amorphous carbon, silica and silicates among others [30]. Due to complex structure and heterogeneous nature multiple complementary analytical techniques should be used to elucidate the structure-functional peculiarities of coal.

Since the early 1990s [33], less than a decade after its original development, the atomic force microscope (AFM) [34] has been increasingly used to measure the surface properties and micro-structure of coal [35]. The AFM research to date has focused on coal maceral [36, 37] or coal surface pore characteristics of surface topography [38]. Here, we use combined multimodal

micro-Raman and functional AFM imaging through band excitation-atomic force acoustic microscopy (BE-AFAM) to resolve chemical, mechanical and structural components of coal on the micron-nanometer scale. Combining these approaches has the advantage that high-spatial resolution of confocal micro Raman and BE-AFAM allows further insight into structure-mechanical properties of coal at the submicron level and furthers the understanding of the deformations (stress and/or strain) on mechanisms of coalification and graphitization [7].

2. Methods

2.1. Sample preparation

A coal sample collected from an underground mine in the subbituminous/bituminous region of the Uinta Basin, Colorado, USA was used in this study. The sample was previously investigated and the calorific value of this coal on a dry basis was 27.9 MJ kg^{-1} (ASTM D388, 2005) [39]. The fixed carbon, volatile material and ash yield on the dry basis were determined as 56.99%, 38.31%, and 4.70% (ASTM D7582, 2010), indicating bituminous rank. The coal sample was securely attached to a sample actuator using two part epoxy (5 min epoxy, Devcon).

2.2. Raman spectroscopy

Raman spectra were collected in backscattering geometry using a confocal micro-Raman Renishaw 1000 equipped with a 50× objective (Leica, NA = 0.55) using 633 nm (HeNe laser) for excitation. The mapping was done on the area without mineral inclusions, thus justifying use of static Raman mapping mode. The point-by-point mapping with 1200 l mm^{-1} grating centered at 1450 cm^{-1} enabled collection of Raman spectra in $1010\text{--}1860 \text{ cm}^{-1}$ spectral range. The point-by-point mapping was done in confocal mode collecting 5041 spectra over an area of $71 \times 71 \text{ }\mu\text{m}$ with a $1 \text{ }\mu\text{m}$ step size and 5 s integration time. The Raman spectra were baseline-corrected and

deconvoluted using a mixed Gaussian–Lorentzian function. The G- and D- peak parameters including intensity, full width at half maximum (FWHM), central frequency were used for further analysis, including calculation of the G/D band intensity and FWHM ratios.

2.3. Band excitation—atomic force acoustic microscopy

To explore the mechanical properties of coal, we introduce a combination of atomic force acoustic microscopy (AFAM) [40] with the band excitation (BE) approach [41]. In AFAM, the probe tip is held in constant force with the sample, while the sample position is mechanically excited using an ultrasonic transducer, emitting longitudinal waves into the sample and causing an out-of-plane surface displacement. The vertical displacements of the surface are transferred through the nanoscale tip-surface contact, exciting flexural oscillations in the cantilever beam, which acts as a resonator amplifying sub-nm surface displacements. Here, we utilize the mechanical contact resonance (CR) of an AFM cantilever in contact with a sample, which changes with variations in tip-sample mechanical properties [40, 42–45]. As shown in figure 1, the cantilever–sample interaction can be represented as two coupled springs in series (i.e. cantilever elastic modulus and sample elastic modulus) and in parallel with a dashpot element (i.e. dissipative sample interactions or viscous behavior of material). In this way, the tip-sample contact is impacted by both conservative (i.e. elastic) and dissipative (i.e. viscous) mechanical interactions. The mechanical tip–sample interactions will be strongly influenced by both *elastic* and *viscous* behavior of the sample, which can be observed through both shifts in the CR frequency as well as broadening of the peak shape (change of Q-factor), respectively. As shown in figure 1(b), when the stiffness of the sample contact changes, the CR frequency (ω_0) shifts conservatively, with a higher ω_0 representing a higher sample stiffness and subsequently a lower ω_0 representing a lower sample stiffness. At the same time, any viscous behavior in the sample

will be reflected as energy dissipated in the tip–surface interactions. The quality factor (Q) of the CR, (i.e. full width half maximum), can be used as a measurement of energy dissipation in the tip–sample interaction, where a lower Q is expected for a more viscous material. The result of which is that information on the ω_0 and Q factor are directly related to the mechanical properties of material in the tip-surface contact, providing a valuable way to map them locally. Determination of both elastic and viscous material properties unambiguously, however, necessitates measurement and analysis methods capable of simultaneously detecting changes in both the ω_0 (elastic response) and Q (viscous response). This requires extension of existing single frequency techniques into the multifrequency domain.

We use the BE method as it allows capturing the entire cantilever transfer function in the band comprising the CR [41]. In BE, the full amplitude and phase response of the cantilever transfer function in the vicinity of the CR is recorded. To achieve this, a digitally synthesized signal is inverse Fourier transformed to generate a signal in the time domain, which is used to excite the transducer sample stage. When operated in the linear regime, the behavior of the cantilever CR can be approximated by a damped harmonic oscillator and described by three independent parameters: ω_0 , amplitude at CR, A_0 , and Q , which can be deconvoluted and stored as images as given by equation (1):

$$A(\omega) = \frac{A^{\max} \omega_o^2}{\sqrt{(\omega^2 - \omega_o^2)^2 + (\omega \omega_o / Q)^2}}, \quad (1a)$$

$$\tan(\varphi(\omega)) = \frac{\omega \omega_o / Q}{\omega^2 - \omega_o^2}. \quad (1b)$$

From these, ω_0 is related to the tip-surface force gradient, A_0 to the driving force, and Q to energy dissipation. The BE detection applied to AFAM is particularly useful as it allows deconvolution of both conservative (ω_0) and dissipative (Q) contributions of the tip–sample

interaction, and hence, separation of elastic (i.e. conservative) and viscous (i.e. dissipative) material behavior simultaneously. Noteworthy, well known contact mechanics models, such as the Kelvin–Voigt model, can be subsequently used to convert these stiffness and dissipation measurements to elastic modulus and loss modulus [46, 47]. However, this requires additional calibration steps and was beyond the scope of this study.

In this work, all measurements were performed using Si cantilevers (*Olympus, AC240*) with nominal resonant frequency and stiffness of 70 kHz and 2.8 N m^{-1} , respectively. A commercial AFM (Asylum Research, MFP-3D) was used, equipped with a highly damped piezoelectric sample holder (Asylum Research, Contact Resonance Module) acting as a sample actuator. All measurements are performed in contact mode where the tip was held in constant force ($\sim 100 \text{ nN}$) with the surface using static deflection feedback. To operate BE-AFAM, data acquisition and arbitrary waveform generator were implemented using NI 5122 and 5412 cards (National Instruments, NI5122 and NI5412) and custom Matlab code (MathWorks).

3. Results and discussion

3.1. Confocal and micro-Raman spectroscopy

Optical imaging, figure 2(a), reveals a variety of maceral components surrounded by a matrix of vitrinite macerals. Vitrinite is a primary maceral component derived from cellulose and lignin (i.e. from cell wall material or woody tissue of plants) and having higher reflectance appearance. A large inclusion across the image can be seen in figure 2(b), a 3D AFM topography image of approximately the same location, and is identified as cutinite, a maceral of the liptinite group, demonstrating a lower reflective optical property than the surrounding vitrinite matrix. Cutinite is a plant cuticle and is typically very long and thin with uniform cusps on one side, is very

elastic and generally stands in relief on a polished surface. Here the cuticle is rather thick and has folded upon itself.

Optical microscopy remains one of the most common and standardized method for characterization of coal type and rank [48–50]. The optical photograph of the sample shows four distinct areas based on their reflectance, listed in the order of decreasing reflectance: 1 (highest reflectance value) > 4 > 3 > 2. Both area 1 and 2 appear uniform whereas area 3 and 4 are heterogeneous. Based on the optical reflectance and morphology we assigned area 1 to inertodetrinite, area 2 to cutinite, area 3 as vitrinite and 4 as semifusinite (a lower reflecting inertinite maceral). The original Raman spectra between 1010–1860 cm^{-1} were deconvoluted using a mixed Gaussian–Lorentzian fit with both peak and relative peak parameters analyzed. Spatially resolved Raman maps are shown in figures 2(c), (d). Here we are primarily interested in crystallinity or degree of order across the sample and, consequently, chose to analyze the I_G/I_D rather than the I_D/I_G ratio. We note that the I_G/I_D ratio is directly proportional to AL_a where A is a constant and L_a is the average crystallite size [51]. Figures 2(c) and (d) are background corrected ratio of the integrated intensity of G- (1599 cm^{-1}) to D- (1323 cm^{-1}) bands and the ratio of peak full widths at half maximum (FWHM), respectively. Data in figure 2(c) can be considered as first approximation of the L_a . However, because both I_G and I_D depend on the excitation wavelength, we used values of FWHMs for G- and D-peaks (figure 2(d)) to estimate the averaged distance between defects, L_d , since the FWHM does not depend on the excitation wavelength [52]. We found that the value of L_d varies between 2–2.5 nm for areas 1, 3, and 4 (note; L_d was not evaluated for area 2 where high fluorescence background did not allow for complete spectral deconvolution). The small distance between defects suggests that conditions for the application of the Tuistra–Koenig approach are not met, and the L_a is proportional to

$(I_G/I_D)^{1/2}$; the carbon in coal sample can be considered as mostly amorphous. Using previously reported correlation between L_a (derived from x-ray diffraction) and the I_D/I_G intensity ratio obtained from the Raman spectra [52, 53], the L_a value was estimated to be less than 3 nm. Defect density can be estimated from the equation $n_d \text{ (cm}^{-2}\text{)} = (1.8 \pm 0.5) \times 10^{22} \times (I_D/I_G)/(\lambda)^4$, where λ is the excitation wavelength of laser. Since excitation laser source was the same across the map, the equation reduces to the $n_d \sim (I_G/I_D)^{-1}$.

From this analysis, figure 2(c) can be interpreted as inverse of the defect density map, with the lowest values of the n_d in area 1 (left part) and area 4. It is worth noting that the inclusions with slightly higher reflectance values located in the area below area 2 are difficult to distinguish optically from its surroundings (figure 2(a)). However, their presence is clear on the I_G/I_D map, suggesting a heterogeneous nature of this location with inclusions demonstrating a lower defect density compared to the surrounding matrix. It should be mentioned that while FWHM of the D- and G- peaks are expected to be excitation wavelength independent, we have not obtained a uniform map of their ratio. This is probably due to the fact that the estimated distance between defects is smaller than the average distance an electron-hole pair travels to scattering with a phonon, making defects contribution interdependent which in turn leads to slightly dispersive nature of the G-band. According to Zerda et al. the difference between L_a in vitrinite and inertinite could be as low as 0.3 nm and as high as 2.3 nm with vitrinite showing the lower value ($L_a \sim 3.3 - 3.8$ nm) as the difference is shown to scale with rank [54].

The optical gap of coal macerals can be derived using a phenomenological three-stage model of the carbon amorphization trajectory, which explains structural transformations of ordered, disordered and amorphous carbons in terms of resonant excitation of π states and the long-range

polarizability of π -binding [55]. Based on the position of the G-peak (1599 cm^{-1}), a non Tuistra–Koenig dependence of L_a , and the dispersion of the G- band, we assign the sample to the second stage of carbon amorphization model (characterized by transition from monocrystalline graphite to amorphous carbon). The value of the optical gap, E_g , increases proportional to the increase in the value I_G/I_D ratio, following the equation [55] $E_g = (CI_G/I_D)^{1/2}$, where C is a constant. The value of the e.g. increases in the series: area 2 < (area 1(right) and area 3) < (area 4, left part of area 1). The optical gap series is related to the changes in bond-angle and bond-bending disorder of sp^2 aromatic double bonds.

3.2. BE-AFAM

To explore the local structural and mechanical properties of the coal microstructure, the same area of the sample was investigated using BE-AFAM and directly correlated to micro-Raman results. The region was located using optical microscopy, allowing the cantilever to be positioned over the same region imaged by confocal micro-Raman imaging, figures 2(c), (d). Here, the cutinite inclusion, area 2, corresponds to the region with a low reflectance in optical image, figure 2(a), and can be easily identified in the AFM deflection image, figure 3(a).

Figure 3(b) shows the CR spectra recorded over dissimilar regions of the sample, as identified in figure 2 by confocal micro-Raman imaging. It can be clearly seen that significant variation in the ω_0 , A_0 , and Q can be observed across the coal surface. For the area 2, the cutinite inclusion (purple square), the ω_0 and corresponding Q factor were found to be $\omega_0 = (301.33 \pm 1.09 \text{ kHz})$ and $Q = (41.56 \pm 14.28)$. These values are significantly lower than all other locations, where $\omega_0 = (312.08 \pm 1.79 \text{ kHz})$ and $Q = (105.63 \pm 32.54)$ was determined for area 1 the small inertodetrinite inclusion; and $\omega_0 = (306.25 \pm 1.18 \text{ kHz})$, and $Q = (96.27 \pm 35.25)$ determined for

area 3 vitrinite and $\omega_0 = (307.53 \pm 1.05 \text{ kHz})$, and $Q = (86.25 \pm 29.38)$ determined for area 4 semifusinite. These results indicate that the cutinite inclusion is considerably softer and more viscous than the other regions, as demonstrated through lower ω_0 and Q factor. The stiffest and least dissipation response of area 1 corresponds to the carbon with the largest optical gap and lowest density of defects.

BE-AFAM resolves inhomogeneous structural and viscoelastic behavior of maceral in coal specimens with a spatial resolution on the order of ~ 10 s of nm, far exceeding the resolution of standard light microscopy and confocal micro-Raman spectroscopy. To explore the structure of the sample at intermediate, $< 100 \text{ nm}$ resolution, the same region was mapped with BE-AFAM. BE-AFAM images, figures 3(c), (d), together with cantilever deflection image, figure 3(a), clearly demonstrate the several inhomogeneous regions, including the inertodetrinite inclusion and surrounding liptinite. In BE-AFAM ω_0 and Q images, brighter values correspond to higher stiffness and lower damping respectively. It is immediately clear that the various macerals components demonstrate significantly different elastic and viscoelastic behavior as is expected from the single CR spectra measurements. It can be seen that the cutinite inclusion demonstrates a lower ω_0 (i.e. lower elastic modulus) and lower Q (i.e. higher loss moduli) than the vitrinite matrix, whereas the embedded inertodetrinite material shows a higher elastic and lower loss moduli than both cutinite or vitrinite matrix. Furthermore, smaller inhomogeneities in the vitrinite matrix are apparent throughout the image, for example the bottom right corner of figures 3(a) and (d), suggesting that BE-AFAM can be used to visualize viscoelastic behavior of coal macerals on submicron scales.

Note that the BE-AFAM is not limited to imaging of the non-fluorescent areas, thus enabling characterization of area 2 (figure 3(a)) in more detail. The area is characterized by the smallest value of the reflectance and e.g., highest density of defects or high disorder of sp^2 atomic double bonds (reduced conjugation of the π system) which is expected from the soft and viscous macerals, which is demonstrated in BE-AFAM with this area having the lowest value of the Q factor and ω_0 . The conclusions on optical, Raman scattering and mechanical properties for the most reflecting maceral (area 1, left side) are complimentary. The high reflectance maceral is the hardest among those studied with lowest e.g. value, lowest defect density and most conjugated π -electron system of sp^2 hybridized carbon. The intermediate values of optical, Raman scattering and mechanical response correlate well, suggesting that multi-analytical technique Raman-BE-AFAM provides complimentary information on visualization and direct correlation of structural and viscoelastic properties of coal macerals on submicron scales. This correlation can also be used on submicron scale to characterize heterogeneous areas of coal (below area 2). We showed that confocal micro Raman allows better resolution for imaging of heterogeneous macerals with close values of optical reflectance.

Here, we consider detection limits of confocal optical and micro-Raman spectroscopy, which allows probing controlled sampling volume using confocal aperture, or slit binning approaches among many others. The laser beam size focused on the sample can be considered a rough approximation of the spatial resolution limit (d_{x-y}) which depends on the laser wavelength λ (assuming single mode laser) and the numerical aperture (NA) of the microscope objective, $d_{x-y} = 0.61\lambda/NA$. The spatial resolution is defined using Rayleigh criterion, which states that two points on two-dimensional image are resolvable if their Airy disk diffraction patterns are distinct. Depth of field which is closely related to the Z-resolution, is defined by the depth of sample which stays

in focus, $d_z = \lambda\eta/(\text{NA})^2$, where η is the refractive index of the media. The Raman mapping with submicron x - y spatial resolution can be achieved with the system equipped with short-wavelength excitation, high numerical aperture objective with the depth of field (z -resolution) decreasing faster than the x - y spatial resolution. The confocal micro Raman system spatial resolution is around $0.6\ \mu\text{m}$.

Because BE-AFAM is not limited by Rayleigh criterion we expect to exceed the spatial resolution of the confocal micro-Raman. We note that the BE-AFAM image of area 1 (right side) indicates a heterogeneous phase with small oriented domains to that of area 1 and 2, which may imply that the area is a result of precipitation of high quality material eventually coalescing to form maceral in area 1. The results on coal maturation where softer phase is reported as a precursor to high quality macerals support this interpretation [3]. We now probe the achievable resolution limit of BE-AFAM imaging technique using correlated Raman-BE-AFAM response for large domains, assuming that coal has fractal structure, and that the domains observed on submicron scale have the same nature and composition as that on micron scale [56, 57]. A high resolution image ($2.5 \times 2.5\ \mu\text{m}$) of the inertodetrinite inclusion (area 1) embedded in cutinite (area 2) shows features spatially resolved below 100 nm length scales, figure 4(e). Three regions and two boundaries are clearly distinguishable in both deflection and BE-AFAM images (figures 4(a)–(c)). Qualitatively, the cutinite demonstrates a softer and more viscous behavior similar to that on the micron scale, indicating continuity of mechanical response on micron to 100 nm scales. From the deflection image each region demonstrates a very different surface structure and can be clearly identified. The mean surface roughness (R_a) from the topography image (not shown) in the three different regions (marked with numbers in figure 4(d)) was found to be; 1.04 nm, 7.78 nm and 4.33 nm for regions 1 2 and 3 respectively. Furthermore, a significant

difference in the relative stiffness is observed through different CR ω_0 as shown in figure 4(d). The ω_0 appears to be more sensitive for distinguishing components in heterogeneous area 2 on figure 4(e). The smallest feature of approximately 0.57 nm in height and 4 nm in radius with a higher relative stiffness than the surrounding matrix was identified on high resolution scans. Based on the increase in stiffness, we assign this feature to mineral inclusions. The observed increase in surface roughness in this interfacial area (area 2) between inertodetrinite and cutinite is likely a result of the polishing process where it's possible that secondary depositions of other organic or mineral matter results in the observed heterogeneous structural and mechanical properties.

4. Summary

The internal structure of coal has been studied using combination of micro-Raman spectroscopy and BE-AFAM on micron and submicron scales. BE-AFAM has been used for the first time to study coal with sub-50 nm resolution and provide detailed chemical and micromechanical maps of macerals. The synergy of BE-AFAM and confocal micro-Raman spectroscopy allows mechanical properties to be probed and correlated to the reflectance, optical gap, average crystallite size, and defect density. Such a synergistic combination of techniques can provide a unique insight into the complexity of coal morphology on nano- and mesoscopic length scales. It will also allow the comprehensive modeling of mechanical behavior of coal during maturation, graphitization, extraction and utilization, opening pathways for knowledge-driven advancement in large-scale energy production.

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Figure Captions

Figure 1. (a) Schematic of conservative and dissipative interactions in BE-AFAM where the elastic response is represented as a spring having a sample stiffness of k and sample dissipation is represented as a dashpot with a damping coefficient b . (b) The frequency of the CR is proportional to sample stiffness and the quality factor of the CR is proportional to the sample dissipation.

Figure 2. Confocal micro-Raman imaging of coal. (a) Optical micrograph of coal region selected for investigation (imaged through Leica 50 $\times$, NA = 0.55 objective) (1- inertodetrinite, 2- cutinite, 3- vitrinite and 4- semifusinite). (b) A 80 $\times$ 80 μm 3D AFM topography image of the same regions (c) background corrected G/D integrated intensity band ratio and (d) G/D peak full width at half of maximum ratio peak 1599 cm^{-1} /1323 cm^{-1} .

Figure 3. (a) Deflection image and (b) average response spectra determined from regions indicated in the deflection image (red- inertodetrinite, purple- cutinite, green-vitrinite and black-semifusinite). BE-AFAM maps of the fitted (c) frequency response and (d) quality factor of the cantilever response.

Figure 4. (a), (d) Deflection images and (b), (c) frequency response and (d), (e) quality factor of the cantilever transfer function. Where (d)–(f) are taken from area indicated by a dashed box in region (a).

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