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Mapping internal structure of coal by confocal micro-Raman spectroscopy and scanning microwave microscopy

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HIGHLIGHTS

- Complexity of coal demands increasing spatial resolution in characterization.
- Scanning probes offer various spatially-resolved characterization functionalities.
- Coal samples were imaged with micro-Raman and Scanning Microwave Microscopy.
- This combination allowed resolving coal structure below a 100-nm spatial resolution.

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ABSTRACT

Structural complexity and variability of the chemical properties define technological applicability of coal and demand increasing accuracy and spatial resolution from the techniques used for coal characterization for development of new, clean, and efficient technologies of coal utilization. Here, we combined spatially-resolved reflectometry, fluorescence, and confocal micro-Raman spectroscopy with high-resolution scanning probe microwave imaging to achieve a nondestructive sub-100-nm spatial resolution mapping of coal structure. It was found that this approach allows for high spatial resolution identification of individual elements in coal architecture, thus potentially generating valuable input for knowledge-driven optimization and design of coal utilization processes.

1. Introduction

Development of the energy strategies based on direct and indirect coal liquefaction, coal gasification, direct carbon fuel cells, or solar-to-fuel cycles necessitates detailed understanding of the structure and functional properties of coals to predict and design the processing pathways. Advancement in this area began in 1950s and 1960s with progress in characterization techniques such as powder X-ray diffraction, infrared (IR) spectroscopy, adsorption measurements, nuclear magnetic resonance (NMR), and electron paramagnetic resonance (EPR). These methods allowed bulk to atomic level insights into complex physical and chemical processes associated with coal utilization [1]. However, fundamentally coal is a highly heterogeneous system on multiple length scales with macro- to nanoscale porosity, mineral inclusions and associations, and a strong variability of local chemical compositions, as well as degree of structural disorder [2]. These heterogeneities include domains of inorganic and organic constituents. Among the inorganic mineral constituents of coal are silicates (quartz, mica, feldspars, zircon, clay minerals such as kaolinite and illinite, as examples), sulfides (pyrite, sphalerite, galena, marcasite), carbonates (calcite, dolomite, siderite), sulfates (gypsum, barite), oxides and hydroxides of iron, aluminum, magnesium, calcium, and others [2–5]. Organic components of coal—macerals—can be recognized by optical microscopy. Originated from different dehydrogenated parts of plants (roots, bark, leaves, pollen), depositional environments, and degradation products, they are different in their chemical composition and optical properties and may have more

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oxygen-rich components (vitrinite), more hydrogen-rich mainly aliphatic components (liptinite), and more carbon-rich highly aromatic components (inertinite) [2,5].

The variability of the chemical properties of macerals defines technological applicability of coal. Improvements in technology of coal require increasing accuracy of characterization with increasing demand on non-destructive real-time measurements employing advanced characterization tools [2]. The multiscale coal structure naturally leads to increasing spatial resolution of the characterization tools up to the length scales of a few nanometers, the length scale typically cited as a length of structural coherence in coal macerals [2]. Evolution of coal analysis techniques—progressively more sophisticated with access to smaller length scales—is needed in chemical and structural identification of different coal constituents in order to understand the chemical behavior of coal during processing and utilization.

Among the old, well-established techniques, optical techniques such as measurements of reflectance and fluorescence can deliver general information about coal structure based on known large-scale properties of coal constituents. However, the spatial resolution of these methods is limited by few micrometers. A widely used high spatial resolution technique—transmission electron microscopy (TEM)—requires special sample preparation and is destructive. Spatial resolution of scanning electron microscopy (SEM) can be below 10 nm, however, low atomic weight of carbon and oxygen do not allow reliable identification of macerals at small-length scales. In turn, micro-Raman spectroscopy with a spatial resolution of about 1 μm was recently employed in studies of inorganic mineral inclusions [4], amorphous and ordered carbon content in coal [2,6–8], coal macerals (collotelinite, fusinite, and macrinite) [9], chars [10,11], coke [12], and fly ash [13]. Complexity and high heterogeneity of the coal structure necessitate application of several different complimentary analytical techniques to gain information about local coal structural and chemical composition. A benefit of structural and functional imaging of the same area of coal using multiple nondestructive, spatially resolved techniques including optical microscopy, micro-Raman spectroscopy, fourier-transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) can be useful for further understanding of structure-properties relationship in coals [4,8,14–18]. However, coal heterogeneity expands below micron scale, making structure–functional characterization with submicron resolution highly desirable. Towards this end, the current fleet of scanning probe microscopy (SPM) techniques combining a variety of non-destructive probing functionalities offers an approach for spatially resolved coal characterization at the length scales down to 5 nm.

Here, further advancing the spatial resolution in non-destructive coal characterization, we use combined confocal micro-Raman and Scanning Microwave Microscopy (SMM) imaging [19,20] to non-destructively resolve the structure of coal at the mesoscopic, sub-micron, lengths scale *in situ*. We combine spatially-resolved reflectometry, fluorescence, and micro-Raman spectroscopy with high-resolution microwave imaging to achieve a sub-100 nm spatial resolution mapping of coal structure at the lithotype, maceral, and sub-maceral levels.

2. Methods

2.1. Sample preparation

The initial candidate for exploration was a block sample of subbituminous/bituminous coal collected from an underground mine in the Uinta basin, Colorado, USA. The calorific value of this coal on a dry basis was 27.9 MJ/kg (ASTM D388, 2005). 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.

2.2. Raman spectroscopy

Raman spectra were collected in backscattering geometry using a Renishaw inVia Raman Microscope with a 50× objective (Leica, NA = 0.75) using 633 nm (HeNe laser) probing light. Raman maps with 0.4-μm spatial resolution were collected using 10-s acquisition time and 150-μW laser power on the sample surface. Reflectance spectra were acquired using Nikon Eclipse microscope with a Filmetrics F40 spectrometer attachment.

Preliminary Raman mapping of the coal sample showed no mineral inclusions in the area of interest, justifying narrow spectral window for Raman mapping between 900 and 3200 cm^{-1}. The point-by-point mapping was done in confocal mode collecting 1115 spectra over an area of 35 × 32 μm^2 with a 1 μm step size. The Raman spectra were fit with a Gaussian–Lorentzian function, and the G and D peak intensity parameters were used to calculate the map of G/D band intensity ratio. To attain insight into the spatial variability of Raman signal, this 3D spectral imaging data set was analyzed using Bayesian deconvolution [21]. This approach represents data as $\mathbf{Y} = \mathbf{MA} + \mathbf{N}$, where the collection of (noisy) observations **Y** is a linear combination of position-independent matrices **M** (called endmembers) with respective relative abundances **A** corrupted by additive Gaussian noise **N**. The endmembers **M** are non-negative, and the respective abundances add up to unity. Hence, the spectrum at each location is decomposed into a linear combination of spectra of individual components in corresponding proportions. The unique aspect of this analysis is that the endmember spectra and abundances are estimated jointly in a single step, unlike multiple least square regression methods where initial spectra should be known.

2.3. Near-field microwave microscopy

Scanning microwave microscopy, Fig. 1, is a near-field scanning probe technique, where electromagnetic field is coupled to a sample through a sharp probe tip connected to a microwave transmission line. Microwaves are sent through a coaxial cable, reflected off the cantilever with corresponding amplitude and phase being measured and recorded. The wave reflection coefficient depends on the impedance of the probe-sample system, and therefore, the reflected waves carry information about the sample's complex dielectric permittivity, namely dielectric constant and electric

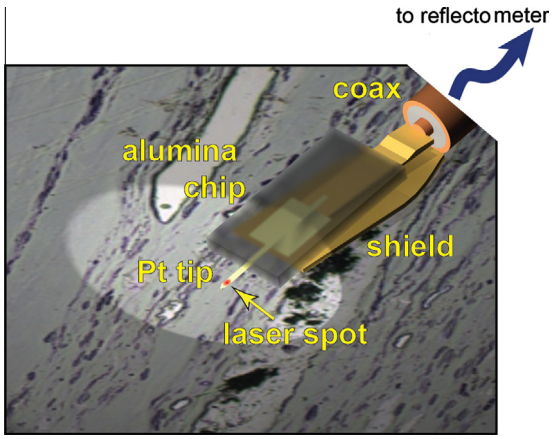

Fig. 1. Layout of the probe and operational principle schematic of a scanning microwave microscope.