Imaging and Spectroscopic Analysis of Bitumen

Ayşe N. Koyun[1] and Hinrich Grothe[2]

(Vienna University of Technology, Institute of Materials Chemistry, Getreidemarkt 9 BC 01, 1060 Wien, Austria),[1] ayse.koyun@tuwien.ac.at , [2] grothe@tuwien.ac.at

Abstract

Atomic force microscopy (AFM) is capable to picture the topology of bitumen at a sub-micrometer level and optical spectroscopy can gather chemical information [1-3]. Here we combine AFM and Raman spectroscopy, which allows a better specification of the chemical origin of bitumen. AFM imaging was performed from the topology, following with Raman imaging from the same area correlating the chemical composition of bitumen with each point of the image. The major challenge in applying Raman is the highly fluorescent character of bitumen, which interferes with Raman and in worst case pyrolysis products are built due to laser absorption at high laser power. Here, this problem has successfully been solved through surface enhanced Raman spectroscopy (SERS) applying silver nanoparticles on the bitumen surface. This application also enables Raman spectroscopy with low laser power, i.e. 0,5 mW at 532 nm. In contrast to former research [4], where Raman spectra were obtained from carbonized bitumen, in this case SERS spectra from virgin bitumen were recorded for the first time. Previous publications [4] only presented carbonized bitumen, which is not suited to draw conclusions regarding the chemical composition of the original bitumen. In the past, several methods for unravelling bitumen microstructure were developed and applied. However, the here presented method will allow additional clues concerning the mechanical properties and the aging behavior of bitumen at a macroscopic level. The high lateral resolution of the new approach is also a step closer to the chemical origin of the structure of the core-shell particles which are situated on the bitumen sample surface.

Keywords: bitumen microstructure, atomic force microscopy, Raman spectroscopy, surface enhanced Raman spectroscopy

1 Literature Review

AFM was first introduced in 1986 by Binning et al. [5] to measure surface topography. A heterogeneous composition on bitumen surface with the *´bee-like´*structure was first observed by Loeber et al. [6]. The alternating higher and lower topography was eponymous for the impression of *bees*, surrounded by a flat area. The *bee-structure* was at this time associated with asphaltenes. When applying AFM on heat-casted bitumen samples three phases on bitumen surface were identified [7] the catana, the peri and the para phase at ambient temperature. The sample was cooled down to -55°C, subsequently a fourth phase occurred, the sal phase. Heating up the sample caused disappearing of the *bee structures* at a temperature range between 50°C and 56°C. After melting the bitumen sample up to 170°C, the temperature was decreased at temperatures above 57°C and the *bee structures* began to form successively.

Pauli et al. [8] discussed that the interaction between crystallizing paraffin waxes and the remaining asphalt fractions is responsible for much of the structuring, including the well-known *bee structures* which has been observed with asphalt materials. According to Hofko et

al. [9] the occurrence of the catana structures is connected with asphaltenes. However, to prove this hypothesis correct spectroscopic mapping analysis on bitumen has to be recorded. Raman spectra of pyrolyzed bitumen do exist [4]. Adam Zofka et al. [10] covered the bitumen sample with a glass slide in order to reduce the heating during laser exposure this method is not suitable for Raman mapping as the contact with the glass is destroying the *bee structures*.

2 Materials and Methods

2.1. Bitumen and Bituminous Specimen

Typical oxidized bitumen 90/10 was provided by an Austrian mineral oil refinery. The term and specification is referred to EN 13304 [11]. The sample was classified and named by needle penetration according to EN 1426 [12] and by ring and ball test according to EN1427 [13] which was measured in Glycerin. The penetration value is 14 1/10mm and the ring and ball test value is 90,5°C. Pro analysis Toluene was used as a solvent. An Alpha300 RS (Witec, Germany), was used for this study, facilitating confocal Raman imaging in combination with Scanning Near-field Optical Microscopy (SNOM) for optical imaging with resolution beyond the diffraction limit. The viscoelastic nature of bitumen requires AFM with non-contact mode, where the cantilever tip with its own resonance frequency is oscillated a few nanometers above the sample surface. Van der Waals forces interact with the cantilever tip and reduce the resonance frequency of the cantilever, which allows the software to construct a topographic image of the sample surface. The light source for Raman was created with a 532 nm Laser. The Laser power was about 0,5 mW. A grating with 600 gr/mm was selected for the spectrometer.

2.2. Experimental

Thin bitumen films were prepared by dissolving bitumen in toluene, spreading the binder solution on the glass slide and rotating by a spin-coater at a constant speed of 5000 r.p.m. Samples with different binder concentrations were prepared. After 120 h relaxation time, the characterization via AFM and Raman spectroscopy were performed. Due to the chemical origin of bitumen, autofluorescence is unavoidable, which is a major challenge in Raman spectroscopic analysis. To overcome fluorescence, surface enhanced Raman spectroscopy (SERS) was used to enhance the Raman bands. Silver colloids were prepared according to Leopold and Lendl method, which has the advantage of a quick synthesis and easy principle [14]. This method enabled us to obtain SERS from bitumen for the first time. Under normal conditions, without applying silver colloids on the surface of bitumen, fluorescence is interfering with the Raman bands (see figure 4). Applying SERS allows an amplification of the Raman bands up to several orders of magnitude and as a result the fluorescence was quenched (see figure 5).

3. Results

3.1. AFM

The preparation of different bitumen concentrations was performed to explain the influence of sample thickness on the forming of the microstructures. Bitumen films were prepared by dissolving bitumen in toluene, spreading the binder solution on the glass slide and rotating by a spin-coater at a constant speed of 5000 r.p.m. Different binder concentrations were prepared as seen in Fig.1. After 120 h relaxation time, the characterization via AFM and Raman spectroscopy were performed. Figure 1 shows the size and amount of catana structures are

decreasing with reducing the concentration of bitumen in toluene. As the aim of this study is to reveal the microstructure of different phases, it is necessary to prepare samples where the microstructures are completely formed and no interaction with neighbor structures is given. Consequently, for our study only 4 w% bitumen in toluene was analyzed.

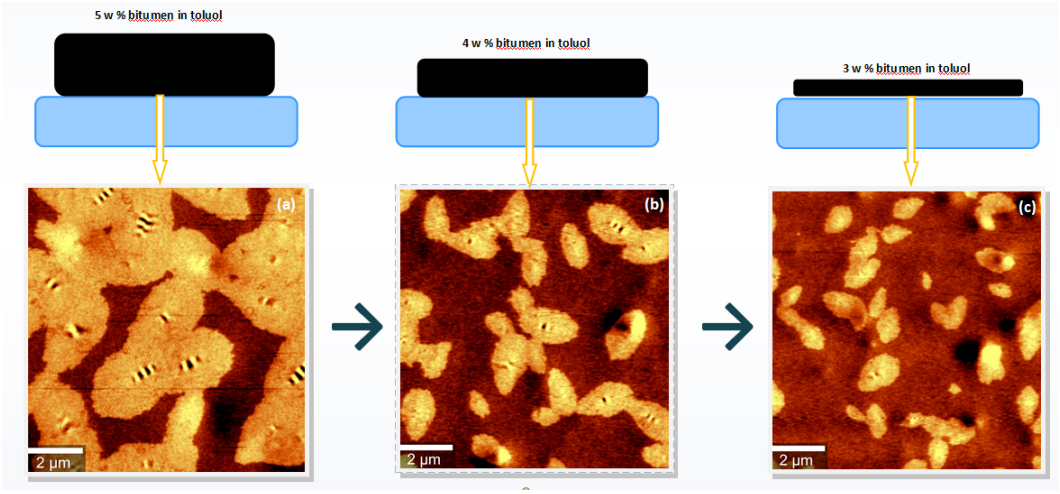

Figure 1. AFM Phase images with different bitumen concentrations and different thicknesses. (a) 5 w% (b) 4 w% (c) 3 w% Bitumen in Toluene.

Figure 2 a and b show a phase image of oxidized bitumen 90/10. It is representing a heterogeneous sample surface, in which different phases occur. Catana phases, visible as dark and light alternations, are referred to as *´bee-structures´*. An illustration of the topography is demonstrated in Fig.3.

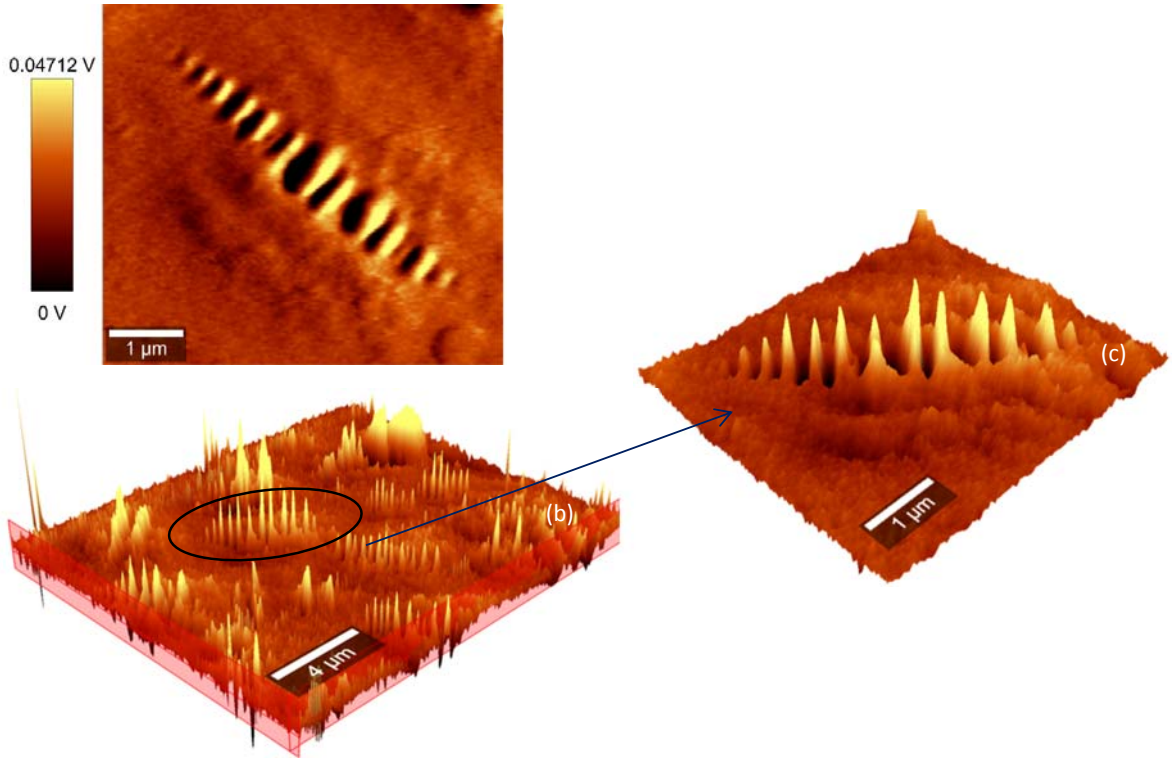

Figure 2. (a) 2D phase image and (b) and (c) 3D phase image of bitumen 90/10.

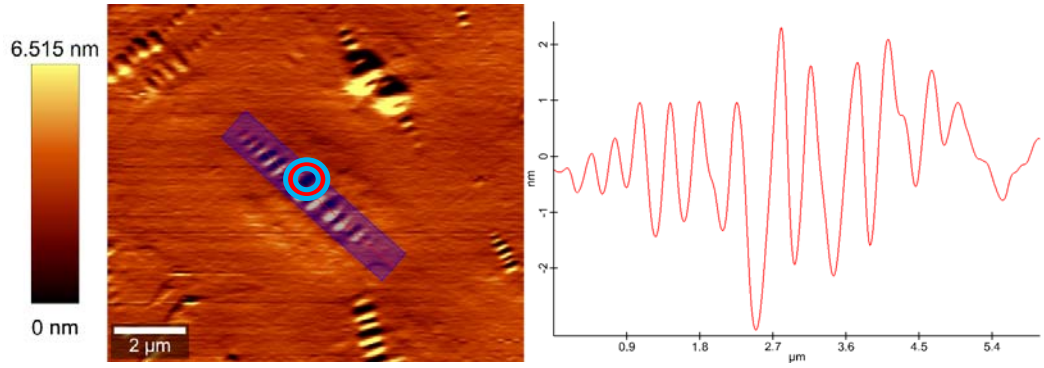

Figure 3. (a) Topographic image, height profile from the marked area in (a) is plotted in (b). Maxima and minima in b respectively correspond to light and dark strips in Fig 3a.

3.2. Raman

Raman imaging and AFM were performed on the same bitumen sample and on the same position. Both images are superposable in a certain range of tolerance (ca. 2µm), which is not precise enough to match microstructures seen in AFM to the Raman spectra corresponding to this position. The Raman spectrum (figure 5) corresponds to the circled area in figure 3, where the tolerance range has to be considered additionally.

This work documents the first Raman spectroscopic study of bitumen, where no glass slide cover is needed, which was done before in order to prevent bitumen pyrolysis. As a consequence of this, switching from AFM to Raman measurements does not implicate the damage of the surface structures, which is caused by the glass slide which was put on the sample surface [10].

The application of silver colloids on the bitumen surface successfully quenched the autofluorescence of bitumen. To better point out the Raman band enhancement and fluorescence quenching – a Raman spectrum of bitumen 90/10 without silver application and a SERS spectrum from the same sample are demonstrated in Fig.4 and Fig.5.

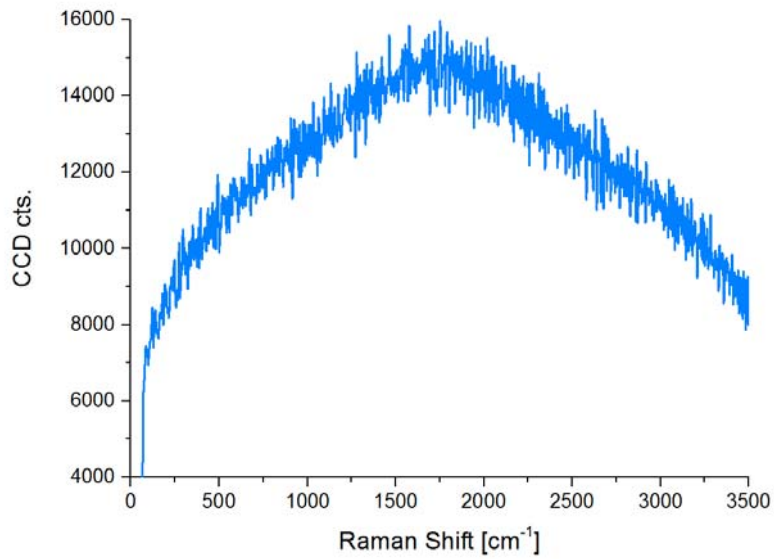

Figure 4. Raman spectra of oxidized bitumen 90/10 without SERS.

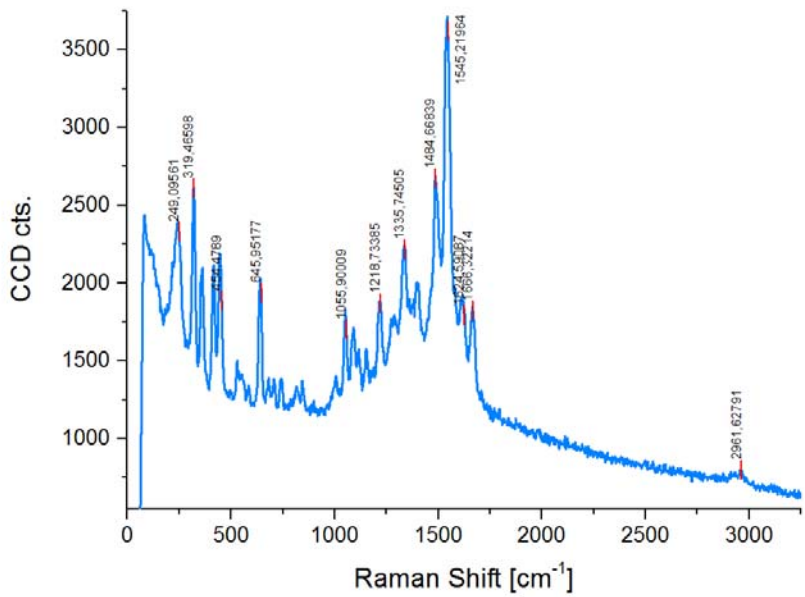

Figure 5. SERS spectra of oxidized bitumen 90/10.

Using Silver nanoparticles makes it possible to apply very low laser power (0,02%) and thus prevents sample damage by carbonization while measuring Raman spectra. Sadezky et al. [15] investigated the structures of highly ordered carbonaceous materials with exciting laser in the visible range and identified the G-Band at 1575 cm^{-1}. Here, the strong Raman G-Band occurs at 1542 cm^{-1} which is normally referring to the ideal graphitic lattice (E_{2g}-symmetry). The presence of the D_1-Band is known to be characteristic for disordered graphitic lattice (A_{1g}-symmetry). The band at 1217 cm^{-1} can be attributed to the D_4-Band - non aromatic polyene - and the band at 1614 cm^{-1} corresponds to the D_2-Band – surface graphene layers. Zofka et al. [10] have observed similar Raman spectra.

4. Conclusion and Outlook

Over the last decades, several Raman spectra of bituminous coal were recorded [16]. Raman spectra from virgin bitumen exist as well, even though the bitumen sample was covered by a glass slide. Receiving Raman spectra of virgin bitumen, where the topography is not interfered by a glass slide, requires low laser excitation power in order to prevent high absorption, which mostly leads to carbonization. Applying SERS on bitumen shows that this method being ideally suited to quench autofluorescence of bitumen as well as enhancing the electromagnetic field of the Raman signal. However, the change of analysis methods from AFM to Raman requires a change in the microscope objectives, where a certain tolerance range has to be accepted. To overcome this problem, SNOM technique could be applied where AFM and Raman spectroscopy are taken simultaneously.

This opens the possibility of matching the microstructures seen in AFM images to Raman spectra where the precision is given. This will allow identifying the chemical origin of each pixel of the AFM images. Thus, the chemical constitution of core-shell particles on bitumen surface will be accessible.

The fundamental spectroscopic investigations could help to close the gap between molecular and microstructural information of bitumen which could help to develop more precise bitumen models and thus innovative pavements.

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6. References

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