PRF#: 58515-DNI10

Project Title: Understanding Asphaltene Aggregation via Nanoscopic Dynamics Imaging

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1. Overview of Goals

The goal of the research supported under this ACS PRF grant is to understand the fundamental mechanism for asphaltene aggregation at the nanoscale, aided by establishing and utilizing an ultra-low dose liquid phase transmission electron microscopy (TEM). Asphaltenes are complex aromatic hydrocarbons in crude oil, whose aggregation deleteriously affects almost all aspects of petroleum utilizations, from oil transport (upstream sector) to oil refining (downstream sector). The innovation of our research is to resolve the in-situ asphaltene aggregation dynamics in model solvents at the unprecedented nanometer and millisecond resolutions. The obtained liquid-phase TEM movies of the asphaltene aggregation were analyzed by single particle tracking to derive a composition–structure–aggregation relationship, which guides new engineering control rules for asphaltene aggregation reduction and prevention in petroleum industry.

2. Research Progress

During the reporting period (9/1/2018–8/31/2019), we have made the following major progress in achieving the proposed goals.

We were able to have a collaboration with Prof. Grace Burke at University of Manchester and to conduct a systematic study on understanding asphaltene aggregation process in solution. From Prof. Grace Burke, we obtained liquid-phase TEM movies (obtained for the first time with nanometer resolution in a solution) of the aggregation dynamics of model asphaltene. Because the aggregation was initiated in-situ, we observed the complete process from nucleation of nanoaggregates (dark under TEM) out of a homogeneous solvent background, to their further clustering into clusters in 10's of mins, over a spatial and temporal domain hard to achieve by all-atomistic simulations (Fig. 1).

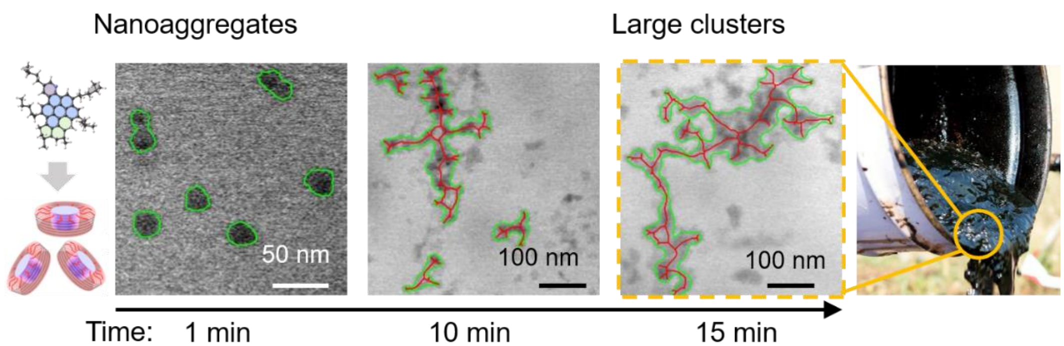

Fig. 1: Asphaltene aggregation dynamics captured by liquid-phase TEM: from nanoaggregates of stacked asphaltene molecules to large clusters, to eventually large clogs that precipitate out of crude oil (unpublished, Chen lab in collaboration with Burke lab).

To quantify the aggregation process, we used our customized image segmentation and analysis algorithm to track each asphaltene aggregate over time. The contour lines (see green lines in Figs. 1–2) were used to track the area and the caliper diameter for each aggregate in the TEM movies over time. The caliper diameter describes the longest dimension of an arbitrarily shaped object as shown by the yellow marker line in Fig. 2a, which serves as a measure of how much the shape deviates from a perfect circle.

By plotting the size of the asphaltene aggregate against caliper diameter, we revealed a hierarchical process of the aggregation dynamics of asphaltene. As shown in Fig. 2b, in the initial growth of asphaltene aggregate, the aggregates formed independently. The relation between its area and caliper diameter was shown by the green filled circles in Fig. 2b. It is noted that the green filled circles follow a trend that is close to the relation of perfect circular aggregates (solid grey lines). The green filled circles follow a power law of 2, suggesting that the nanoaggregates grew symmetrically in the radial directions. Next, as the aggregates grow larger (caliper diameter $\geq$ 60 nm), we observed that individual aggregates tend to coalescence with each other in a branched manner to form into fractal clusters (Fig. 2a). On the area versus caliper diameter plot, we saw the corresponding data denoted as blue filled circles deviates from the power law of 2 dependence as the stage I, due to the empty space in clusters compared to highly filled structure in the early stage. We name this second stage as fractal growth since the clusters are composed of branched aggregates. It is clear that using our quantitative analysis of the real-space shape evolution of the aggregates (otherwise not accessible by other means), we can distinguish two stages of the aggregation process associated with vastly different shaped aggregates.

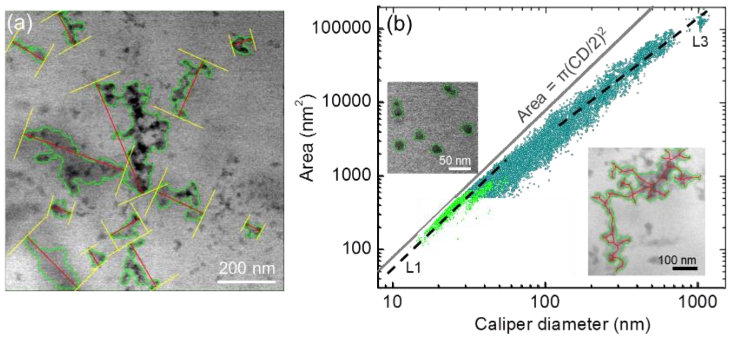

Fig. 2. Growth and fractal formation in asphaltene aggregation. The cluster size (area) of the aggregation of asphaltene is plotted as a function of the caliper diameter of the cluster, as obtained from the liquid-phase TEM movies of the aggregation process of asphaltene. Different colors mean different experiment data. The inset TEM images show the typical cluster morphology of asphaltenes when the cluster size is below (left) and above (right) 10,000 nm^2 (unpublished, Chen lab).

The petroleum implications based on this fundamental understanding can be manifold. For example, maybe fractals are more easily to be removed than the densely packed circularly shaped aggregates under external shear, so can we shift the transition point of the two stages, or can we make the slope even lower by changing flow rate or adding molecular additives? We see the opportunity here is that this curve plotted for this model system can be measured systematically for many other depositions at a matrix of conditions for comparison, for screening, and even for predictive design of prevention strategies.

3. Mentoring Opportunities

This project has supported (partially) educational and training opportunities for one PhD student and one postdoctoral researcher. The PI has provided close guidance and training for them in liquid-phase TEM imaging, composition mapping, statistical mechanics, and TEM movie analysis. Moreover, the PI has provided training on developing scientific communication and presentation skills, and manuscripts and fellowship proposals writing, especially their oral presentations in international conferences, which have been shown as a great opportunity for them to connect with the experts in the field and to put their work in the context of the colloidal community.

Specifically, the PhD student has presented his work on early-stage establishment of liquid-phase TEM imaging platform using model nanosized colloids:

Title: Polymorphic Self-Assembly of Nanoarrows

Author list: Chang Liu, Qian Wang, Binbin Luo, Limin Qi, Qian Chen

Date and time: 2019-04-24, 4:30 pm – 4:45 pm

Conference: 2019 MRS Spring meeting, Symposium CP02: Design and In Situ TEM Characterization of Self-Assembling Colloidal Nanosystems

and the postdoctoral researcher will present his work on composition mapping and 3D imaging of organic materials:

Title: 3D Analysis of Nanostructured Polyamide Membranes using Quantitative Electron Tomography

Authors: Hyosung An, John W. Smith, Wenxiang Chen, Nestor J. Zaluzec, Matthew A. Kulzick, Qian Chen

Date/time: 2019-11-13, 4:21 pm – 4:38 pm

Conference: 2019 American Institute of Chemical Engineers Annual Meeting

The visual appeal of the liquid-phase TEM movies has made the group to play a host role in the High School Summer Research program at UIUC (2019) by providing a 6-week lab experiences for high school students. The PI has given a GSOFT Short Course on “Structures and Order in Soft Matter Physics” in the American Physics Society March Meeting, Denver, CO (Mar 3, 2019) with a 45-min lecture on “Structure and Dynamics Determination by Electron Microscopy” on tutorials of this liquid-phase TEM imaging tool to the broad community of soft matter concerning colloidal, polymeric and biological matter.