Experimental report

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Proposal: 9-12-565 **Council:** 4/2019

Title: Nano and micro structural characterization of polymer-Au nanorod hybrid electronic ink by SANS and NR

Research area: Chemistry

This proposal is a new proposal

Main proposer: Peng ZHANG

Experimental team: Peng ZHANG
Zhen LIU
Lucas HUPPERT
Mariano LAGUNA MORENO
Mariano LAGUNA
Aljosa HAFNER

Local contacts: Philipp GUTFREUND
Sylvain PREVOST
Leonardo CHIAPPISI

Samples: Gold nanoparticle
poly[2-(3-thienyl)-ethyloxy-4-butylsulfonate]

Instrument	Requested days	Allocated days	From	To
D11	2	2	12/02/2020	14/02/2020
D17	2	2	10/02/2020	12/02/2020

Abstract:

Anisotropic metal nanoparticles such as gold nanorods (AuNR) are now accessible in a variety of shapes, sizes and surface properties using wet-based chemical synthesis. Conductive polymers with electrical conductivity and good mechanical property have recently been used as the ligands to fabricate polymer-Au hybrid systems and to achieve unprecedented electrical properties in a range of applications.[1-3] Such objects are used in “electronic inks” to combine high electrical conductivity and mechanical elasticity and can be printed to prepare flexible conductive electrodes, as illustrated in Figure 1. While the process engineering of electronic ink drying is well-established, little is known about the nano and microscopic structure formation in drying hybrid nanoparticle films and its effect on the properties (conductivity, mechanical flexibility, etc.) of the final coating. We plan to investigate the hybrid material with SANS and NR.

Experimental report for

Nano and micro structural characterization of polymer-Au nanorod hybrid electronic ink by SANS and NR

Zhen Liu[1], Lucas Huppert[2],Philipp Gutfreund[3], Aljosa Hafner[4], Sylvain Prevost[3], Xin Li[1], Mariano Laguna Moreno[2], Tobias Kraus[2,5] and Peng Zhang[1*]

1.School of Materials Science and Engineering, PCFM Lab, Sun Yat-sen University, Guangzhou 510275, China

2. INM-Leibniz Institute for New Materials, Saarbrucken 66123, Germany

3. Institute Laue-Langevin (ILL), Grenoble 38042, France

4. CERIC-ERIC, Trieste 34149, Italy

5. Institute of Colloid and Interface Chemistry, Saarland University, Saarbrucken 66123, Germany

[*]Corresponding authors: Peng Zhang, E-mail: zhangpeng3@mail.sysu.edu.cn

We have performed SANS and NR measurements of PEDOT:PSS hybrids in solution and in solid thin-film at D11 and D17 beamlines, respectively. The PEDOT:PSS hybrids are used in "electronic inks" to combine high electrical conductivity and mechanical elasticity and can be printed to prepare flexible conductive electrodes. The SANS and NR experiments help to illuminate nano and microscopic structure formation in drying hybrid films and its effect on the properties (conductivity, mechanical flexibility, etc.) of the final coating.

Figure 1a shows the SANS data of PEDOT:PSS (W) and its hybrid with LiTFSI. We analyzed the SANS data with an empirical broad peak model [1, 2], i.e., equation 1

$$\mathrm{I(q)} = \frac{\mathrm{A}}{q^n} + \frac{C}{1+(|q-q_{max}|L)^m} + \mathrm{B} \qquad (1)$$

where *n* is the low-q scaling exponent, *m* is the high-q scaling exponent, q_{max} is the interchain correlation peak position, *L* is the electrostatic screening length of the interchain correlation, and *B* is the background incoherent scattering. In general, as the increase of LiTFSI content, a decreased screen length (from 39 Å to 26 Å) is observed due to the interchain charge repulsion. Meanwhile, an increased correlation length (280 Å to 1039 Å) is found, indicating that the distance between charged-rigid segments of polyelectrolyte chain increased. Similar phenomenon has been reported by Muthukumar *et. al.*[2]. The structure change mentioned above could be correlated with the resistivity of the hybrid samples, as shown in Figure 1b. Adding salt into PEDOT:PSS causes the decrease of the sample resistivity, i.e., enhance the conductivity. It should be mentioned that the decrease of sample resistivity is not monotonic with the increase of the salt content. For example, the resistivity reached a minimum with 1.5 wt% salt, agreeing well with our recent study of the PEDOT:PSS/LiTFSI system [3]. However, we could not decipher the microphase structure of the PEDOT:PSS hybrid since the limited electron density contrast among PEDOT and PSS. During this SANS experiment, we used the deuterated water that is a good solvent for PSS and enhances the signal of PEDOT microdomains, thus we could track the microphase structure change of the PEDOT:PSS hybrid as a response of salts' mixing. Meanwhile, we find that the resistivity value of the solution sample also decreases with the increase of the salt content. We suspect that the structure change in solution contributes to the conductive network formation in the dried film. Further details are summarized in a manuscript titled "Deciphering the quaternary structure of PEDOT:PSS solution by combining small angle X-ray scattering with small angle neutron scattering characterizations", which is going to be ready for submission in a few months.

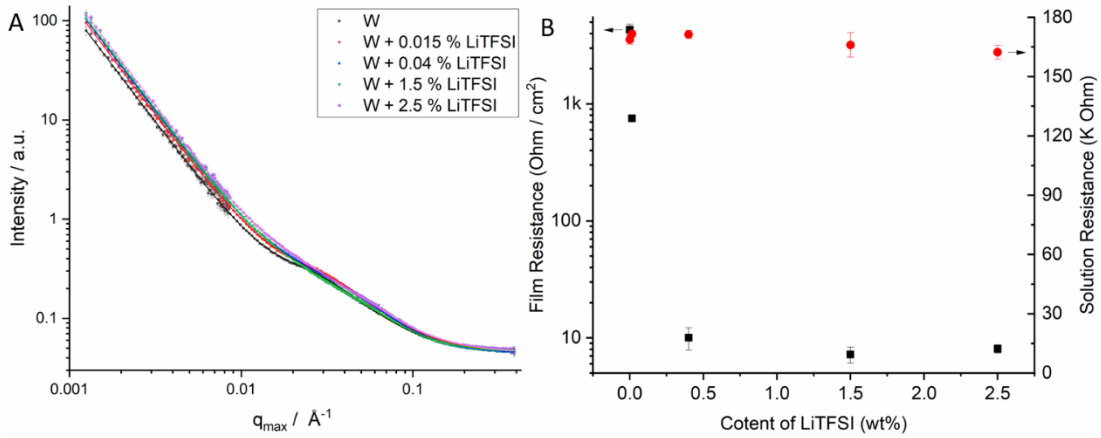

Figure 1. (A) SANS measurement of W solution with content of LiTFSI. The scatters and the lines across the scatters are the original data and fitted results, respectively. (B) Solution and film resistivity of W with different content of LiTFSI. The black square and red circle represent the film and solution conductivity, respectively.

Moreover, we measured some other polymer hybrids, like mixture of PEDOT:PSS with different salts, Au-PEDOT:PSS and Au-PTEBS, in solution and dried films with SANS and NR, respectively. Figure 2 shows the 2D NR data of the PEDOT:PSS and its hybrid with the gold nanoparticle in dried films. By analyzing the NR data, we could extract the arrangement of PEDOT:PSS along the layer thickness. Therefore, we could decipher that how could the selective interaction among gold nanoparticle and conjugated polymer would influence the molecular assembly and thus the conductive network. A series of complementary characterizations like DLS, UV-vis, TEM, (gi)SAXS and resistivity measurement have been partially completed. These experimental data are expected to help us design electronic ink with better performance based on the fundamental understanding of the complex structure and structure formation process during the ink preparation.

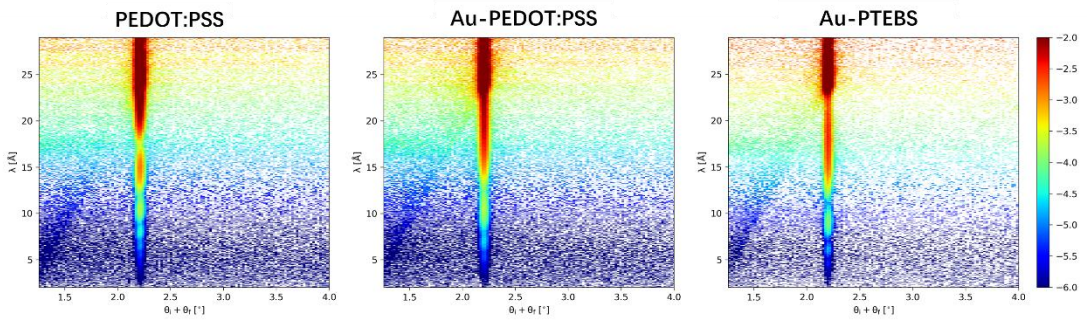

Figure 2. 2D NR data of the as-prepared PEDOT:PSS, Au-PEDOT:PSS and Au-PTEBS dried films.

However, the SANS measurements at room temperature took much longer time than what we expected, partially because we spent some time to prepare contrast-matching samples on site, that we did not have time to finish the proposed measurements at higher temperature. We expect that we could finish them via “mail-in” mode measurements, considering the influence of the pandemic Corona- 19 virus. Furthermore, we are eager for a combined USAXS-SAXS-SANS measurement at ILL and ESRF to decipher the quaternary structure of PEDOT:PSS hybrid, covering from atomic to micron length scales. We are looking forwards the next call for proposal.

Reference

1. Horkay, F.; Hammouda, B., Small-angle neutron scattering from typical synthetic and biopolymer solutions. *Colloid and Polymer Science* **2008,** *286* (6), 611-620.

2. Murphy, R. J.; Weigandt, K. M.; Uhrig, D.; Alsayed, A.; Badre, C.; Hough, L.; Muthukumar, M., Scattering Studies on Poly(3,4-ethylenedioxythiophene)–Polystyrenesulfonate in the Presence of Ionic Liquids. *Macromolecules* **2015,** *48* (24), 8989-8997.

3. Li, X.; Liu, Z.; Zhou, Z.; Gao, H.; Liang, G.; Rauber, D.; Kay, C. W. M.; Zhang, P., Effects of Cationic Species in Salts on the Electrical Conductivity of Doped PEDOT:PSS Films. *ACS Applied Polymer Materials* **2020,** in press.