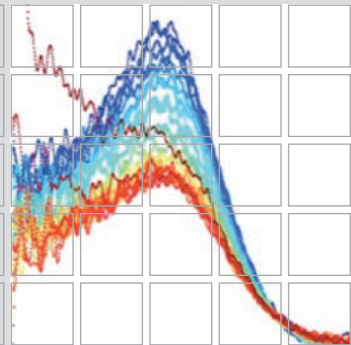
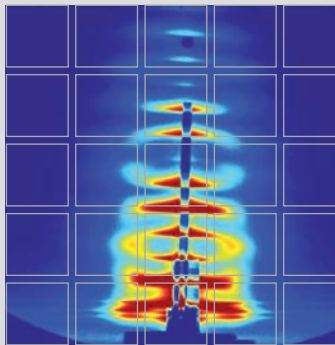
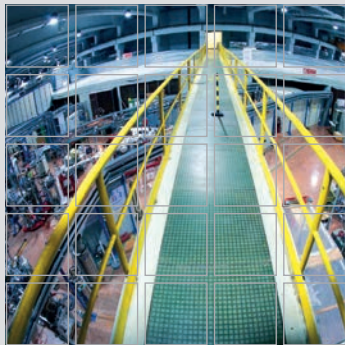
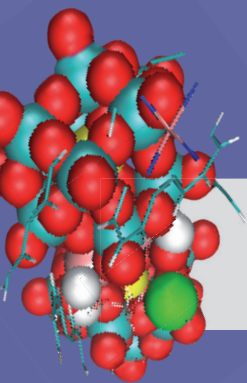


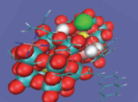
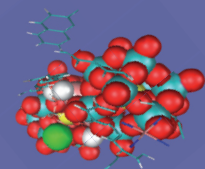
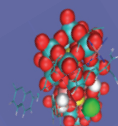
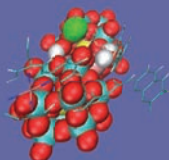
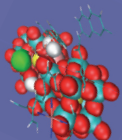
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Austrian SAXS Beamline at



Austrian Small Angle X-ray Scattering (SAXS) Beamline at ELETTRA

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FORMATION OF P123-MEDIATED AU-NANOPARTICLES IN AQUEOUS SOLUTION: IN-SITU X-RAY SCATTERING STUDY

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Metal nanoobjects are attracting significant attention because of their size dependent optical, magnetic, electronic, and catalytic properties. Among them, gold nanoparticles (AuNPs) with desirable structures and functions are of special interest due to their various applications in biology, medicine, catalysis and sensors [1,2]. There are various physical and chemical methods for the synthesis of AuNPs. Among them, the solution-phase chemical reduction method is one of the widely used methods to synthesize and stabilize monodispersed AuNPs. The whole process involves the use of four basic materials, namely solvent, metal salt, reducing agent and stabilizing agent. Recently, a lot of work is going on to develop simple, versatile, environment-friendly and economically viable methods for the preparation of AuNPs. In this direction, attempts are made to synthesize and stabilize AuNPs in a single step from aqueous solution of gold salt using water-soluble triblock copolymer (TBP) at ambient temperature [3-5]. TBPs belong to a special category of nonionic surfactants. The most widely used TBPs (with the commercial name of Pluronics) are polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO) with different composition of hydrophilic PEO and hydrophobic PPO blocks. In the aqueous solution, TBPs form micelles. The hydrophobic PPO blocks form the core of these micellar aggregates, whereas the hydrophilic PEO ones form the corona. TBP can act as reducing and stabilizing agent and has been utilized to form nanoparticles. However, the control the size of the nanoparticles and their yield are poor, which need large improvement. For that monitoring the formation of the nanoparticles, in-situ, using different complementary techniques, is very essential. X-ray scattering in general [6-9], while SAXS and WAXS in particular, can provide complementary information about polymer coated AuNPs and core AuNPs.

In order to monitor the formation of the nanoparticles, solutions were prepared by dissolving TBP and Au salt in water. P123 [PEO₂₀-PPO₇₀-PEO₂₀] is taken as TBP, while hydrogen tetrachloroaurate (III) hydrate [HAuCl₄.3H₂O] as Au salt. Solutions were prepared in glass beaker for 5 wt% of P123 and four different concentration (1, 2, 3 and 4 mM) of Au salt. After preparation, the solution was transferred quickly to a Kapton window based teflon cell and was placed to the sample stage of the goniometer (SAXS beam line, Elettra), where *in-situ* SAXS or WAXS measurements were carried out separately at energy 8 keV. For SAXS measurements a 2D detector (image plate mar300, Marresearch GmbH, having 2000 x 2000 pixels with pixel size 150 x 150 μm²) was placed about 135 cm downstream of the sample, while for the WAXS measurements a 2D detector (PILATUS 100k, Dectris, having 487 x 195 pixels with pixel size 172 x 172 μm²) was placed about 20 cm apart from the sample. The transparent colourless solution of P123 becomes colourful with time due to the AuNPs formation. Such coloration become fast compared to that observed in India, where UV-vis and DLS studies were carried out.

The SPR peak position obtained from the UV-vis spectra of the solutions increases with Au salt concentration, suggesting an increase in the AuNPs size. However, the intensity of the SPR peak increases with concentration up to 3 mM then decreases, indicative of some optimum value of Au salt concentration for conversion. LMCT peak intensity increases with Au salt concentration, however, for 1 and 2 mM solutions the intensity decreases gradually with time, while for 3 and 4 mM solutions the intensity increases up to about 30 min then decreases. A fast increase in the SPR peak intensity is also observed for 3 and 4 mM solutions

up to 30 min. This suggests that the LMCT complex formation continues up to 30 min, which is visible for the 3 and 4 mM solutions. The SPR peak intensity for all the solutions nearly saturate after 2 h. Considering different parameters, such as SPR and LMCT peak intensity for normalized concentration and corresponding P123 amount, optimum conversion observed for solution of 3mM Au salt. The size distribution of normal P123 micelles and after inclusion of Au salt are obtained from DLS measurements. The average size for the normal P123 micelles is found to be 18 nm. With the addition of Au salt large size particles (about 200 nm) are formed. This is due to the AuNPs loaded hybrid micelles. The amount of this hybrid particles increases with the Au salt concentration in expense of normal size micelles. Maximum amount is reached for 3 mM solution.

SAXS patterns show two peaks corresponding to two different size particles/clusters. The positions of the peaks remains fixed with time indicating no change in size of the particles/clusters, while a small increase in intensity is observed indicating an increase in the number of the particles/clusters. Such change is prominent within 20 min. WAXS patterns of the solution were also collected with time. After proper background subtraction, prominent (111) and weak (002) peaks of Au are visible. Almost no change in the width of the prominent peak, indicating no change in size of the Au particles, while a small increase in intensity is observed indicating an increase in the number of the particles. It can be noted that an increase in the background or amorphous intensity is found with time. Even considering that the peak (i.e. difference) intensity first increases and then saturates. Such change is again within 20 min. Similar is the situation for the other concentrations as well.

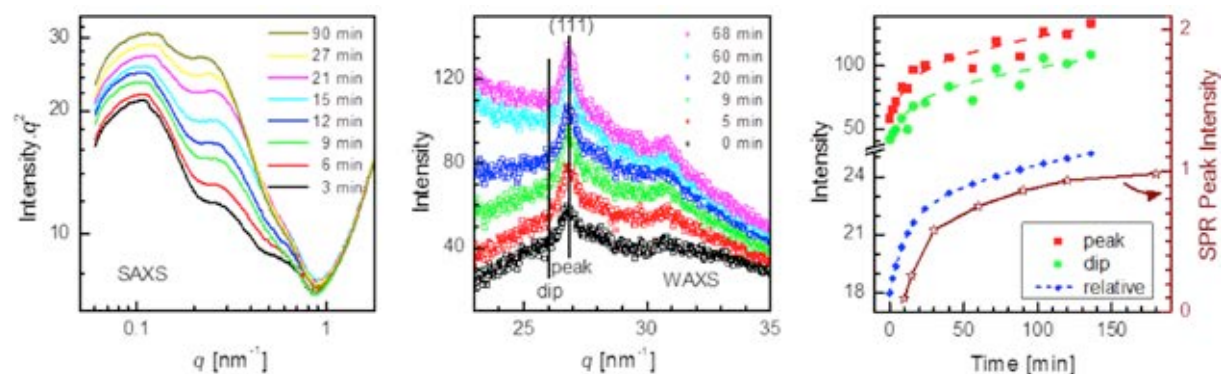


Figure 1. Left: Time-evolution of SAXS pattern of a P123 + HAuCl_4 + H_2O ternary mixture solution (intensity is multiplied with q^2 to enhance the features), Middle: Time-evolution of WAXS pattern of a P123 + HAuCl_4 + H_2O ternary mixture solution, Right: Corresponding variation of peak, dip and their expected difference in intensities with time. Also time-evolution of the SPR peak intensity as obtained from UV-vis spectra.

The Au NPs formation dynamics is found fast from the SAXS and WAXS studies, which is in contrary to the study carried out in India using in-situ UV-Vis and DLS techniques (see Fig. 1). We really need to understand the reason behind such fast dynamics. It is often found that light can also play some role in the growth of nanoparticles, which needs to be taken care. Thus the present experimental result is really interesting but needs further verification, which we are planning for next time. On the other hand, if the dynamics is really fast then special experimental arrangement is needed for proper understanding.

References:

- [1] I. H. El-Sayed, X. Huang and M. A. El-Sayed, *Nano Lett.* **5**, 829 (2005)
- [2] M.-C. Daniel and D. Astruc, *Chem. Rev.* **104**, 293 (2004)
- [3] T. Sakai and P. Alexandris, *Langmuir* **20**, 8426 (2004)
- [4] P. Khullar, A. Mahal, V. Singh, T. S. Banipal, G. Kaur and M. S. Bakshi, *Langmuir* **26**, 11363 (2010)
- [5] D. Ray, V. K. Aswal and J. Kohlbrecher, *Langmuir* **27**, 4048 (2011)
- [6] S. Hazra, *Appl. Surf. Sci.* **253**, 2154 (2006)
- [7] P. Chatterjee, S. Hazra and H. Amenitsch, *Soft Matter* **8**, 2956 (2012)
- [8] H. Koerner, R. I. MacCuspie, K. Park and R. A. Vaia, *Chem. Mater.* **24**, 981 (2012)
- [9] P. Chatterjee and S. Hazra, *J. Phys. Chem. C* **118**, 11350 (2014)