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Artefacts Induced on Soft Layer of Hybrid Metallic Nanoparticles in TEM

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Hybrid organic shell - inorganic core nanoparticles (NPs) are of interest in a wide range of applications, such as drug delivery and nanosensors. The structural and chemical arrangement of organic layers plays a crucial role in the function of hybrid NPs, therefore physicochemical characterization can help us to understand and control the synthesis processes. Transmission electron microscopy (TEM) has been applied to the visualization and measurement of organic shell thickness of hybrid NPs [1]. However, there are some challenges to be overcome, including the awareness of artefacts when applying TEM to characterize organic layers. One typical challenge concerns the electron beam induced hydrocarbon contamination (HC), which predominates when examining NPs deposited from solution and could cause the improper analysis of soft layers of hybrid metallic NPs.

HC sources, HC observation in EM and mitigation approaches have been discussed and reported in previous work [2]. However, in order to visualize and analyze the soft layer of hybrid NPs made in solution, most HC mitigation approaches cannot be applied. For instance, UV cleaning, plasma cleaning and heating in vacuum may damage and remove the soft layers or increase the layer thickness before TEM analysis. Here we show evidence for a thickness increase of the soft layer and investigate its cause. Proper mitigation approaches are then recommended for analysis of such hybrid NPs in TEM.

The citrate-capped 40 ± 3.2 nm gold NPs were purchased from BBInternational, with a concentration of 9 x 10^{10} particles/ml. AuNPs were modified with 4-Nitroazobenzene (dNAB) using the method introduced by Laurentius et al. [3]. The modified Au/dNAB NPs were separated from solution by centrifugation at 8000 rpm for 10 minutes in a micro-centrifuge. Next the NP pellet was redispersed in deionized water. A second centrifugation step was added to wash the particles further. The suspended modified particles are stable and were stored at 7^{o}C before use. A 5 µl droplet of Au/dNAB solution was placed on TEM grids. Excess solution was blotted after one minute and then grids with NPs on were air-dried at room temperature for half to one hour before imaging in TEM. All zero-loss bright field (BF) images were recorded in a JEM2200FS TEM at 200 kV with a 10 eV energy-filter slit.

The HC was severe for the Au/dNAB NPs specimen on holey carbon film, as shown in Fig.1. The holey carbon film was used as provided commercially. The dark ring (red arrow marked) represents HC built up around the edge of illumination area. Meanwhile, it was observed that the soft layers of AuNPs near to or even about 300 nm away from the illumination area became asymmetrical. The thickness of the soft layer is larger on the side facing towards the illuminated area, compared to the other side of the NPs, whereas the soft layer of Au NPs on carbon film within the illuminated area is symmetrical. The AuNPs near the edge of holes (Fig. 1b) have asymmetrical layers inside the illuminated area and their thickness observed to increase during irradiation. To mitigate the HC source, the holey carbon film and SiN membrane were cleaned in a UV TEM Zone cleaner and evaluated in TEM before applying solution, in which case there was no HC built up. However, the same phenomenon of asymmetrical thickness of the soft layer was observed, as shown in Fig.2, although a lighter

HC ring built up compared with the sample used in Fig.1.

In order to properly measure the thickness of the soft layer in the TEM, heating, cryogenic imaging and beam shower approaches were carried out. The asymmetrical thickness phenomenon disappeared when the specimen was heated but the layer thickness increased. The most effective method of avoiding HC contamination was imaging under cryogenic conditions, as shown in Fig. 3, but with a longer setting-up time and the possibility of ice interference. The beam-shower method was also evaluated for measuring the layer thickness and proved also to be effective. As a result, we successfully measured the layer thickness of different functionalized AuNPs, for comparison with theoretical values.

In summary, the possibility of artefacts in thickness measurement or composition analysis of soft layer in hybrid NPs or nanowires needs to be recognized. An increase of layer thickness can be caused by hydrocarbon contamination from grid supporting films or the organic residuals from solution.

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[4] The authors acknowledge Masahiro Kawasaki from JEOL USA, Inc. for his useful discussion.

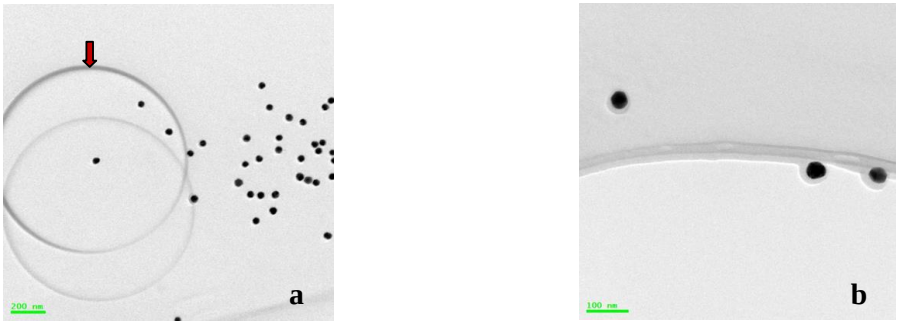

Figure 1. Zero – loss BF TEM image of Au/dNAB NPs on holey carbon grid:
a) taken at lower magnification to include previous illuminated areas at higher magnification;
b) taken near the edge of the hole of carbon film.

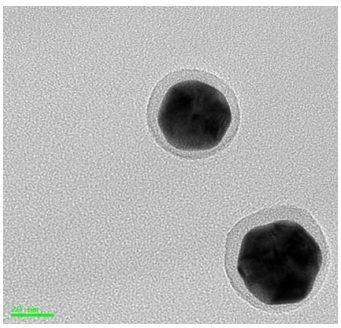

Figure 2. BF TEM images of Au/dNAB NPs on UV cleaned SiN membrane.

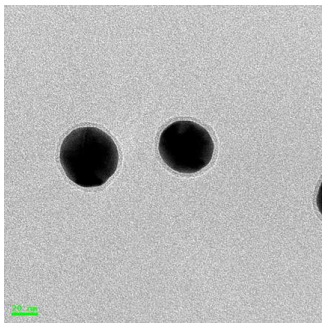

Figure 3. BF TEM image of Au/dNAB on UV cleaned carbon film and imaged at LN_2 temperature.

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