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1216 – Imaging of Molecular Coating on Nanoparticle Surface Using AFM Ringing Mode

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The molecular coating of nanoparticles is important for particle functionalization. Direct imaging of the molecular coating on the nanoparticle's surface with a sufficiently high lateral resolution is important though challenging. Recently introduced Ringing mode of atomic force microscopy (AFM) allows for simultaneous imaging of several maps of physical properties of a sample surface [1, 2], including imaging the height of the molecular coat. To the best of our knowledge, there is no other technique capable of measuring the presence of a thin layer of organic molecules on organic nanoparticles. The rival NIR AFM technique allows measuring of the presence of an organic layer on a nanoparticle core which has a substantially different coefficient of thermal expansion [3]. The lateral resolution of the coating reported in the literature is not well defined though but could be estimated in the range of 10 nm. Here we demonstrate that Ringing mode allows imaging of PEG on mesoporous silica with the lateral resolution down to ~1 nm. Furthermore, PEG coating on cellulose acetate particles can also be imaged in Ringing mode (though it is hard to estimate the resolution because of a rather smooth coating of cellulose acetate particles).

Figure 1 shows a representative example of Ringing mode imaging of a nanoparticle made of mesoporous silica [4] and cellulose acetate [5, 6]. Panel (a) shows the path of the AFM probe oscillating above the surface in a sub- resonance mode. Panel (b) shows the definition of two channels collected in Ringing mode: 1) the pull-off height or height of the neck formed between the AFM probe and sample surface during the probe – sample disconnection, and 2) the disconnection distance or height of the molecular coat on the sample surface. The molecular interaction between the AFM probe and surface / surface coating is nonspecific and formed mainly by van der Waals forces and capillary bridge between the probe and surface.

Panel (c) shows the adhesion images of a nanoparticle made of silica and cellulose acetate. The zoomed area, shown by the rectangular, are presented in panel (d). These 20 x 20 nm^2 zoomed images show the distribution of the height of the molecular coat. One can clearly see the difference of the molecular coat of these two types of particles. The coating shows virtually no defects on the cellulose acetate particle, whereas there are a number of defects clearly seen on the coating of the mesoporous silica particle. A statistical analysis made for a dozen particles shows a statistically significant difference between the PEG coating on mesoporous silica and cellulose acetate particles.

It is interesting to note that there is no one-to-one correspondence between the adhesion and the size of the molecular coating. Figure 2 shows an example of simultaneous imaging of adhesion, neck height, and the size of the molecular coat (disconnection distance). While some correlation between the adhesion and neck height can be seen, heterogeneity of distribution of the neck height is much richer than the adhesion map. The distribution of the height of the molecular coat is substantially different from the neck height. These images indicate a high complexity of the formation of the molecular coat on nanoparticles. The mechanism of formation of the coating layer is not well understood. Therefore, Ringing mode may be instrumental in the understanding of formation of such a layer.

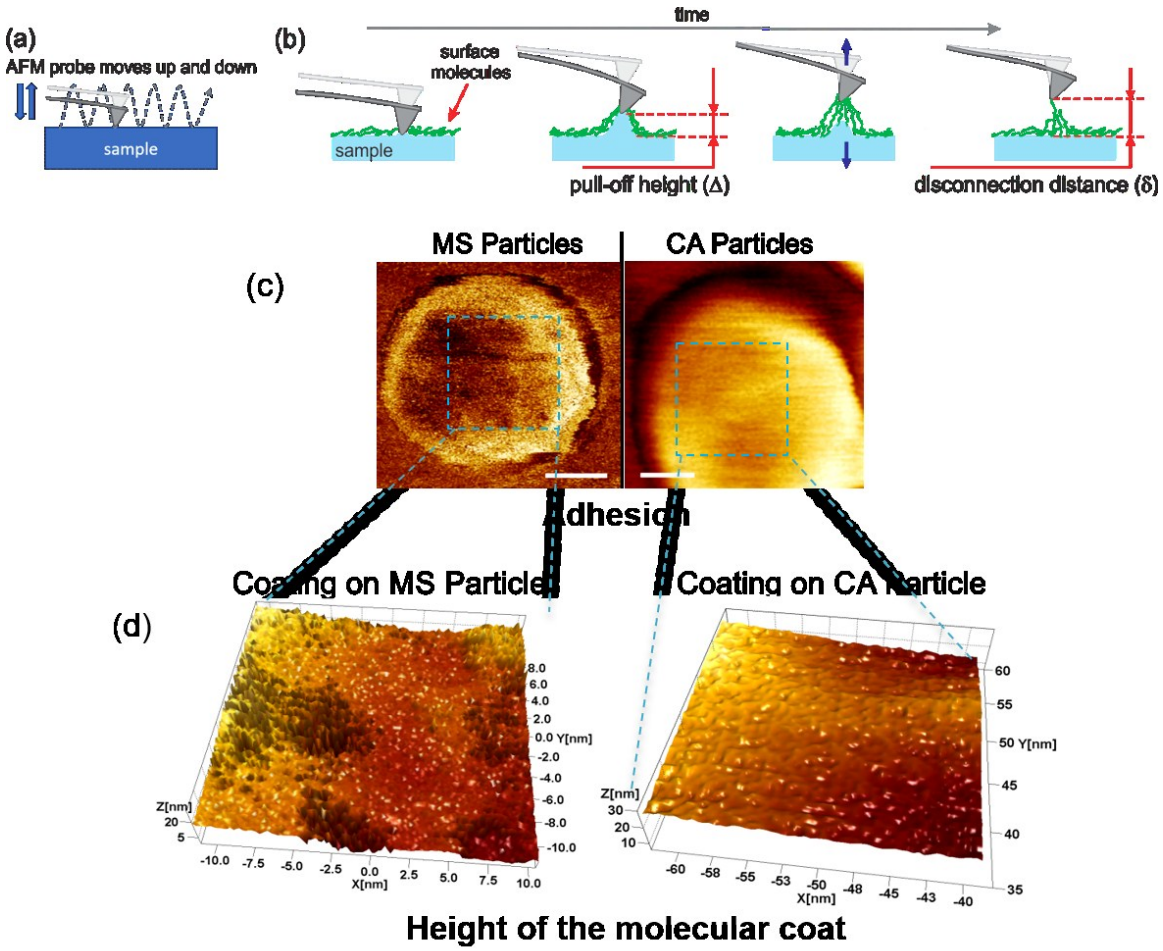

Figure 1. Figure 1. Imaging in AFM Ringing mode of the PEG coat on nanoparticles made of mesoporous silica (MS) and cellulose acetate (CA). (a) Schematics of the motion of the AFM probe during the imaging; the probe oscillates in a sub- resonance mode. (b) graphical definition of meaning of two channels imaged in Ringing mode: the pull off neck height and disconnection distance (height of the molecular coat). (c) the adhesion images of a mesoporous silica and cellulose acetate nanoparticles. The scale bar is 10 nm. (d) 20 x 20 nm2 zoomed area (shown in panel c by a dashed rectangular) showing the height of the molecular coat (disconnection distance channel of Ringing mode).

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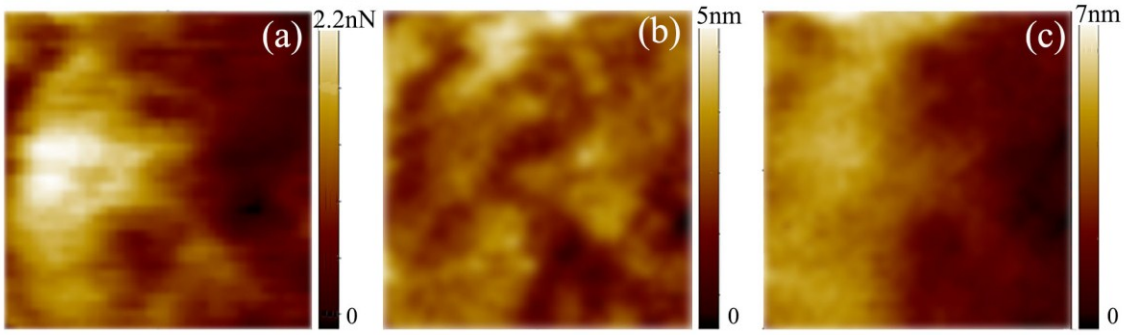

Figure 2. Figure 2. 70x70 nm2 area of a cellulose acetate nanoparticle imaged in Ringing mode. Three channels recorded simultaneously are shown: (a) adhesion force, (b) neck height, (c) disconnection distance.

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