Electrochemical Dissolution and Redeposition of Metallic Nanostructures Revealed by Liquid Phase Transmission Electron Microscopy

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Converting small molecules in the atmosphere by using of electrochemical energy devices can generate higher-value products by coupling to renewable energy [1]. Metallic and alloy electrocatalysts play a key role in the energy conversion because they can greatly promote the reaction process [2]. The electrocatalyst performance in terms of activity, durability, and selectivity can be optimized by modifying the structural parameters. Meanwhile, the structures also dynamically change under working conditions, including the hash liquid environment and high overpotential or current density, which affect the catalytic performance accordingly. Real-time study of the structural dynamics of metallic nanostructures is crucial to understanding the degradation mechanism and design advanced catalysts.

A wide range of *in-situ* spectral and imaging techniques have been employed to study dynamics of metallic nanomaterials. Comparing to those techniques, transmission electron microscopy (TEM) shows its unique advantages, *i.e.*, simultaneously offering imaging, structural and compositional information with significantly high spatial and energy resolution. Thanks to modern microfabrication, *in-situ* liquid phase transmission electron microscopy (LPTEM) method, based on customized closed liquid cells (i.e. MEMS-based sample carriers) and the corresponding holders, has been attracting much attention in the past years [3, 4]. In our previous studies, we successfully used this technique to study the chemical stability of metallic nanostructures with different morphologies in gold(III) chloride trihydrate ($HAuCl_4$) aqueous solution [5].

In this work, we use LPTEM for real time observation of the dynamics of metallic nanostructures under biasing conditions in a $NaHCO_3$ aqueous solution. As a typical example, Silver (Ag) nanostructures were synthesized by a simple one-pot solution phase method. The samples were then transferred on the working electrode of the functionalized chip with three-electrode configuration. To achieve reliable electrochemical measurements and good imaging contrast, the working electrode and counter electrode were made of glassy carbon (GC), while the reference electrode is made of polycrystalline Platinum (Pt). In addition, the electrodes were encapsulated with insulating layers to decrease the interfacial surface area outside the observing area. The working electrode was scanned with a potential range of -1.0 V to +1.2 V (vs. Pt) and a sweep rate of 100 mV s^{-1}. Figure 1 shows the morphology evolution of Ag nanostructures under the potential scanning process. Some conclusions can be obtained from the real time observations. (1) The dynamics is size dependent. When positive potentials are applied, thin nanowires (diameter D < 30 nm) are unstable, which are dissolved along the axis direction, or broken from a specific position. The thick nanowires (D > 30 nm) are stable under the oxidation condition. (2) The dynamics are morphology dependent. Comparing to the nanowires, the triangular nanoparticle keeps the morphology during the experiments, indicating that the electrochemical dissolution depends on the exposed facets of the nanoparticles. (3) Under reducing condition, no morphology change of the Ag structures is observed. The additional depositions (indicated by the blue arrows) are formed by the reduction of the dissolved silver ions in the solution. Control experiments excluded the electron beam

effect during the observation (Figure 2).Our results provide new insights in the electrochemical stability of metallic nanostructures.
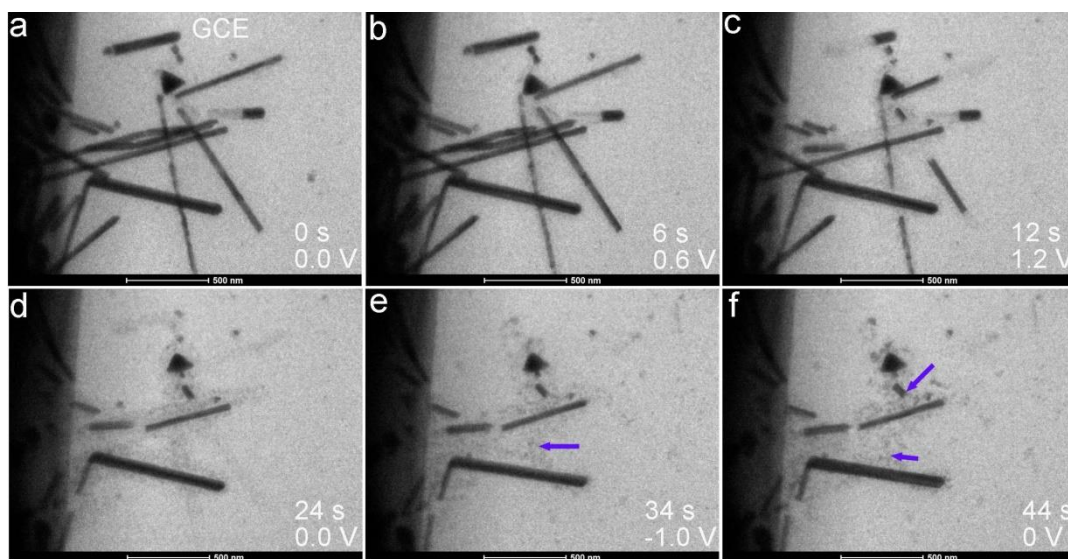

Figure 1. Time series of TEM images showing the evolution of Ag nanostructures on GC working electrode under potential scanning from -1.0 V to +1.2 V (vs. Pt) with a sweep rate of 100 mV s^{-1} in 0.1 M NaHCO$_3$ aqueous solution. The dissolution under positive scan and redeposition (indicated by blue arrows) during negative scan can be clearly observed.
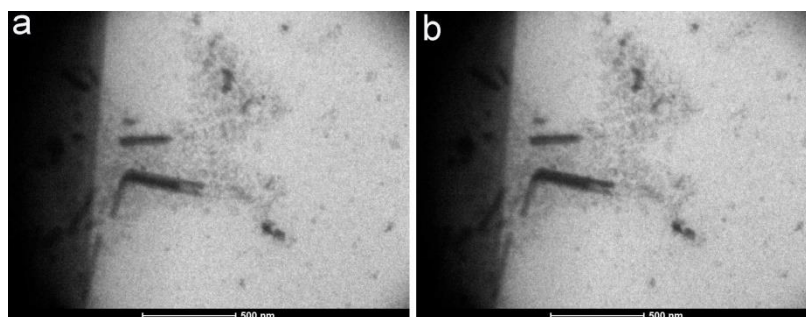

Figure 2. TEM images of Ag nanostructures before (a) and after 30 s (b) electron beam irradiation. No obvious morphology change can be seen from the nanowires, indicating the beam induced dissolution can be excluded.

References:

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