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In Situ Transmission Electron Microscopic Investigation of Coalescence Dynamics of Au Nanoparticles Embedded in Solid Potassium Bromide

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Understanding dynamic behaviors of nanoparticles under different circumstances is of essential importance to tune their sustained functionalities in any given application [1-3]. Thanks to the advances in the *in-situ* transmission electron microscopy (TEM), coalescence dynamics of Au nanoparticles (AuNPs) in aqueous solution have been extensively investigated [4,5]. However, there is rare attention on the study of these activities in the presence of solid surfactants, such as potassium bromide (KBr).

Our group recently reports Br ion (Br^-), serving as the surfactant, can direct the anisotropic growth of gold nanocrystals [6,7]. It is thus of interest to devise experiments to explore detailed interactions of KBr, the provider of Br^-, with gold clusters/nanoparticles. In this report, we demonstrate a novel approach to prepare AuNPs in solid KBr environment. We monitor the coalescence kinetics of AuNPs with KBr and reveal that KBr has dominant effects in the fusion process of AuNPs.

As is known, halogen salts such as NaCl and KBr are vulnerable to high-energy electron beams [8]. It is, therefore, challenging to monitor their activities in TEM in terms of a long period (e.g. more than a few seconds). Here, we employed graphene sheet as the support for both KBr and AuNPs. Figure 1 (a) shows a representative TEM image of AuNPs associating with KBr on the graphene substrate. Interfaces of solid KBr and AuNPs are highlighted in the red box, demonstrating nanoparticles are entirely surrounded by KBr crystallites. The higher magnification image in Figure 1(b) clearly illustrates a typical (100)-orientated crystalline structure. The fast Fourier transformation (FFT) of highlighted area is presented in the inset of Figure 1(b). The lattice distance is measured as 3.3 Å, corresponding to $d_{spacing}$ of KBr (200). It is surprising to observe KBr crystallites preserve certain stability against the high energy electron beam (dose rate of 1.6×10^5 $e^-/Å^2 \cdot s$ at 300 keV). It has been reported graphene has the capability of stabilizing nanocrystals such as gold nanowires [9] and the square ice [10]. We will discuss the mechanism of graphene-stabilized KBr under the electron irradiation.

We then investigate the electron bean induced coalescence of AuNPs in the presence of KBr. Figures 2 (a)-(e) are time-lapsed TEM images of the fusion process from 10 s to 87 s. Overall, coalesced nanoparticles get contacted, form the neck, and complete the fusion when the neck area is filled up. In this study, three nanoparticles finally evolve to a Au nanorod at 87 s. Neck growth, which is driven by surface energy minimization and realized by surface atom diffusion, characterizes the coalescence kinetics [11]. We record the growth rate of the neck between particle 1 and 2 and summarize the relation (neck width $\boldsymbol{D}$ versus time $\boldsymbol{t}$, $\boldsymbol{D \sim t}$) in Figure 2 (b). It is of interest to note two obvious differences in this relation from AuNPs coalesced with and without KBr. First, the neck grows significantly faster associated with KBr . Second, two growth stages exist in the case of AuNPs with this capping agent. We will extend our discussions to the dynamic state of KBr under electron irradiation and provide plausible explanations to these impressive phenomena. This work will enhance the understanding of the role of solid surfactants in directing the growth of nanocrystals.

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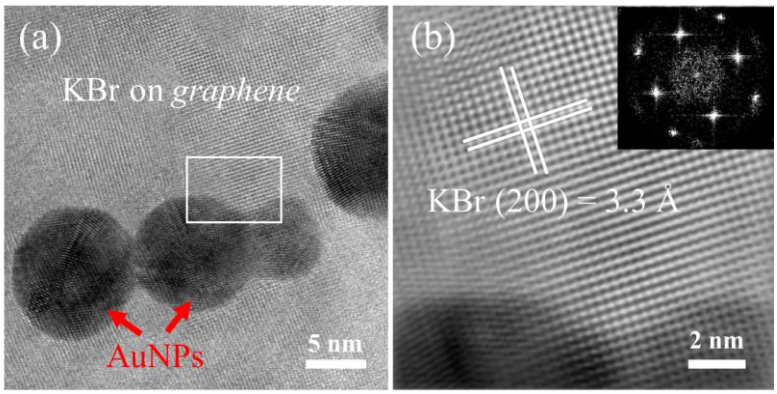

Figure 1. (a) A representative TEM image of Au nanoparticles embeded in solid KBr crystallites. (b) High resolution image of the interface between Au nanoparticles and KBr. Crystalline structure of KBr is clearly identified.

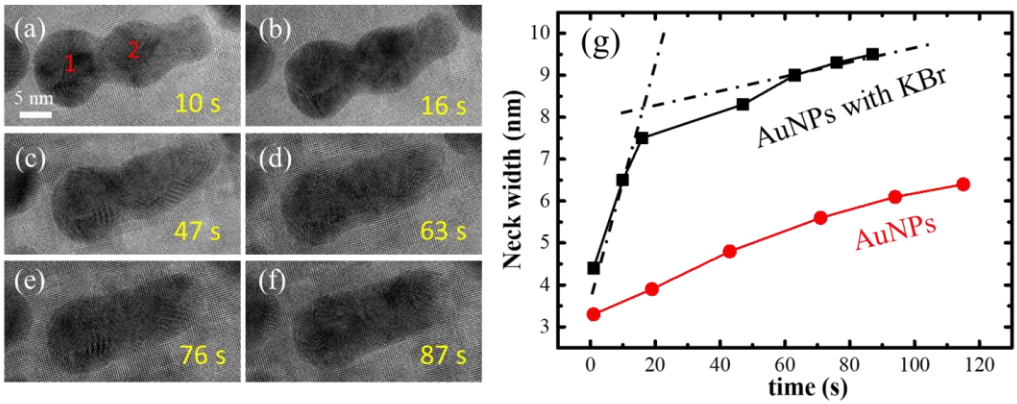

Figure 2. Coalescence kinetics of Au nanoparticles capped with KBr. (a)-(f) Time-lapsed TEM images of the coalescence process. (g) Neck growth over time between particle 1 and 2. For comparison, the neck growth of AuNPs free of KBr is also provided (red curve).

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