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In situ TEM Observation of the Nucleation and Growth of Metal Oxide Nanoparticles on Graphene

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Depending on their shape, size and crystal structure, nanoparticles exhibit different catalytic, electronic, and optical properties for numerous real world applications including gas-sensing, drug delivery, and heterogeneous catalysis [1]. Over the past decades, an unprecedented wealth of knowledge has been gathered in the synthesis of nanoparticles with controlled shape, size and uniformity. Recently, the graphene based nanocomposites have attracted prevailing attention due to its potential to tune desired properties together by building multifunctional architectures in nanoscale [2]. However, complicated structures bring more challenges to the synthesis approaches. Traditional synthesis studies rely on the *ex-situ* characterization techniques after processing encounter the time-consuming optimization process as well as difficulties of precision-tailoring resulting in the loss of expected properties.

The limitations of traditional synthesis studies can be overcome by the use of *in situ* TEM techniques which provide real time information during processing such as nucleation, growth, and ripening of the nanoparticles as well as the real time monitoring the phase change, *e.g*. amorphous to crystallized structures [2]. By using an *in situ* heating stage, the temperature required for nanoparticle growth can be mimicked inside the microscope column. We here report the dynamic TEM observation of the *in situ* synthesis of cobalt oxide nanoparticles on graphene support with comparing to that directly from dried cobalt precursors.

Synthesis experiments are performed on a 120 KV S/TEM (Hitachi® HT-7700) which minimizes the beam effect to the nanoparticle synthesis with a Gatan® heating holder capable of heating up to 875ºC. Graphene and precursor solution were dropped in turn onto lacey carbon TEM grids. Fig. 1A and B present *in situ* bright-field TEM images showing the Co oxide nanoparticles nucleate on the bare graphene sheet at 300ºC after a 30mins incubation time. The oxide nuclei show a large nucleation density ($1.18\times10^4 \mu m^{-1}$) with a narrow size (equivalent disk radius) distribution (1.2±0.2nm) with no preferential sites of nucleation. Fig. 1C and D present the ripening of nanoparticles at elevated temperature. Increasing temperature to 500ºC, the average size of nanoparticles increases from ~1.2nm to ~2.1nm accompanied with the coalescence of small nanoparticles. Above results demonstrate the growth of metal oxide particles on graphene with great uniformity can be achieved inside the microscope and the size of nanoparticles can be tuned by the following thermal treatment.

Fig.2 presents a comparison between the nanoparticles nucleated on graphene and directly in precursor (without graphene as support) at 300ºC by *in situ* TEM imaging. The nucleation rate of the nanoparticles in the precursor is much faster than that with graphene as support. However, after 60mins' growth, the nanoparticles on graphene have a larger lateral size and smaller nucleation density than those in precursor. The nucleation of nanoparticles is dominated by the supersaturation of metal ions and their diffusion rate in the system. In the precursor without graphene support, there could be abundant metal ions that leaded to a high supersaturation rate, which was suspected as the cause of the observed fast

nucleation and a large nucleation density. Meanwhile, the graphene sheets promote the surface mobility of the metal ions providing sufficient mass transport for nanoparticle growth (ripening), which leads to the formation of nanoparticles with a large averaged size in the same period of time.

These results show the *in situ* nucleation, growth and coalescence of nanoparticles in real time on different supports. It demonstrated that we may have the flexibility to tailor the size and density of the nanoparticles by using graphene as the support. This detailed information could guide the synthesis of nanoparticle-graphene composites.

References:

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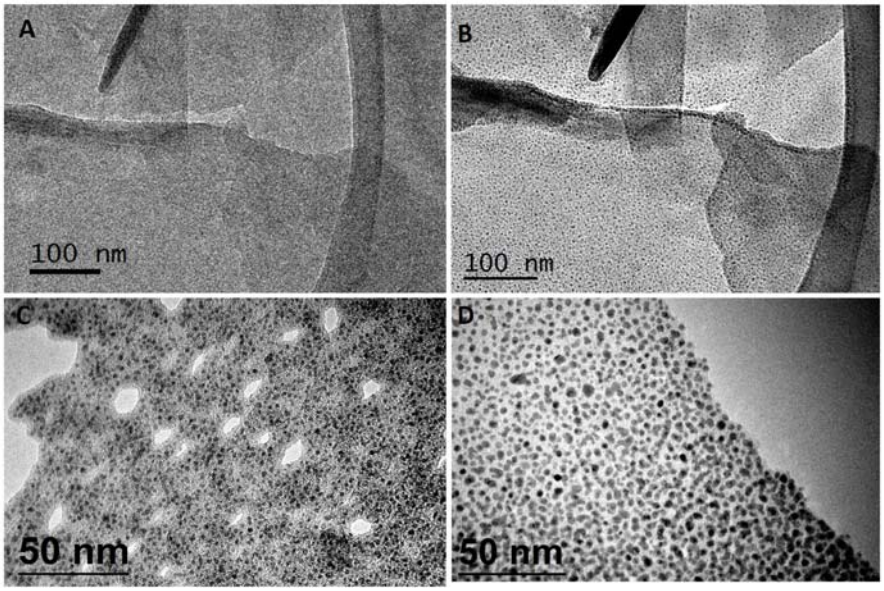

Figure 1. *In situ* TEM images of Co oxide nanoparticles growth on graphene at 300ºC A) 0min; B) 30mins. Ripening of Co oxide nanoparticles C) 300ºC and D) 500ºC for 30mins.

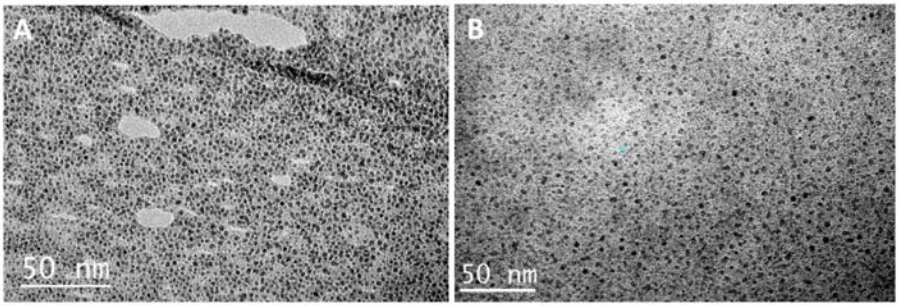

Figure 2. *In situ* synthesized Co oxide nanoparticles A) in precursor without graphene as substrate and B) on graphene at 300ºC after 60mins.

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