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Investigating Dynamic Processes of Nanomaterials Using in Situ Liquid Phase TEM Technologies: 2014-2019

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The dynamic processes of nanomaterials are common phenomena in material science and biological system. Liquid-phase transmission electron microscopy (TEM) with high resolution provides unprecedented insights into dynamical processes by in situ imaging. This review summarizes the technical developments and the breakthroughs during 2014-2019 in the field of nanoparticles nucleation and growth, nanoparticles corrosion, self-assembly of nanomaterials, dynamical processes *in vivo,* in situ electrochemistry and radiolysis induced reaction in energy systems. The recent research developments in the liquid-phase TEM will promote advancement for material science and bioscience.

Keywords: Dynamic processes; Nanomaterials; Liquid phase transmission electron microscopy; In situ imaging

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1. Introduction

The dynamical processes during formation and transformation of nanomaterials in solution, most importantly water, are widespread phenomena in material science and bioscience, ranging from liquid-based synthesis to self-assembly, biological activity and electrochemical reactions in energy conversion. In order to control those dynamic processes in solution, it is important to get the structural and compositional information and unravel the basic mechanisms. Moreover, in order to take an insight into the basic mechanisms, a microscopy with both high temporal and spatial resolution is needed. However, it is beyond the capability of common microscopy techniques such as optical microscopy, atomic force microscopy (AFM), and conventional transmission electron microscopy (TEM).

Hereinto, conventional TEM provides structural and compositional information with atomic resolution, but unfortunately, because of the indispensable vacuum working environment, it can only allow ex situ imaging samples in dried state. Construction of "liquid cells" in TEM is a reasonable resolution that comes into peoples' mind at the beginning of TEM development, and has only been realized by modern microfabrication techniques.[1] Combined with development of other techniques, such as control of electron dose and quantitative analysis, liquid cell TEM allows direct observation of samples in liquid with both high temporal and spatial resolution and provides both structural imaging and elemental analysis. Recently, liquid cell TEM reveals unprecedented information of dynamical processes of nanomaterials in solution, [1-5] such as nanoparticles nucleation and growth, [3]

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nanoparticles corrosion,[6] self-assembly of nanomaterials,[7] dynamical processes *in vivo,*[8] in situ electrochemistry[9] and radiolysis induced reaction in energy systems.[10]

In this review, we summarize the development of the technology for liquid phase TEM and its application in studying dynamic processes of nanomaterials in recent years (2014-2019). Meanwhile, we foresee the possible further development and application of liquid phase TEM.

2. Technical Developments

2.1 Design and Fabrication of Liquid Cells

The prime need for liquid phase TEM is reliable liquid cells with electron-transparent windows for liquid enclosure; while in the high vacuum environment required by TEM, the windows should be both strong enough to hold an adequate volume of liquid and small enough to avoid bulging too much under differential pressure between internal and external.

In 2015, Chen *et al*. have summarized the developments of liquid cell technology for in situ TEM.[11] Liquid cells have been classified into four broad categories: 1. liquid cells with silicon nitride windows sealed by polymer O-rings; 2. liquid cells with silicon nitride windows sealed by other materials; 3. liquid cells using low vapor pressure liquids such as ionic liquids, called opened liquid cells elsewhere;[12] 4. graphene-sealed liquid cells (GLCs). Besides, liquid cells are classified according to its purpose: static cells are used for static liquids while flow cells allow for flow of solutions.[3] The flow cells is more commonly used in materials formation, where fresh solution is needed in process. Especially, liquid cells are designed with two flow lines for reagent mixing. As shown in Fig. 1, a flow cell was fabricated with silicon nitride windows and sealed with O-rings, and two inlet flow lines and one outlet line are incorporated. The flow cell was designed to observe the $CaCO_3$ nucleation by mixing of $CaCl_2$ and $NaHCO_3$.[13] Commercial liquid cells with silicon nitride windows are available recently, even with flow lines.[14]

Hereinto, graphene-sealed liquid cells (GLCs) are liquid cells using one or two graphene sheets with atomic thickness

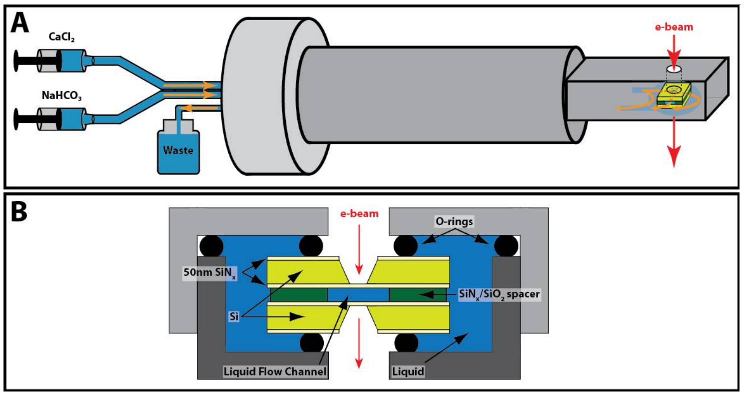

Fig. 1 (A) Schematic illustration of Flow cell with two inlet lines and one outlet line mounted on holders and connected to syringe pumps; and (B) Flow cell sealed by O-rings. (Reprinted with permission Ref.13. Copyright 2014, AAAS.)

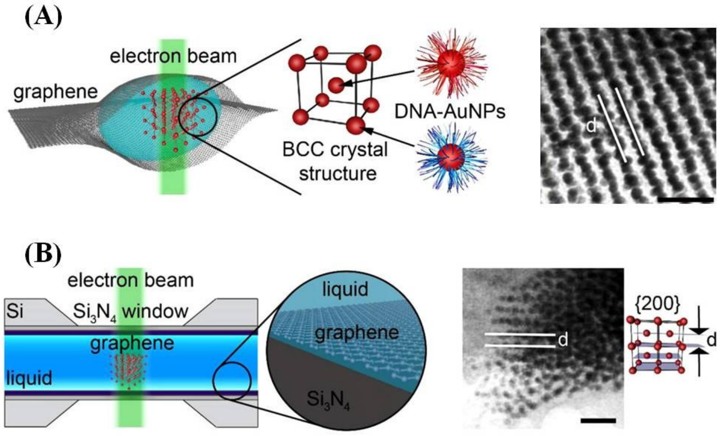

Fig. 2 Experimental setup of (A) graphene liquid cells and (B) graphene-coated silicon nitride cell. The insets are representative TEM images of DNA-Au nanoparticles, respectively, the scale bar is 50 nm. (Reprinted with permission Ref. 15. Copyright 2017, ACS.)

to encapsulate liquid specimens which allows the excellent image resolution at an atomic level;[11] and owing to the electrical conductivity, GLCs can be even used to protect radiation-sensitive specimens, such DNAs[15] and proteins[16], by efficiently scavenge reactive radical species (Fig. 2). Great efforts have been taken to assemble GLCs. Strategies about how to transfer graphene to a liquid surface in a reproducible way and with less imperfections have been pushed forward.[17-18] Compared to GLCs, silicon nitride cells have lower imaging contrast, however they are also highly attractive because of their mechanical strength, chemical inertness, and their capacity for additional functionalities and improvements. Recent research reported that two dimensional MoS_2 sheets have been used as windows and functional substrates.[19]

2.2 Control of Electron Dose

It is well-known that the long-lasting interaction of the specimen with electron beam could lead to damage or transformation of components in the specimen.[20] Therefore, ultralow-dose electron or/and high image-acquisition rates are required for liquid phase TEM. New strategies, both hardware and software based, have emerged and provide possibilities to optimize the image-acquisition process of liquid phase TEMs. In 2015, Migunov *et al*. have demonstrated that the use of direct electron detector has reduced total the electron dose by more than an order of magnitude. The direct electron detector with a pnCCD sensor is from PND detector GmbH. The detector is fully depleted and sensitive over its full thickness. The maximum pixel full well capacity enables that the full image was read out at a rate of 1150 frames per second with absolute intensity information. And a tomographic tilt series of inorganic lanthanide misfit nanotubes containing 3487 images was recorded successfully in only 3.5 s.[21]

Base on the principle that a signal can be recovered from far fewer samples than required through optimization, compressing sensing is a signal processing technique to reconstruct a signal from a series of sample measurements. Compressing sensing was used to increase image-acquisition rates instead of replacing the existed TEM detectors with expensive direct electron detectors. For example, by using compressing sensing, Stevens *et al*. have demonstrated that electron dose was significantly reduced and the image-acquisition rates were increased by more than an order of magnitude.[22,23] In 2018, Hujsak *et al*. applied a Multi-Objective Autonomous Dynamic Sampling (MOADS) method as a software add-on to accelerate spectrum mapping in electron energy-loss spectroscopy (EELS) or energy-dispersive X-ray spectroscopy (EDS) by a factor of 10.[24]

2.3 Quantitative Analysis

It was anticipated that liquid phase TEM has the potential for quantitative study of various phenomena in solution; the factors that influence quantitative analysis of liquid phase TEM include electron dose, accelerating voltage, imaging mode, depletion of precursor and accumulation of residual radicals.[20] It was suggested that great care should be taken to correctly interpret quantitative information.

As depicted in Fig. 3, two 3D structures of individual Pt nanocrystals at near atomic resolution have been obtained with a hybrid method combining a graphene liquid cell, high-resolution TEM, a direct electron detector and an ab initio algorithm for single-particle 3D reconstruction by Park *et al*. in Alivisatos's group in 2015.[25] Soon after, Ye *et al*. in Alivisatos's group have observed the short-lived, nonequilibrium nanocrystals and rationalized their structure through Monte Carlo simulations.[26] Moreover, quantitative analysis of the dynamics of a solution-phase superlattice assembled from gold nanoprisms at the single particle level has been carried out based on a combination of direct liquid phase TEM imaging, small angle X-ray scattering and theoretical modeling.[27] And later, rotational dynamics of gold nanoparticles in aqueous solution was studied by 4D TEM with liquid cells, which demonstrated that the possibility of liquid cell 4D TEM for time-resolved 3D structure reconstruction of individual nanoparticles including biomolecules in the native environments.[28]

3 Dynamical Process Investigation

3.1 Nanoparticles Nucleation, Growth and Corrosion

Various nanomaterials with different sizes, shapes and architectures have been synthesized in solution in the last 20 years, which leads to the "nanomaterial era". Meanwhile, the fundamental understanding dynamic processes of those nanomaterials, such as nucleation, growth, attachment, diffusion, corrosion and so on, is urgently needed and cannot be implemented with common analytic techniques. Fortunately, advanced liquid phase TEM enables in situ imaging of those dynamic processes with adequate resolution.[6, 29] Enormous great works focused on formation and transformation of nanomaterials by using liquid phase TEM have been reported.

Notably, liquid phase TEM has made breakthroughs in investigation of nanoparticles nucleation and growth. The application of liquid phase TEM spreads rapidly from nanoparticle nucleation and growth in pure liquid water,[13, 30-32] in solution with mediator such as polyelectrolyte[33] or protein[34], and on other nanoparticles,[35-36] to nucleation and growth of metal-organic framework[37] and protein crystals[38], even involving synthesis of polymeric nanoparticles from a Pt(II)-containing monomer.[39] Those works are elaborated in some excellent perspective articles and reviews.[2-4, 9, 40-41] For example, in 2016, De Yoreo *et al*. have reviewed investigation of materials formation with liquid phase TEM, including the dynamics of nanoparticle nucleation, assembly dynamics in soft matter systems, and also the formation of inorganic

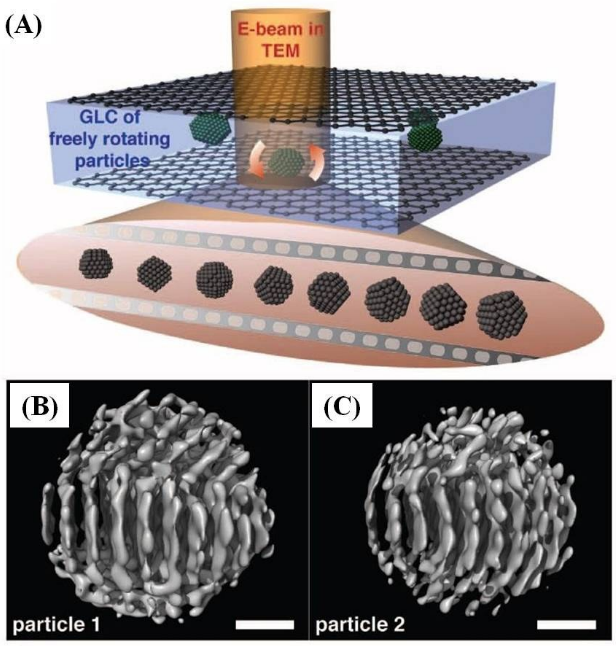

Fig. 3 (A) Schematic illustration of Pt nanocrystals rotating freely in a GLC and being captured by in situ TEM imaging; (B) and (c) 3D density map of two Pt nanocrystals obtained from 3D reconstruction. (Reprinted with permission Ref. 25. Copyright 2015, AAAS.)

nanomaterials directed by biomolecular or biomimetic constituents.[3] In 2018, Kim *et al*. have summarized the application of liquid phase TEM in the studying of colloidal inorganic nanoparticles in the aspect of the growth mechanism, transformation and motion of those nanoparticles.[40] Most recently, in 2019, Shi *et al*. have described the formation of nanocrystal electrocatalysts studied by liquid phase TEM.[6] It shows that liquid cell TEM promises great potential for promoting the science of nanoparticles synthesis.

Besides nanoparticles nucleation and growth, nanoparticles corrosion is another important issue concerned. Better understanding dissolution kinetics at nanometer scale can help better manipulate the surface structure of nanoparticles and improve the stability of nanoparticles, which is especially important for nanomaterials used as electrocatalysis. By using liquid phase TEM, the real-time corrosion processes of nanoparticles under harsh liquid environments have been investigated, such as oxidative etching of palladium nanocrystals[42] and platinum nanoparticles[43]. Particularly, palladium-platinum core-shell nanomaterials have been employed as a model system, asymmetrical corrosion[44] and facet-dependent thermal stability[45] have been found during nanoparticles corrosion.

3.2 Self-Assembly of Nanomaterials

Due to driving forces including van der Waal forces, interactions among capping agents, ligands and nanomaterials, and magnetic forces (for magnetic materials), it is commonly for nanomaterials to self-assemble into chains, loops, sheets and three-dimensional crystals. Assembled nanoparticles with controlled patterns are dispensable for nanodevices; therefore, it is necessary to control self-assembly processes by understanding the driving forces and building models. Liquid phase TEM is used to observe directly self-assembly of nanoparticles.[7, 27, 46-47] For example, in 2017, Powers *et al*. have applied liquid phase TEM corroborated with computational methods. The results offer a quantitative understanding of underlying self-assembly mechanisms of $PtFe_3$ nanoparticles.[7]

Self-assembly is also an important process for soft materials, such as polymers and biomolecules. Although soft materials are always composed with low atomic numbers elements which usually means low contrast for TEM imaging, liquid cell TEM still shows its potential to visualize soft materials in liquid without staining. During 2014-2019, liquid cell TEM has been used to investigate micelle-micelle fusion process[48] and self-assembly[49] of amphiphilic block polymers, movements of individual water-soluble polymers[50] and proteins.[16, 51-52]

3.3 Dynamical Processes *In Vivo*

Direct observation is significant for understanding how the therapeutic agents or other items works in the body. The ability of liquid cell TEMs to study dynamical processes *in vivo* at the nanoscale is attractive, however, the response of organisms provoked by electron beam is confirmed to be inevitable. de Jonge *et al*. even have argued that the utilization of electron microscopy to investigate live cell is probably impossible, because minimal electron dose required to obtain contrast in electron microscopy is many orders of magnitude above lethal dose of reproductive-cells in a prior paper.[53] And researchers have made great effort to evaluate experimental results and choose the convincing ones.[14] Therefore, the application of in situ imaging with liquid phase TEM in biological systems is relatively limited and not as widespread as in materials science.

Liquid cell TEM has been used alone or associated with optical microscopy to image *in vivo* systems, such as magnetotactic bacteria,[54] the infection of a living biological cell with virus,[55] movements of Au nanoparticles embedded in MDCK cellular matrix in solution,[56] delivery of nanoparticles into cancer cells,[57] etc. For examples, in 2014, Woel *et al*. have combined liquid cell TEM with fluorescence microscopy to image magnetotactic bacteria in liquid.[54] In 2015, Park *et al*. have observed the structure of influenza viruses and cells, and also movements of Au nanoparticles embedded in MDCK cellular matrix in solution with high contrast at nanometer scale resolution by using GLCs and low-dose electron beam.[56] Varano *et al*. have presented the time-resolved movies of virus particles in solution for the first time.[58] de Jonge's group have reported in 2017 that single-membrane proteins within whole eukaryotic cells were studied with quantum dot labels by using electron microscopy with GLCs and low electron dose.[59] Thereafter, Piffoux *et al*. have exploited the morphology and dynamical behavior of cell-derived extracellular vesicles in physiological media with liquid phase TEM.[8]

3.4 In Situ Electrochemistry

In situ electrochemistry process can be observed by TEM with integrated electrodes inside the liquid cells. It is flexible to fabricate electrodes with arbitrary geometry by using a wide range of materials. Fig. 4 shows a representative electrochemical liquid cell for TEM imaging. During 2014-2015, in situ electrochemistry process, such as the electrodeposition of metals[60-61] and anode/cathode reactions of lithium-ion batteries have been widely studied with electrochemical liquid cells. The study of lithium-ion batteries by liquid phase TEM reveals the direct observation of lithiation/delithiation of MoS_2 nanosheets,[62] lithium dendrite growth,[63] lithium ion distribution,[64] lithiation of an Au electrode,[65] formation of a solid-electrolyte interphase,[66] degradation mechanisms in electrolytes solutions,[67] etc. All these exciting works about in situ electrochemistry by liquid phase TEM have been summarized in literatures.[4, 9, 12, 68] Additionally, in 2018, Lutz *et al*. have studied the charge/discharge mechanism in Na-O_2 batteries by using fast imaging TEM with electrochemical liquid cells.[69]

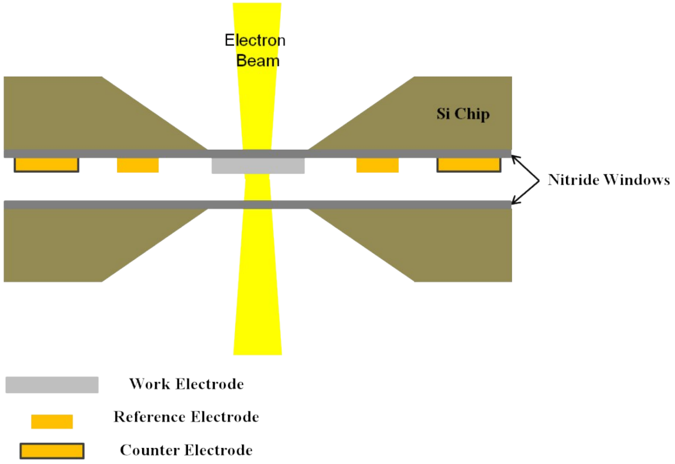

Fig. 4 Schematic illustration of a TEM holder for in situ electrochemistry.

3.5 Radiolysis Induced Reaction in Energy Systems

Researchers have taken great attention to the electron beam effects on samples, especially for the liquid samples. When the electron beam interacts with the solution, radiolysis of liquid water happens, followed by the generation of highly reactive species and alternation of pH, ion concentration and reaction rates in the solution, which is often considered as a source of undesirable sample damage and imaging artifact of liquid phase TEM.[70-72]

However, in another perspective, these highly reactive radiolytic species, for example, hydroxyl radicals and solvated electrons, are crucial for energy research areas, such as battery systems, electrochemistry, photocatalysis, etc.[10, 73] Liquid phase TEM is the right tool to directly reveal nanometer-scale dynamics of energy-related materials without introducing additional materials or energy. In 2018, Rehn *et al*. have set forth the development and prospect of liquid-phase TEM in probing energy systems.[10] In this article, Rehn *et al*. have presented the statement of problem and perspective of tailoring radiolysis firstly. Then three potential approaches to tailoring radiolysis have been highlighted, which are engineering the lifetime of free radicals, engineering the lifetime of solvated electrons, and regulating radiolytic products via beam dose, respectively.

4. Conclusions and Perspectives

In conclusion, owing to its ability to direct observation of dynamics processes of nanomaterials in liquids with high temporal and spatial resolution, liquid phase TEM shows its unique advantages to provide unprecedented experimental results of dynamic processes, including nanoparticles nucleation and growth, nanoparticles corrosion, self-assembly of nanomaterials, dynamical processes *in vivo,* in situ electrochemistry, radiolysis induced reaction in energy systems.

Despite its advantages, liquid phase TEM has its limitations. The major limitation comes from electron beam radiation which could affect pH, ion concentration and reaction rates in the solution, and bring damage and byproducts to the sample. To avoid these effects, low electron dose has been advised by researchers. The second limitation is the fabrication of liquid cell. It is a great challenge to fabricate a liquid cell to hold an adequate volume of liquid in the high vacuum environment with electron-transparent windows small enough to avoid bulging, and meanwhile thin enough not to reduce resolution of TEM. The third limitation is the dynamic processes being imaged, which could reduce the resolution of TEM compared to vacuum methods. Additionally, some influence factors of liquid phase TEM that different from normal conditions should be concerned, such as local temperature, reactant mixing, differential pressure, molecular adsorption on substrates, and so on. Accordingly, expensive direct electron detectors and complicated quantitative analysis are needed to get high quality of liquid phase TEM results.

Hopefully, liquid cell TEM will open tremendous opportunities to study dynamics processes of nanomaterials in liquids with high spatial and temporal resolution by fully take advantage of advanced liquid cells and detectors, computational design and data analysis, and other technical developments. An promising and exciting future are expected for the expansion of liquid cell TEM applied in the field of materials science and bioscience.

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