Showcasing work from the Key Laboratory for the Physics and Chemistry of Nanodevices, Peking University, Beijing, China.

Constant-rate dissolution of InAs nanowires in radiolytic water observed by *in situ* liquid cell TEM

Liquid cell technology enables studying liquid by transmission electron microscopy (TEM). Despite the extensive study on nanoparticles, 1D nanowires (NWs) have not been studied a lot in liquid. Here, we observe the dissolution process of 1D InAs NWs in radiolytic water by *in situ* liquid cell TEM. Unlike most size-dependent dissolution of nanoparticles, the dissolution rate of InAs NWs is found to be constant with reduced diameter down to ~5 nm. Through analyzing the dissolution kinetics, we find our results are consistent with surface reaction limited dissolution.

As featured in:

See Qing Chen et al., *Nanoscale*, 2018, 10, 19733.
Constant-rate dissolution of InAs nanowires in radiolytic water observed by in situ liquid cell TEM†

Mei Sun, a Xing Li, b Zhiqiang Tang, a Xianlong Wei c, a and Qing Chen d, a *

Understanding the dissolution process and mechanism of materials in a liquid at the nanoscale is very important for both science and technology in many fields. Although the dissolution process of nanoparticles has been studied by many groups, the dissolution of one-dimensional (1D) nanomaterials with a high aspect ratio has seldom been directly observed with a high spatial resolution. In this paper, the dissolution process of 1D nanowires (NWs), InAs NWs as an example, in radiolytic water is studied by in situ liquid cell transmission electron microscopy. Different from most size-dependent dissolutions of nanoparticles, the dissolution rate of InAs NWs is found to be constant with reducing size down to ~5 nm in diameter. The kinetics of InAs NW dissolution in radiolytic water is investigated by analyzing the source supply, surface reaction and product diffusion steps in the dissolution process. We find surface reaction limited dissolution fits well with our experimental results and the activation energy should be constant during the whole dissolution process even when the diameter of InAs NWs is as small as 5 nm. The present results are significant for a quantitative understanding of liquid phase reactions for 1D systems and for design and optimization of dissolution processes.

Introduction

Nanomaterials have unique properties which are significantly different from their bulk counterparts, and have great potential in numerous applications, a large part of which involves liquid. However, most of the liquid phase processes of nanomaterials, such as dissolution or etching, liquid phase growth, chemical reactions, processes of bioscience, etc., are still unclear due to technical constraints. The recently developed liquid cell technology has made it possible to in situ observe liquid phase reactions by transmission electron microscopy (TEM) with nanoscale or even atomic scale resolution. Up to now, liquid cell TEM has been applied to study nanoparticle nucleation and growth, nanoparticle motion and self-assembly in solution, electrochemical reactions, Li-ion batteries, dissolution, bioscience, etc. Focusing on the study of dissolution by liquid cell TEM, there have been many novel reports on nanoparticles, such as Pd nanocrystals, Pt nanoparticles, core–shell nanoparticles, Ag nanocables, Au nanorods, etc. The dissolution of metal nanoparticles has been found to start first from apexes and edges and then facets. Through controlling the etching rate, the nonequilibrium morphology evolution of Au nanorods and Au nanoparticles has been observed and simulated, driving-force-dependent near-equilibrium and nonequilibrium transformation pathways have also been exhibited. The chemical wet etching process of amorphous Si nanopillars in alkaline solution has been monitored by liquid cell TEM and some transient reaction intermediate clusters have been found around the surface of Si. The dissolution of metal oxides has also been studied by liquid cell TEM, and oxygen vacancies induced by electron beam irradiation have been found to boost the dissolution of metal oxides. Besides many studies on nanoparticles, the dissolution of some nanorods with an aspect ratio smaller than 5 has also been studied by several researchers. However, so far, there is still a lack of reports on the dissolution of one-dimensional (1D) systems with a high aspect ratio (such as higher than 20) by liquid cell TEM, to the best of our knowledge. The behaviour of 1D materials, such as nanowires (NWs) and nanotubes, could be different from that of nanoparticles or nanorods with a low aspect ratio. It is well known that many NWs have great potential in numerous fields, such as electronic devices, photoelectronic devices, energy, sensors, chemistry, etc. A large number of NW-related processes are carried out in the liquid phase, such as fabrication, cleaning, modification and also in many applications. Studying liquid phase processes of
NWs by *in situ* liquid cell TEM can provide a deep understanding of the relevant phenomena at the nanoscale.

Due to the high electron mobility, small $g$ factor and ease of forming ohmic contact with most of the metals, InAs NWs have great potential in high performance as well as high speed electronic devices and even quantum devices.\(^{21,22}\) However, the native oxide layer on the surface strongly disturbs the physical properties and applications of InAs and other III–V materials.\(^{23}\) Wet-chemical etching methods are most commonly used to remove the native oxide layer and passivate the surfaces,\(^{24,25}\) but most of the solutions used also etch InAs. Precisely controlling the etching process is very important for the application of thin InAs NWs which are the basic channel materials for advanced scaling-down devices. Etching InAs NWs properly can even create fascinating structures for quantum devices.\(^{26}\) Consequently, it is demanding to explore the dissolution kinetics of InAs NWs in solutions.

Here, using *in situ* liquid cell TEM, we study the dissolution process of 1D systems, InAs NWs as an example, in radiolytic de-ionized water. The dissolution rate is found to be constant during the whole dissolution process and the kinetics of InAs NW dissolution in radiolytic water is investigated by analyzing three possible rate control steps in the dissolution process. We find that surface reaction limited dissolution could be responsible for the constant dissolution rate of InAs NWs. Although the dissolution observed by *in situ* liquid cell TEM may not be the same as the dissolution outside TEM, which is the common problem of an *in situ* TEM study, our observation is significant for understanding the dissolution of 1D systems.

**Experimental**

InAs NWs studied in this work were synthesized by molecular beam epitaxy (MBE) and metal–organic chemical vapour deposition (MOCVD).\(^{27,28}\) TEM characterization indicates that most of the MBE-grown InAs NWs have a wurtzite (WZ) structure and grow along the <0001> direction without stacking faults (Fig. 1a). In contrast, the MOCVD-grown NWs have mixed phases containing zinc blende (ZB) and WZ sections separated by stacking faults and grow along the <0001>-WZ/<111>-ZB direction (Fig. 1b). The diameter of the MOCVD-grown InAs NWs is normally larger than the MBE-grown InAs NWs. Although both types of NWs are coated with an amorphous native oxide layer with a thickness of $\sim 2$ nm, the oxide layer outside the MOCVD-grown NWs is more uniform.

For the liquid cell TEM study, InAs NWs were transferred onto a silicon nitride (SiNx) film window of liquid cell chips using a nanomanipulator (Kleindiek MM3A) on a scanning electron microscope (SEM, FEI Quantum 600F),\(^{29,30}\) as shown in ESI Fig. S1.\(^{†}\) The liquid cell TEM experiments were carried out using a liquid cell holder (Hummingbird Scientific) on a FEI Tecnai F20 TEM operated at 200 kV. InAs NWs and de-ionized water were sealed by two silicon chips with electron transparent SiNx windows (about 50 nm thick) in the center area for imaging. In order to improve the spatial resolution of TEM imaging, we introduced a bubble in the liquid cell to reduce the thickness of the water layers in the window region.\(^{31}\) The electron beam dose rate used here is in the range of 23 to 36 electrons per Å² per s. We note $N_a$ as the average counts per pixel in the blank picture captured by using a CCD camera under the same microscopy conditions as in the experiments. The electron beam dose rate $I$ is obtained by dividing $N_a$ by the exposure time ($t$) of the picture, the pixel area of the images ($A_p$) and the conversion efficiency ($r$) of the CCD camera, $I = N_a/(t \times A_p \times r)$. Videos were taken with an exposure time of 0.2 s for each video frame, and all the experiments were carried out at room temperature.

The diameter of the InAs NWs was measured using Photoshop software from the video frames. The main error in

---

**Fig. 1**  HRTEM images of typical MBE-grown (a) and MOCVD-grown (b) InAs NWs. The black dotted lines indicate the native oxide layer covering the InAs NWs.
the diameter measurements comes from the low contrast between the water background and InAs NWs. In order to obtain accurate data, the diameters of the InAs NWs at the same positions were measured many times. The points and the error bars in the figures correspond to the average values and the range of multiple measurements, respectively. The present measurement error is larger than the pixel size (0.5 nm) of the images.

Results and discussion

First of all, the stability of the InAs NWs on the SiNx film under high energy electron beam irradiation is checked in a vacuum in TEM (ESI Fig. S2†). As can be seen, no obvious structure change on dry InAs nanowires under electron beam irradiation is observed. The amorphous layer covering the InAs NWs is the native oxide layer formed before electron beam irradiation, and it does not change obviously either. The InAs NWs are stable under vacuum for a long time (more than 500 seconds), with high dose rate (~1800 electrons per Å² per s) electron beam exposure. Such an electron dose rate is much higher and the exposure time is much longer than what we use in the liquid cell experiments. Therefore, the electron beam exposure effect itself on InAs NWs can be ignored.

The MBE-grown InAs NWs are observed to dissolve rapidly in water under electron beam irradiation (Movie S1†). With the increase in irradiation time, the contrast of the NWs fades together with the diameter reduction, indicating that the NWs dissolve roughly uniformly around their perimeter (Fig. 2). The NWs dissolve almost completely after 32 s. As the temperature variation in water caused by high energy electron beam irradiation is usually insignificant,32 the chemical composition changes of the solution should be the main reason for the InAs NW dissolution. High energy electron beam irradiation is known to excite various reducing and oxidizing radicals in water, such as $e_{aq}^-$, H-, H₂, H₂O⁺, OH⁻, H₂O₂, OH⁺, O₂, etc.33 As H₂O⁺ and H₂O₂ can etch bulk InAs,24,25 they should also etch InAs NWs in radiolytic water here. The main role of H₂O₂ and H₂O⁺ is to accelerate the surface oxidation and to etch the oxidation layer. The primary oxidizing radical OH⁻ may also be the etching agent of the InAs NWs. The main oxide etching products of InAs include In³⁺, As₂O₃, AsO₂⁻, AsO₄³⁻, HAsO₄²⁻, etc.25 These products may not be stable in water as the thermodynamically stable states of In and As in water (when pH = 7) at room temperature have been reported to be In₂O₃ and As₂O₅.25 Also, $e_{aq}^-$ existing in the radiolytic water may reduce some of the above ions. However, we do not observe regrowth of any nanoparticles (precipitates containing In or As) in the irradiation area or outside the irradiation area in our

Fig. 2  (a)–(i) TEM images taken from the same area of a single MBE-grown InAs NW at different times during the dissolution process of the NW. The scale bar is 100 nm for all the images. (j) The plots of the InAs NW diameter as a function of the dissolution time. The labels d1, d2, d3 and d4 represent the diameters at different positions on the InAs NWs indicated by the black, red, green and blue arrows in (a).
experiments, as shown in ESI Fig. S3.† The regrowth of nanoparticles has been reported in some systems, e.g. Ag precipitation has been reported in oxidative etching Ag nanocable experiments using liquid cell TEM. However, the mechanism of observable nanomaterial precipitation is very complex, and should be different for different systems. The extremely low concentration of In/As may be one of the reasons that no regrowth cluster or nanoparticles can be observed here.

To quantitatively analyze the dissolution processes, the diameters of the NWs at four positions are measured at different dissolving times and the results are shown in Fig. 2j. It shows that the dissolution rates at different positions of these NWs are almost the same. More importantly, the diameter \( d \) of the NWs reduces roughly proportionally to the dissolving time \( t \) until we cannot see the NWs clearly when the diameter is around 5 nm. Linear fitting the experimental data gives a diameter reduction rate of 18.6 nm min\(^{-1}\).

Normally, the dissolution rate is characterized by the surface normalized mass dissolution rate \( dm/(dt \times S) \), where \( m \) is the mass, \( t \) is time, and \( S \) is the surface area. In the case of NWs, the surface area can be expressed as \( 2\pi rl \), so that \( dm = \rho 2\pi rdl \), where \( \rho \) is the mass density, \( r \) is the radius of the NWs. Therefore, the dissolution rate, \( dm/(dt \times S) = \rho dr/dt \), is proportional to the diameter reduction rate. The constant diameter reduction rate indicates a constant dissolution rate, even down to a small diameter of about 5 nm, as shown in Fig. 2j. The constant dissolution rate of the InAs NWs in water during the whole dissolution process is unexpected. Previously, lots of studies suggested that the dissolution rate \( (dr/dt) \) of particles increases with decreasing size. This implies that the dissolution mechanisms of NWs may be significantly different from that of nanoparticles.

To find out whether the above dissolution phenomenon is universal for InAs NWs, we further study the dissolution process of MOCVD-grown InAs NWs. In order to have a controlled comparison, we transferred MOCVD-grown InAs NWs and MBE-grown InAs NWs onto the same area of a SiNx window and observed their dissolution behavior under the same conditions (the same solution, the same electron beam dose rate and the same total electron beam dose) at the same time. Fig. 3 shows the morphology evolution of the two types of InAs NWs in radiolytic water, where the MOCVD-grown NWs have a larger diameter. In the early stage with the irradiation time shorter than ~90 s, the MBE-grown InAs NWs gradually dissolved, evidenced by a diameter decrease and contrast fading (Fig. 3a–e). At the same time, no obvious dissolution trace can be observed from the MOCVD-grown InAs NWs. After the MBE-grown InAs NWs dissolved completely in 90 s, the MOCVD-grown InAs NWs moved to the center of the field of view (Movie S2†). When the irradiation time was prolonged to ~110 s, the MOCVD-grown InAs NWs started to dissolve obviously. The diameter of the MOCVD-grown NWs reduced continuously with time, exhibiting slightly different radial dissolution rates at the two ends of the NWs. As shown in Fig. 3g, one end of the NWs became thinner than the other one after some time. Finally, the thinner end of the NWs dissolved completely first and the NWs started to dissolve also along the axial direction but with a faster speed than along the radial direction (Fig. 3h–i). In addition, it is also worth mentioning that the surface roughness increased with the dissolving time for both types of InAs NWs. The delay of the dissolution of the MOCVD-grown InAs NWs could be due to the more uniform oxide layer and the larger size of the MOCVD-grown InAs NWs than the effective thickness of the water layer (30–40 nm). High-resolution TEM (HRTEM) images of the InAs NWs cannot be taken during the dissolution process because the high electron beam dose needed by HRTEM accelerates NW dissolution.

Quantitative analysis on the dissolution rate of these two InAs NWs is illustrated in Fig. 4. The diameter of the InAs NWs is measured at different positions during the whole dissolution process. For the MBE-grown InAs NWs, at the positions pointed by the red and dark arrows in Fig. 3a, both the diameter decrease and contrast fading are observed, indicating a uniform dissolution around the perimeter. The diameter of the NWs decreases continually with roughly the same rate of 5.1 nm min\(^{-1}\) (Fig. 4a), similar to the case shown in Fig. 2. However, at the positions indicated by the green and blue arrows in Fig. 3a, the diameter of the NWs did not decrease obviously after 30 s and only contrast fading can be observed, indicating that the etching mainly happened in the direction parallel to the electron beam and perpendicular to the SiN window. Such phenomena could be caused by direct contact between the NWs and the SiN window. In such a case, the dissolution rate cannot be obtained by measuring the diameter.

For the MOCVD-grown InAs NWs, obvious dissolution happened after ~120 s electron beam exposure, evidenced by a diameter decrease as well as contrast fading (Fig. 3). Fig. 4b shows that the diameter changes with the irradiation time at different positions of the MOCVD-grown InAs NWs. Similar to the case of the MBE-grown InAs NWs, the diameter of the MOCVD-grown InAs NWs decreases with time with a roughly constant speed. However, the dissolution rates at different positions of the MOCVD-grown InAs NWs range from 19.6 nm min\(^{-1}\) to 34.9 nm min\(^{-1}\), and all of which are higher than those of the MBE-grown NWs. The unintentional carbon-doping and the defects in the MOCVD-grown NWs could possibly increase and influence the dissolution rate, and we will discuss it in more detail later.

Fig. 4c shows the relationships between the length of the MOCVD-grown InAs NWs in the visual field (as indicated in Fig. 3h) and the time starting from the point when the thinner end of the NWs completely dissolved. The length of the InAs NWs also reduced roughly linearly with time but at a speed of about 441 nm min\(^{-1}\) after one end of the NWs dissolved completely (Fig. 4c). This is understandable as the tip end is etched not only in the axial direction but also in the radial direction.

Other MBE or MOCVD-grown InAs NWs are also studied here and some results are shown in ESI Fig. S4.† The diameters of the NWs are also measured at different times. The quantitative results from another MBE and another MOCVD-
grown InAs NWs are shown in Fig. 5a and b. The diameters of these MBE-grown InAs NWs decrease from the beginning and decrease linearly with time with a constant dissolution rate of about 8.9 nm min\(^{-1}\). These MOCVD-grown InAs NWs also do not dissolve obviously at the beginning similar to that shown in Fig. 3 and 4, and after about 110 s, the diameters of these NWs reduce continuously with a constant speed of 18.2 nm min\(^{-1}\).
Totally nine MBE and eight MOCVD-grown InAs NWs are studied by in situ liquid cell TEM in radiolytic water. So far, all the NWs show a constant dissolution rate even when the diameter has decreased to about 5 nm. The dissolution rates of the MOCVD-grown InAs NWs are all higher than the MBE-grown InAs NWs. In order to make a reliable comparison, we have transferred a MOCVD and a MBE-grown InAs NWs onto the same center area of the SiNx window as shown in Fig. 3 and tried our best to use the same experimental conditions for the two types of NWs. It should be noted that in the results shown in Fig. 3 and 4, the MBE and MOCVD-grown InAs NWs are just separated by about 200 nm, both located at the center of the electron beam exposure area at the center of the SiNx window, and are observed at the same time in the same experiment. Therefore, the experimental conditions, such as the electron beam energy, the electron beam dose rate, the total dose at a specific time, the thickness of the water layer, the concentration of the etching agents in the water, etc., are all the same for these two NWs. The different dissolution rates between these two NWs must be due to the NWs themselves. Although they are all InAs NWs, the MBE-grown InAs NWs have a perfect WZ structure, while the MOCVD-grown InAs NWs have mixed phases containing ZB and WZ sections separated by stacking faults, as shown in Fig. 1b. Besides, it is well known that the MOCVD-grown InAs NWs show unintentional doping (mainly carbon) due to the precursors used and the growth process of MOCVD.\(^\text{37}\) Dense defects have been proposed to cause surface roughening of bulk materials\(^\text{34}\) and the irregularities of InAs NWs\(^\text{26}\) during the chemical wet etching process. In the synthesis process of metal nanocrystals, oxide etching has been widely used to remove highly reactive metal seeds with dense defects and then uniform, single-crystalline nanocrystals can be obtained in the final products.\(^\text{36,39}\) Here, the dense stacking faults and the unintentional doping are the main reasons for the higher dissolution rate of the MOCVD-grown InAs NWs than that of the MBE-grown NWs.

For the same kinds of NWs, the dissolution rates of different individual NWs are not exactly the same, possibly due to the following reasons. The electron beam dose rate is not exactly the same for different experiments. There might be a little amount of salt in the solution unintentionally introduced during the sample preparation step. We observe that a small amount of unintentionally introduced KCl in water could obviously accelerate the dissolution of InAs NWs (ESI Fig. S7†). This is unsurprising considering that the etching rate of InAs bulk material in HCl/H\(_2\)O\(_2\) solution depends on the presence of Cl\(^-\).\(^\text{24}\) However, we would like to emphasize that the dissolution rate is observed to be independent of the diameter of every NW even when the diameter is as small as about 5 nm, with or without KCl.

As discussed above, H\(_2\)O\(^+\), H\(_2\)O\(_2\) and OH\(^-\) excited by an electron beam in water are the main etching agents for InAs NWs, and knowing the concentration of these etching agents is important to understand the dissolution mechanism of InAs NWs. It has been reported that the concentration of radiolysis products (etching agents) is influenced by many factors, such as radiolysis time, dose rate, chemical composition of the solution, position relative to the electron beam center, electron beam energy, electron beam dose rate, etc.\(^\text{40}\) According to the reaction–diffusion equation, it can be deduced that the radiolysis products generally reach the steady state concentration within seconds under continuous irradiation in liquid cell TEM. The steady state concentration has been reported to be a power exponent function of the dose rate.\(^\text{32,33,41}\) For the water under 200 keV electron beam irradiation in our experiment, the steady-state concentrations of H\(_2\)O\(^+\) and H\(_2\)O\(_2\) in radiolytic water depend on the dose rate \(I\) (electrons per Å\(^2\) per s) by:\(^\text{20,33}\)

\[
\begin{align*}
[H_2O^+] &= 5.11 \times 10^{-6} \times I^{0.51} \text{ (M)} \\
[H_2O_2] &= 1.86 \times 10^{-4} \times I^{0.44} \text{ (M)}
\end{align*}
\]

In the present experiments, the electron beam dose rate is in the range of 23–36 electrons per Å\(^2\) per s, and the concentrations of H\(_2\)O\(^+\) and H\(_2\)O\(_2\) at the steady-state are calculated to be \(\sim 10^{-3} \text{ M} \) (pH is \(\sim 4.5\)) and \(10^{-5} \text{ M}\) in the irradiated area. The dissolution rate of bulk InAs in the solution with the same concentrations of H\(_2\)O\(^+\) and H\(_2\)O\(_2\) is calculated\(^\text{24}\) to be 0.2 nm min\(^{-1}\), which is smaller than the dissolution rate of InAs NWs.
in radiolytic water we observed presently. This is understandable because other oxidizing radicals (\(\text{OH}^+\)) in the radiolytic water can also accelerate the dissolution of InAs NWs during \textit{in situ} liquid cell TEM.

Generally, the dissolution rate is mainly controlled by the dissolution reaction and can be affected by the crystal size, surface roughness, crystal aggregation degree, temperature, solution, etc.\textsuperscript{16,42,43} The effects of these factors have also been observed by performing liquid cell TEM experiments. The dissolution rate of Pd nanocrystals has been found to be a function of particle size (\(-\text{d}r/\text{d}t \sim 1/r\)) by \textit{in situ} liquid cell scanning transmission electron microscopy (STEM). The increase of the dissolution rate with decreasing diameter has been attributed to the higher surface energy of smaller particles.\textsuperscript{13} The multimode dissolution kinetics of faceted Pt nanocrystals has been reported to depend on the dominant dissolution site which changed with time.\textsuperscript{14} The etching of Au nanorods in FeCl\(_3\) solution has been studied by \textit{in situ} graphene liquid cell TEM, and the longitudinal dissolution rate (\(\text{d}r/\text{d}t\)) has been found to increase with the increasing tip curvature.\textsuperscript{16} However, no attention has been paid to the dissolution of 1D NWs. Here, we find that the dissolution rate of 1D NWs is constant during the whole dissolution process, even when the diameter is as small as around 5 nm.

Overall, the dissolution in a liquid experiences three main steps: reactant diffusion, surface reaction and product diffusion steps, which could influence or even control the dissolution rate. Fig. 6 shows schematically the dissolution process of InAs NWs in radiolytic water, where the main reactants are \(\text{H}_3\text{O}^+\), \(\text{H}_2\text{O}_2\), and \(\text{OH}^-\). It has been reported that the concentrations of \(\text{H}_3\text{O}^+\), \(\text{H}_2\text{O}_2\), and \(\text{OH}^-\) can reach the stable state within seconds after electron beam irradiation.\textsuperscript{30} As the dissolution process of InAs NWs happens in tens of seconds, the concentration of the reactants should remain stable in the irradiated area regardless of the reaction consumption. So the effect of reactant diffusion on the reaction speed can be ignored for the dissolution of InAs NWs. If product diffusion is the key factor controlling the dissolution, there will be product accumulation near the surface of the NWs. However, we did not observe extra material accumulation presently, indicating that the present constant speed dissolution is not controlled by product diffusion.

Therefore, surface reaction is the key process controlling the present dissolution. Generally, if the surface roughness and structure difference can be ignored, the reaction rate is proportional to the surface area:

\[
\frac{\text{d}m}{\text{d}t} = A v
\]

where \(m\) is material quantity, \(t\) is the dissolution time, \(A\) is the surface area and \(v\) is the surface reaction rate. InAs NWs can be treated as an infinitely long cylinder, and dissolution occurred only on the cylindrical side surface. Therefore

\[
\frac{\text{d}m}{\text{d}t} = 2\pi rl v \frac{\text{d}r}{\text{d}t} = 2\pi rl v
\]

so that

\[
\frac{\text{d}r}{\text{d}t} = \frac{v}{\rho}
\]

where \(l\) and \(r\) are the length and radius of the NWs, respectively, and \(\rho\) is the mass density of InAs. The present experimental results show that the diameter of InAs NWs decreases linearly with the dissolution time with a constant speed, which is consistent with eqn (3) as \(\rho\) is roughly constant. In the steady state, the surface reaction rate is related to the activation energy by an exponential function.\textsuperscript{20} The constant surface reaction rate indicates that the activation energy should be constant during the whole dissolution process even when the diameter of InAs NWs is as small as 5 nm.

**Conclusions**

In summary, we quantitatively study the dissolution of 1D systems (InAs NWs) in radiolytic water by \textit{in situ} liquid cell TEM. We find that both the MBE and MOCVD-grown InAs NWs dissolve rapidly in radiolytic water with a constant speed throughout the dissolution process even when the NW diameter is as small as around 5 nm, which is in contrast to previously reported particle cases where the dissolution rate increases with reducing size. The MOCVD-grown InAs NWs with dense stacking faults dissolve faster than the MBE-grown InAs NWs with a perfect crystal structure. The dissolution kinetics of constant speed InAs NW dissolution in radiolytic water is found to be surface reaction limited dissolution, and the reaction activation energy should be constant during the whole dissolution process even when the diameter of InAs NWs is as small as 5 nm under the present experimental conditions.
Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Key R&D Program of China (2016YFA0200802) and the National Natural Science Foundation of China (61621061). The authors would like to thank Dr Dong Pan, Dr Xianghai Ji, Prof. Jianhua Zhao and Prof. Tao Yang in the Institute of Semiconductors, Chinese Academy of Sciences for the supply of InAs NWs. We would also like to thank Dr Xiumei Ma from Electron Microscopy Laboratory, Peking University for helping with the TEM instrument.

References


