Scanning Probe Microscopy Investigation of Metal Oxides Nanocrystalline

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Abstract: Scanning probe microscopy techniques (SPM) have been applied to a rapid improvement in the characterization of metal oxide nanocrystalline. These materials are widely used in photon-to-electricity conversion devices, such as dye-sensitized solar cells. The surface properties of such nanocrystalline determine the devices’ performance. SPM imaging of nanocrystal surfaces and nanoscale systems has demonstrated great potential for new advances in science and technology of renewable energy production. With the invention and recent development of the scanning tunnelling microscope, atomic force microscope, and scanning electrochemical microscopy used in the ultra-sensitive non-contact mode, the door has now been opened to detailed studies of the whole range of insulating metal oxide surfaces, and result in new and challenging issues, especially within the field of heterogeneous catalysis. In this chapter, the basic principles of SPM and its characterization of the interface between nanocrystalline and various mediators in the atomic-scale are reviewed with respect to their structure and the charge transfer dynamics.

Keywords Scanning Tunnel Microscopy; Scanning Electrochemical Microscopy; Metal Oxide Nanocrystalline; Probing Electron Transfer

1. Introduction

In order to control the physical and chemical properties of materials, scientists need detailed knowledge about the behavior of the atoms and their interplay with other atoms. Nanotechnology has been described as the scientific striving towards precise control of atoms, molecules and larger atomic structures [1]. However this control at the most basic level does not come into true without fully understanding even the simple building blocks and how they interact. Fortunately with the advent of new techniques and instrumentation, that allows analysis and manipulation of matter on the atomic scale, there are now possibilities to design and produce advanced nano-structured materials. Among the new surface characterization techniques, the scanning probe microscopy (SPM) has attracted most of attention, including the scanning tunneling microscope (STM), the atomic-force microscope (AFM), the scanning electrochemical microscopy (SECM), and so on. In the subsections below we begin with a basic overview of the principles and instrumentation for the SPM, introduce the modeling techniques needed to understand the underlying processes and analyse experimental data, before considering specific methods and applications. We conclude with a brief overview of recent developments and potential future developments, including hybrid techniques that involve various SPMs.

1.1 The history of SPM

The STM was invented in 1981 by Gerd Binnig and Heinrich Rohrer which revolutionized the field of surface science. STM was the first surface analysis technique to image surface in real space and with atomic resolution [2, 3]. The authors of this seminal discovery were awarded the Nobel Prize in Physics as early as 1986. The field of surface science has quickly taken the momentum to realize the commercial products incorporating “SPM”, which is now being used as a standard tool in many groups around the world [4]. Figure 1 presents a schematic view of the interactions between the fundamental components of a generalized STM. STM is based on the ability to position, with extremely high precision, a sharp metallic tip in very close proximity (a few angstroms) to the conductive sample under investigation. When a voltage is applied onto the tip and the sample, there is a flow of electric current between them due to the tunnelling of electrons. The current depends exponentially on the tip–sample separation. This gives STM its high spatial resolution. STM scans the surface of a sample with a tip in a raster movement and creates a topographic/electronic image of the surface.

STM can provide information about the density of states of the sample by scanning tunneling spectroscopy (STS), also referred to as differential conductance (dI/dV) measurements. In this mode, the position of the tip is held fixed and the feedback loop is disabled. By sweeping the voltage between the tip and the sample, the current as a function of voltage is acquired.
The AFM was invented by Binnig and Quate in 1986, having its origins in the invention of STM [5]. Unlike the STM, the AFM can image nonconducting samples surfaces using the force between the tip and the sample as the feedback parameter. There are different modes of AFM operation based on the distance between the tip and the sample, or alternatively, based on whether the tip–sample interaction is attractive or repulsive. Besides a topographic image of the sample, the AFM can carry out phase imaging [6].

Originally the STM and AFM were used to image the topography of surfaces, but by modifying the tip it is possible to measure other quantities (for example, electric and magnetic properties, chemical potentials, friction and so on), and also to perform various types of spectroscopy and analysis. The STM and AFM act now the foundations on which a wide range of SPM techniques have been built, such as magnetic force microscopy and dynamic force microscopy [7].

Later works showed that STM could be used in liquids and hence also in electrochemical cells (i.e., it could be used as an in situ technique), leading to an electrochemical scanning tunneling microscopy (EC-STM) [8]. In situ EC-STM has been recognized as a powerful tool for the elucidation of structure of surface and electrochemical reactions in solid/liquid interface at molecular or atomic levels [9, 10]. One of achievements in the STM that have attracted much interest is to build nanoelectronics with STM tips. These approaches are of great importance for molecular electronics, nanoscale device fabrication, and heterogeneous catalysis investigation. For example, Meier et al. introduced and described a new route to study local reactivity of nanoparticles using an STM tip electrode as a local sensor, which aided the understanding of the interfacial electron-transfer dynamics of single nanoparticle possible [11].

Using a similar working strategy with the EC-STM, scanning electrochemical microscopy (SECM) is a specific technique that is used to measure the local electrochemical behaviour of liquid/solid, liquid/gas and liquid/liquid interfaces [12]. Initial characterization of the technique was credited in 1989 to Professor Allen J. Bard, an electrochemist at the University of Texas. Since then, the theoretical underpinnings have matured to allow widespread use of the technique in chemistry, biology and materials science [13, 14]. A schematic of a SECM setup is shown in Figure 2. The spatially resolved electrochemical signals can be acquired by measuring the current at an ultramicroelectrode (UME, with a diameter of 10–20 μm) tip as a function of precise tip position over a substrate region of interest. The SECM signal can be interpreted with the concept of diffusion-limited current [14]. The technique has proven complementary to other surface characterization methods such as EC-STM [15] and AFM [16] in the interrogation of various interfacial phenomena. In addition to yielding topographic information, SECM is often used to probe the surface reactivity of solid-state materials, electro-catalyst materials, enzymes and other biophysical systems [17].
1.2 The application of SPM

Compared to large area averaging techniques like Auger, LEED, XPS etc, the SPM utilizes a local probe for the investigation of local structure of the surface. Theoretically, the resolution of images, containing the local physical properties, is imposed by the interaction, typically a precision of 1Å or better [1, 18, 19]. The SPM is an ideally suited technique to study low-dimensional materials such as semiconductor nanocrystallines because it directly probes the electronic properties at the surface. Different properties of the surface can be revealed based on the interaction between the probe and the surface.

1.3 Metal Oxide Nanocrystalline

The synthesis and study of the preparation and characterization of so-called “nanocrystalline materials”, particles with diameters in the range of 1-20 nm, has become a major interdisciplinary area of research over the past 20 years [20]. The ratio of surface atoms to those in the interior increases as particle sizes become smaller, leading to the surface properties playing an important role in the material. Most of the earth’s crust consists of solid oxides, the result of elements being oxidized by the oxygen. Metal oxide nanocrystalline, by reducing the size of the grains in existing materials, can behave several new properties, typically showing optical, electronic, and mechanical properties distinct from those of the corresponding bulk material. Metal oxides are of considerable interest because of their technological importance, e.g. in the field of heterogeneous catalysis. Spatial enclosure of the electronic charge carriers can take place due to the quantum confinement effect, a major feature of nanocrystals [21]. Two fundamental factors, both related to the size of the individual nanocrystal, distinguish their behavior from the corresponding macrocrystalline material: high dispersity associated with the particles (determining the physical and chemical properties of the semiconductor) and the actual size of the particle (determining the electronic and physical properties of the material).

Nanocrystalline metal oxides have been currently under intensive investigation, such as TiO_2, ZnO and SnO_2 etc. The microstructure and properties of nanocrystals depend in an extreme manner on the synthesis method as well as on the processing route. Unraveling the size- and shape-dependent materials properties entails synthesis of homologous nanoscale materials with monodispersity in size, shape, internal structure, and surface chemistry. Thus, it is of utmost important to select the most appropriate techniques for preparation of nanoparticles and films with desired properties and property combination. The metal oxide nanocrystal materials can be prepared in several ways [22]; several routes involve colloidal chemistry, with others involving the kinetically controlled precipitation of nanocrystallites [23].

1.4 The Application of Metal Oxide Nanocrystalline

Research efforts to explore such nano-structured material have transformed many fields such as material science, biology, chemistry, etc. in many profound ways and visible impact is more in energy-related field. Dye sensitized solar cells (DSC) are a prominent example of nanocrystals based photovoltaic devices, which are currently attracting extensive attention of research and academic interest [24, 25]. Figure 3 shows a schematic of a DSC device. The general working principle of DSC is based on a light harvesting sensitizer, which is anchored to a high surface area semiconductor nanocrystalline film.

DSCs possess properties of low cost, high conversion efficiency and simple to fabrication. Metal oxide nanocrystalline semiconductors (TiO_2, ZnO, Nb_2O_5 etc) are critical component of DSC due to their unique physical properties and potential use for a wide range of applications. These metal oxide nanocrystalline semiconductors possess high surface to volume ratio required for the high absorption of dye molecules to improve light harvesting efficiency. Furthermore, with increasing surface atom exposure the presence of surface states becomes important, since such can provide pathways for non-radiative recombination of photo-generated charge carriers. The challenges of enhancing electron transport rate, reducing recombination are still associated with metal oxide semiconductor based DSCs. Thus, various photo electrodes made of metal oxides nanostructures, including nanoparticles, nanorods, nanowires and

[Fig. 3 The operating principles of the dye-sensitized solar cell.]
nanotubes, have been investigated for the augment of photovoltaic performance. Figure 4 shows a TiO\textsubscript{2} films with various structures as used in DSCs.

![Image](image.png)

**Fig. 4** TiO\textsubscript{2} nanocrystallines for dye sensitized solar cells applications.

1.5 The critical requirement for SPM study of metal oxide nanocrystalline

The characterization of metal oxide nanocrystalline materials in the forms of films demands special techniques with allow for the structural and chemical analysis with a sufficient lateral resolution. Experimental difficulties such as oxidation/reduction at surface, the disordered structure at the grain boundaries and other internal interfaces and substantial porosity can be present in these materials. The extremely high surface and interface areas also have to be considered. SPM methods allow the simultaneous mapping and correlation of surface topography and other physical properties. Fundamental studies of metal oxide surfaces have figured prominently in the development of SPM, particularly STM, and have led to dramatic progress in our understanding of atomic-scale surface phenomena in nanocrystals. In addition, STM and related techniques have been used to explore adsorption, bonding, and removal of atoms and molecules on metal oxide nanocrystalline surfaces during processes, such as epitaxial crystal growth, etching, and deliberate modification of surfaces via tip-sample interactions. Other techniques based electronic spectroscopy, such as X-ray diffraction spectroscopy, electron diffraction spectroscopy, and transmission electron microscopy, typically provide indirect information about sample structure, and obviously, while offering the ability to probe certain structural or compositional features at the atomic scale, inevitably average these properties over substantially larger areas or volumes [2].

SPMs have several advantages compared to normal optical or electron microscopy: the SPM provides a flexible environment for sample observation; the resolution of the SPM is only limited by the point spread function; new structures can be created by utilizing the probe interaction; the measurement of small local differences in object height is unparalleled. Though the SPM shows remarkable performance in metal oxide nanocrystals characterization, the quest to find suitable modification with this technique is still under intensive investigation due to a number of reasons: the detailed shape of the scanning tip is sometimes difficult to determine, leaving effects on the results of the specimen with a large variation in height; the scanning techniques are generally slower in acquiring images; the maximum image size is generally small.

2. SPM Investigation on Surface Engineering of Metal Oxide Nanocrystalline

2.1 The STM and AFM study of metal oxide naocrystalline

TiO\textsubscript{2} is a wide band gap semiconductor and has a broad range of applications. TiO\textsubscript{2} crystalline in three major structures: rutile (tetragonal, a=b=4.58 Å, c=2.935Å), anatase (tetragonal, a=b=3.78 Å, c=9.50Å) and brookite (rhomboedral, a=5.44 Å, b=9.17 Å, c=5.14Å). However, only rutile and anatase play important role in the application of TiO\textsubscript{2} and are here of interest [26]. Figure presents the unit cells of rutile and anatase TiO\textsubscript{2}. Complementary theoretical DFT calculations have predicated a bipyramidal appearance of the anatase nanoparticles, which recalls the crystal habit of the natural crystals.
In both structures, the basic building blocks consist of a titanium atom surrounded by six oxygen atoms in a more or less distorted octahedral configuration. The bulk structure of reduced TiO$_{2-x}$ is quite complex with various types of defects such as doubly charged oxygen vacancies, Ti$^{3+}$ and Ti$^{4+}$ interstitials, and planar defects. The defect structure varies with oxygen deficiency which depends on temperature, gas pressure, impurities, etc. These intrinsic defects result in n-type doping and high conductivity, which allows spectroscopic and STM measurement to scan the surface [26,27]. Figure 6a shows STM images with a resolution of (100×100) nm$^2$ of a clean TiO$_2$ (110) surface, on which large flat terraces are observable.

O. Bikkondoa et al reported on the STM investigation of the reaction of water molecules with bridging-oxygen vacancies on rutile TiO$_2$ (110) [28]. The reaction of water on titania has been intensively studied due to the potential application of TiO$_2$ as photocatalysts for water splitting [29, 30]. Previously study of TiO$_2$ with STM showed that point defects appear among the Ti rows [28]. It was suggested that these defects consist of O vacancies (larger brighter defects, referred as A$_b$), and H adatoms (smaller, darker defects, referred as A$_d$) as illustrated in Figure 7. By applying voltage pulse (from 2.6 to 4.5 V) from the STM tip, Bikkondoa demonstrated that the A$_b$ defects can be selectively removed by scanning the clean surface, whilst leaving the A$_d$ defects intact. By using water as the probe, the attribution of defects has been tested. This is important to understand the interaction of water with oxide surface for technological applications. This work could shed further light on the interplay between O vacancies and hydroxylation on oxide surfaces.

Though atomic resolved STM images on TiO$_2$ nanocrystal can be observed, the analysis of a large number of experimental SPM images recorded with different tips reveals that no general correlation exists between the contrast observed in the AFM and the tunneling current (I$_t$) images on TiO$_2$(110) surface. A new method to obtain realistic atomistic models based on experimental and theoretical calculations, that were used to image a TiO$_2$ (110) surface, was demonstrated by G. Enevoldsen et al [31]. By carefully evaluating the contrast of a handpicked library of SPM tips, the authors proposed a very accurate model of the SPM tip used in experiments.

Usually, STM senses the density of unoccupied states at titanium and defect sites. Electronic structure effects dominate over the contrast in images [32]. Hence, the bridging oxygen atoms are invisible. Non-contact atomic force microscopy (NC-AFM) has the capability of imaging either the bridging oxygen atoms (hole mode) or the titanium atoms (protrusion mode) [33]. R. Bechstein et al studied rutile TiO$_2$ (110) surface using NC-AFM and density functional theory, revealing both bridging oxygen and titanium atoms simultaneously [34]. Furthermore, C. Sánchez-Sánchez et al reported on the understanding atomic-resolved STM images on TiO$_2$ (110) surface by DFT calculations [35]. Figure 6b shows a high resolution STM image recorded on the clean (1×1) surface TiO$_2$ (110) at positive bias voltage (1.5 V). In this situation, the atomic resolved STM image could be exclusively contributed to the unoccupied electronic states of the sample, which accept the electron from the tip. Based on the theoretic calculation, the bright rows running along [001] direction in the STM image on Figure 6b represent Ti$_{5f}$ lines. The discussion on typical point-defects the based on the experimental measurements and theoretical evaluation have revealed the difference of OH adsorption and oxygen vacancies on the surface.

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The principle of the DSC invented by Grätzel et al is based on natural photo-synthesis, where dye is fixed to a TiO$_2$ surface, incoming light photo-excites the dye and an electron is injected in the conduction band of the substrate. The absorption process ideally occurs at the interface between the DSC semiconductor film and a liquid electrolyte. In such systems, the dye is recycled by electron transfer from redox couples in the electrolyte. A transparent back contact of doped tin oxide is used. The importance of TiO$_2$ as a semiconductor material for DSC is clear reflected in the large number of publications during the last three decades. STM, with the ability of atomic resolution and real-space imaging, provides valuable information about the organic-inorganic interface properties in the DSC. In DSC, the common used dye molecules are bipyridine type ruthenium complexes, which are attached to the TiO$_2$ electrode by carboxylate groups. Since the mode of dye attachment to the surface is critical, a detailed picture of the surface chemical bond is needed. The crystal morphology and surface structure of TiO$_2$ nanoparticles are very important for its applications [36]. A. Sasahara et al reported on the STM observation of an individual Ru (4, 4’-dicarboxy-2, 2’-bipyridine) : (NCS)$_2$ (coded as N3) molecules adsorbed on a TiO$_2$(110) surface [37]. The study showed that the number density of the N3 molecules on the steps was higher than that on the terraces due to a lower steric obstacle or less distortion. A Selloni et al have studied the growth and the organization of catecholate monolayer on the TiO$_2$ nanocrystal surface in detail and found that the occupied electronic states of organic molecule adsorbed on a rutile (110) resemble the one on anatase (101), by correlating the ultra-violet photoemission spectroscopy (UPS) results with STM data and ab-initio calculations (direct techniques to measure atomic and molecular structure) [38, 39]. R. Bartynski et al investigated the interfacial electronic interaction though systematic molecular level variation (by chemical modification on Zn-porphyrin) between dyes and dyes/nanoparticles [40, 41]. After sensitizing single crystal TiO$_2$ (110), an effective dipole layer formed on the surface would shift the molecular orbitals on the porphyrin ring with respect to the substrate levels by generating a change in electrostatic potential. The presence of the dipole on the linker chain shifts the energy levels as observed in UPS [40, 41]. It was found that the Zn-porphyrin with carboxylate anchoring group results in a flat adsorption geometry on the oxide surface.

M. Zuleta et al report experimental results of STM imaging of cis-bis (isothiocyanate)-bis-(2, 2’-bipyridyl-4,4’ dicarboxylate) ruthenium (II) bis(tetrabutyl-ammonium) dye (known as N719) adsorbed on a anatase TiO$_2$(100) single crystal [42]. Figure 8 shows the details of the packing mode of N719 on TiO$_2$ (100). The STM image shows that N719 completely covers the surface. Because electron injection occurs from the dye to TiO$_2$, the STM images reveal dynamic photovoltaic processes taking place at the N719/TiO$_2$ (100) interface. Their work clear demonstrates the potential of STM in the study of interactions at the organic layer/metal oxide interface. The authors described a successful method for the chemisorption and STM imaging of ruthenium complex N719 on a single crystal anatase (100) surface. The results demonstrate the potential of STM in the study of interactions at the organic layer/metal oxide interface.

![Fig. 7](image1.png)

**Fig. 7** Sequential (150×150) Å$^2$ STM images of as prepared TiO$_2$ (110), a) before a voltage pulse and b) after the voltage pulse. The voltage pulse (3 V, 0.35 nA, 300 ms) was applied to the Ab defect circled in a. In b, Ab and Ad defects are marked with red and blue crosses, respectively. (Figure taken from Reference 28).

![Fig. 8](image2.png)

**Fig. 8** N719 adsorption on anatase TiO$_2$(100). 40×40 nm$^2$ STM image scanned in the dark; ±2.0 V and 45 pA. (Figure taken from Reference 42).
2.2 The SECM study of metal oxide nanocrystalline

SECM allows probing electrochemical reactivity and topography of a wide range of sample surfaces and phases [43, 44]. SECM can be operated with different working modes, such as feedback (FB), generation-collection (GC) and redox competition (RC). (The basic principles of these working modes see references *). The basic idea of SECM is to place a ultra microelectrode (UME, $r_T \leq 50 \mu m$) near to the sample (or substrate) and to use the flux of electrochemically active molecules as a probe for visualizing the substrate and investigating its chemical properties [45]. The UME behaves differently to macro electrodes, due to the mass transport occurring by hemispherical diffusion (Figure 2). For a microelectrode, a measurable steady-state current can be obtained due to an enhanced radial diffusion (see Figure 9). The steady state limiting current $i_T$, passing at a micro- disc UME is given by $i_{T,\infty} = 4nFDc^*r_T$, where $D$ is the diffusion coefficient of the mediator, $c^*$ is the bulk concentration of the reactant, $r_T$ is the radius of the active part of the UME [46, 47].

A major advantage of SECM for nanocrystalline characterization is that this technique is capable of the detailed quantitative treatment of many experiments. For example, SECM has been developed into a useful and powerful technique of determining electron transfer kinetics at various interfaces. Several review articles and books have been published on this subject [17]. The application of SECM to study electron-transfer processes at the dye-sensitized semiconductor/electrolyte interface has been introduced to allow a more detailed study of the regeneration reaction in DSC [48-52].

The overall efficiency of light-induced charge separation in DSC depends on the kinetic competition between back electron transfer and dye regeneration processes by the redox electrolyte. Y. Shen et al first investigated the regeneration process of photo-oxidized dye molecule using the feedback mode of SECM [48]. Figure 10 illustrates the principle of the SECM feedback mode in a DSC system under short circuit conditions. The Pt UME of a SECM was used to generate a defined flux of the mediator (I). When the substrate (ZnO/eosin Y film) was illuminated from the back, the $I_3^-$ molecules reaching the ZnO/eosin Y film can be varied within one experiment by variation of the distance between the dye-sensitized surface and the UME. The experiment gives a current variation on the UME as a function of distance to the sample (see Figure 11). Using the mathematical description of the mass transport and interfacial kinetics a pseudo-first order rate constant for the reaction at the sample can be extracted.
A quantitative model was developed and verified by studying the regeneration rate at different excitation wavelength, light intensities and mediator concentrations. The exact IT(L)-V curve in Figure 11 can be described by Eq. 1 for a first order reaction at the sample and infinitely fast reaction at the UME.

\[ I_t(L) = I_{t,\text{ins}}(L) + \left( 1 - \frac{I_{t,\text{ins}}(L)}{I_{t,\text{cond}}(L)} \right) I_s(L) \]  

Where \( I_{t,\text{ins}}(L) \) represents the effect of hindered diffusion only, \( I_{t,\text{cond}}(L) \) being the current that results if the reaction at the sample is diffusion controlled. Based on the SECM measurements, the rate constant \((k_{ox})\) for the reaction of \( \text{I}^- + \text{D} \rightarrow \text{Dads} + \text{I}_3^- \) was estimated to be \( 1.4 \times 10^8 \text{ cm}^{9/2} \text{ mol}^{-3/2} \text{ s}^{-1} \). Therefore, the photo excitation cross-section of the adsorbed dye molecule can be estimated as \( 4 \times 10^{-2} \text{ Å}^2 \). Further refinement of the model was performed to consider detailed molecular mechanism of the regeneration process that involves intermediate species, due to the \( \text{I}^-/\text{I}_3^- \) system is a two electron redox couple. By taking the modified model, the approach curves agreed within experimental error with the theoretical approach curves [49, 53]. This example illustrates the wide range of processes, including a quick screening of organic dyes and redox shuttles, that can be addressed with SECM [47, 54]. Further more, a SECM substrate-generation/tip-collection (SG-TC) mode was used to examine the homogeneous distribution of illumination at a small scale on ZnO/D149 film electrodes [51]. The SECM image result shows that the photo electrochemical generation of \( \text{I}_3^- \) is confined to the illuminated regions. The currents obtained at the UME above non-illuminated and illuminated regions were 0.2 nA and 1 nA, respectively. The shape of the spot roughly reflects the distribution of the light intensity within the illuminated area. Dye regeneration kinetics in dye sensitized TiO\(_2\) or ZnO electrodes in various compositions of electrolytes was also studied by SECM approach curves in feedback mode. Compared with AFM and STM, SECM measurement has the advantage of directly revealing the electrochemical specific information of substrates. It measures the combined effect of dye regeneration kinetics and recombination processes, offering new complementing aspects to established methods of DSC characterization.

3. Conclusions and Outlook

Here, we begin our conclusion by reviewing the results in previously described. STM, AFM and SECM can be applied for the investigation of numerous surfaces of oxides and their interfaces. These methods provide a direct image of the topography and reactivity. These studies are the first step, which were done on single crystal surfaces in ultra high vacuum environment, to keep control of surface properties and to form a solid base of experimental data that can be used for theoretical calculation. In order to reveal effects of atomic and electronic structure and defects, various substrate materials and surfaces in different atmospheres should be investigated in the future. Specially, we can study how lateral interactions and bonding within the organic layer influence electronic structure and charge transfer process at the oxides interface. In order to develop better DSC for energy production, a more complete understanding of the adsorption and charge transfer modes at the organic molecules/oxide semiconductor interface is very attractive. SECM coupling with EC-STM can be suitable for this purpose. As the reactions at the dye-sensitized nanocrystal surface are complicated, carrying out simulations for each experimental approach images by developing numerical models which is specific to process in the DSC is required.

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