1

The History/Development of Single Particle Nanocatalysis

Since the evolution of nanosciences at the end of the 1990s, the concept of "nanocatalysis" has come up with indicating the catalysis occurring on all kinds of nanomaterials or nanocatalysts. Ideally, these nanocatalysts should be able to speed up the wanted or slow down the unwanted chemical reactions with high efficiency, selectivity, and stability. Specific reactivity or utilization efficiency of the active components can be anticipated because of the unique tiny size in nanodimension that can afford specific properties that cannot be achieved with regular, bulk, or non-nanomaterials. In recent decades, nanocatalysis is one of the most exciting subfields of catalysis. Its central aim is to speed up some useful chemical reactions by varying the size, morphology, or surface chemical compositions of the nanomaterials with distinct and tunable chemical activity, specificity, and selectivity.

About 10 years ago, the nanocatalysis was usually studied at ensemble level. In this way, all the information obtained for nanocatalysis was from the average of thousands of nanoparticles. Therefore, the knowledge about the structure–activity relationship of nanocatalysts obtained at ensemble level was usually not so precise because of the fact that the surface properties of nanoparticles are intrinsically heterogeneous, owing to their structural dispersions, heterogeneous distribution of surface sites, and surface restructuring dynamics. This intrinsic heterogeneity can cause both nanoparticle-dependent and temporally varying catalytic properties. To address such heterogeneity challenge in nanocatalysis or reveal more precise structure–activity relationship of nanocatalysts, it is very desirable for us to study the catalytic process of nanocatalysts at the single-nanoparticle level in real time.

In the last decades, with the fast development of detection techniques for weak electric or photonic signals, the nanocatalysis study has been extended from bulk ensemble level to single molecule or single particle level via different detection methods, including electrochemical methods, single molecule fluorescence microscopy, surface plasmon resonance (SPR) spectroscopy, X-ray microscopy, and surface-enhanced Raman spectroscopy, etc., or their combination. It has been known that single molecule or single particle measurements of nanocatalysis can reveal the catalytic properties of individual particles or molecules and then obtain distribution of catalytic properties of nanoparticles in inhomogeneous systems. The distributions, which can be either static or

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dynamical, usually cannot be revealed by ensemble-averaged measurements. Such new information usually can further improve our understanding to the surface nanocatalysis process. In the following, the history of some typical study methods for single particle nanocatalysis is introduced concisely.

1.1 History of Single Particle Nanocatalysis Based on Single Molecule Fluorescence Microscopy

The single molecule fluorescence microscopy was initially developed for the study of biological systems, such as single enzymes, cells, or other types of single biological macromolecules. In the early time, the traditional fluorescence microscope uses fluorescence signals from samples, such as large biological objects (such as cells and neurons), to generate an image with low spatial resolution ($\sim\lambda/2$, λ is the wavelength of photons) limited by the optical diffraction and the sensitivity of photon detectors. With the development of science and technologies for photon detection, after 1940s, based on different mechanisms, many types of photodetectors were invented to detect individual photons, including photomultipliers, Geiger counters, single-photon avalanche diodes, superconducting nanowire single-photon detectors, transition edge sensors, or scintillation counters, etc. Single-photon detection is useful in many fields including fiber optic communication, quantum information science, quantum encryption, medical imaging, light detection and ranging, DNA sequencing, astrophysics, and materials science. Especially with the development of charge-coupled devices (CCDs, 1969), the fluorescence of single molecule could be detected via electron-multiplying (EM) CCD camera cheaply.

For the typical application of single molecule fluorescence microscopy in biology, in 1998, Sunny Xie and coworker studied the single molecule enzymatic dynamics of single cholesterol oxidase molecules by real-time monitoring the emission from the enzyme's fluorescent active site [1]. In this work, for the first time, statistical analyses of single molecule trajectories were adopted to reveal the reaction rate fluctuation, the molecular memory effect, and the static and dynamic disorder of reaction rates at single molecule level, which are essentially indistinguishable in ensemble-averaged experiments. This pioneering work exemplified explicitly the advantages of single molecule methods over traditional ensemble approaches. After that, such method has been applied extensively to study many other biological systems at single particle (or molecule) level [2].

The first single particle nanocatalysis with the above-mentioned single molecule fluorescence microscopy was done in 2006 [3]. In this work, by counting the single turnovers on catalysts of individual large (>10 um) layered double hydroxide (LDH) particles, the crystal-face-dependent catalytic activity was spatially resolved half-quantitatively without detailed kinetic analysis. The first catalytic kinetic and dynamic study of single nanoparticles was done two years later by Peng Chen and coworkers [4, 5]. In this work, a Langmuir–Hinshelwood mechanism for the catalytic kinetic study of a single particle was proposed for the first time. Such mechanism is applicable for the product formation and dissociation processes on individual nanoparticles or enzyme molecules with the number of active sites larger than 1; based on such mechanism, with the same single particle approach with single-turnover resolution under single molecule fluorescence microscopy, they studied the redox catalysis of individual colloidal Au nanoparticles in about 5 nm. It was revealed for the first time that the product formation process on individual Au nanoparticles indeed follow the Langmuir–Hinshelwood mechanism but with heterogeneous catalytic activity probably because of the size difference among different individual nanoparticles; as for the product dissociation process, three different dissociation behaviors were revealed to exist in these nanoparticles; also, the indirect or substrate-associated dissociation pathway of product molecules and the spontaneous- and catalysis-induced dynamic surface restructuring of individual Au nanoparticles were revealed for the first time. Such new information undistinguishable from ensemble experiments exemplified the power of the single particle method in the modern surface nanocatalysis.

After this work, the catalytic kinetics of some other nanocatalytic systems (such as Pt, Au, Pd, and TiO_2) were also studied similarly with such method and mechanisms at single particle level [6–10].

Besides the catalytic kinetics of nanocatalysts at single particle level, the catalytic thermal properties of individual nanocatalysts could also be studied at single particle level based on a temperature-controllable single molecule fluorescence microscopy [11].

On the other hand, tremendous efforts have also made to improve the spatial resolution of such optical microscopy. Because of a diffraction limitation, the spatial resolution of a conventional optical microscopy is only about 200 nm for visible light. To visualize and then study the nanoscale properties reliably, early researchers made great efforts to break the optical diffraction limit by bringing the resolution of optical microscopy down to few nanometers [12]. Such breakthrough expedited a new technique of super-resolution (SR) fluorescence microscopy, through which many nanoscale structure or dynamics now can be visualized and then investigated directly. Recently, such technique has been extended successfully from biological areas to heterogeneous nanocatalysis [13–18].

1.2 History of Single Particle Nanocatalysis Based on (Localized) Surface Plasmon Resonance

SPR is the resonant oscillation of conduction electrons at the interface between two types of materials with different refractive indices, stimulated by incident light. Or, simply, it is a physical process that can occur when plane-polarized light hits a thin metal film under total internal reflection conditions. SPR is the basis of many standard tools for measuring adsorption of material onto planar metal (typically gold or silver) surfaces or onto the surface of metal nanoparticles. Its first use in a real-time analysis of a biological system was in 1990s, after that, as a label-free optical method, the SPR has become a popular optical sensing technology in many kinds of biological and medical areas because of its real-time and noninvasive nature.

For nanoparticles, in the early time, the SPR signal was usually adopted to study the shape- or size-dependent variation of radiative, nonradiative and photothermal properties of nanoparticles at ensemble level [19]. The first SPR-based single particle catalysis was done in 2010 [20]. In this work, Tao and coworkers introduced a strategy to image the electrocatalytic current of single nanoparticles by sensing local electrochemical current via SPR. Such technique possesses high spatial resolution and sensitivity because the signal varies with current density rather than current. The imaging technique is noninvasive, scanning-free, and fast, making it a powerful tool for studying heterogeneous surface reactions and for analyzing trace chemicals. Based on the strategy mentioned above, recently, this method was further used to study the electrocatalytic reaction of individual Pt nanoparticles by observing the decrease of the refractive index or the variation of SPR signal near the electrode surface because of the formation of hydrogen reduction process [21].

Furthermore, the localized surface plasmon resonance (LSPR) is the plasmon oscillating locally around a particle with diameter much smaller than the wavelength of incident light. The LSPR is also sensitive to the changes of surroundings of a nanoparticle, which make LSPR being an ideal tool to sense chemical reactions around or on a single particle, including its catalysis. Similar to SPR, the LSPR was also widely used in biological and biomedical sensing. In recent two decades, the LSPR was applied to study the various chemical reactions, such as electrochemical reaction, heterogeneous catalysis, and photocatalysis. Many kinds of LSPR-based strategies were developed based on the catalytic systems at single particle level. However, most of these studies are at the stage of sensing reactions and not deep yet to the explanation of catalytic mechanism.

1.3 History of Single Particle Nanocatalysis Based on Scanning Electrochemical Microscopy

Scanning electrochemical microscopy (SECM) based on an ultra-microelectrode (UME) was invented by Allen J. Bard et al. [22]. SECM can be used to study the local electrochemical behaviors of liquid/solid, liquid/gas, and liquid/liquid interfaces by measuring the diffusion-limited current at a UME tip as a function of precise tip position over a substrate region of interest. Two-dimensional raster scan of the UME can generate images of surface reactivities of all kinds of materials, such as electrocatalyst materials, enzymes, and other biological systems [23].

In 1997, Bard and coworker observed the single electron transfer events at a nanometer electrode, indicating a single molecule resolution achieved on UME [24]. Later on, many efforts have been made to prepare UMEs with all kinds of methods, including the transfer or deposition of single metal nanoparticles to/on the tips of UMEs [25]. After that, very few studies have been done for the real single particle nanocatalysis with SECM as most of the relevant studies are actually about the collisions of single nanoparticles on UMEs by monitoring the current generated through the single-particle-catalyzed reactions [26]. The first study of single particle nanocatalysis based on SECM was done by Stimming and coworkers in 2003. In this work, they studied the catalytic reactivity of supported single Pd nanoparticles for hydrogen evolution reaction using an electrochemical scanning tunneling microscopy (STM) setup [27]. Later on, in 2005, based on rapid-imaging mode, SECM was adopted to screen rapidly the arrays of bimetal electrocatalysts with compositions in a wide range for high efficient oxygen reduction reaction [28].

In recent years, the SECM technique was mainly used extensively in the field of analytical chemistry, while very rare for single particle nanocatalysis.

1.4 History of Single Particle Nanocatalysis Based on Vibrational Spectroscopies

Vibrational spectroscopies, including Raman spectroscopy and infrared (IR) spectroscopy, have been the most common technique to identify the components and structures of samples. However, because of the low Raman scattering and infrared adsorption cross sections of molecules, the studies of normal vibrational spectroscopy are limited in ensemble level. The discovery of surface-specific signal enhancement by plasmonic material led to a fast development of vibrational spectroscopy. The high sensitivity of them even enables single molecule detection at single particle level.

The phenomenon of Raman scattering was discovered in 1928 [29], whereas the first observation of enhanced Raman scattering (ERS) was in 1973 [30] and single molecule ERS in 1977 [31, 32]. It was realized that the tremendous enhancement of Raman signal can somehow rival the fluorescence signal. The application of ERS in single particle catalysts is still very rare mainly due to the usually low enhancement factors from a single particle, the small number of detected molecules, and the high requirement for instrument. Some early representative work was mainly about the studying or monitoring of catalysis on a single particle or at the nanoscale via ERS technique [33].

On the other hand, the technique of surface-enhanced infrared adsorption spectroscopy (SEIRAS) was commercialized in the early 1980s [34]. It allows sub-monolayer detection of molecules absorbed at a surface. Based on it, in the last year (2017), Wu et al. used the synchrotron-radiation-based infrared nanospectroscopy to map the surface catalytic activity of individual particles with high spatial resolution [35]. It is the first case or the only case reported by now with IR for the study of single particle nanocatalysis.

Even though, with the fast development of science and technologies, it can be expected that the techniques based on vibrational spectroscopies will be applied widely in more single particle catalysis because of their advantages of revealing the structural information of molecules.

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