Nanobubbles: An Effective Way to Study Gas-Generating Catalysis on a Single Nanoparticle

Shuping Li,†‡‖ Ying Du,†‡‖ Ting He,†‡‖ Yangbin Shen,†‡‖ Chuang Bai,‖ Fandi Ning,‖ Xin Hu,§ Wenhui Wang,† Shaobo Xi,† and Xiaochun Zhou†‡

†Division of Advanced Nanomaterials, Suzhou Institute of Nano-tech and Nano-bionics, Chinese Academy of Sciences (CAS), Suzhou 215123, China
‡University of Chinese Academy of Sciences, Beijing 100049, China
§Key Lab of Nanodevices and Applications, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences (CAS), Suzhou 215123, China

ABSTRACT: Gas-generating catalysis is important to many energy-related research fields, such as photocatalytic water splitting, water electrolysis, etc. The technique of single-nanoparticle catalysis is an effective way to search for highly active nanocatalysts and elucidate the reaction mechanism. However, gas-generating catalysis remains difficult to investigate at the single-nanoparticle level because product gases, such as H₂ and O₂, are difficult to detect on an individual nanoparticle. Here, we successfully find that nanobubbles can be used to study the gas-generating catalysis, i.e., H₂ generation from formic acid dehydrogenation on a single Pd–Ag nanoplate, with a high time resolution (50 ms) via dark-field microscopy. The research reveals that the nanobubble evolution process includes nucleation time and lifetime. The nucleation rate of nanobubbles is proportional to the catalytic activity of a single nanocatalyst. The relationship between the catalytic activity and the nucleation rate is quantitatively described by a mathematical model, which shows that an onset reaction rate (r_onset) exists for the generation of nanobubbles on a single Pd–Ag nanoplate. The research also reveals that a Pd–Ag nanoplate with larger size usually has a higher activity. However, some large-sized ones still have low activities, indicating the size of the Pd–Ag nanoplate is not the only key factor for the activity. Notably, further research shows that Pd content is the key factor for the activity of single Pd–Ag nanoplates with similar size. The methodology and knowledge acquired from this research are also applicable to other important gas-generating catalysis reactions at the single-nanoparticle level.

INTRODUCTION

Gas-generating catalysis is important to many energy-related research fields, such as photocatalytic water splitting,3–5 water electrolysis,6 dehydrogenation,7–12 and the electro-oxidation of small organic molecules, including methanol,13 ethanol,14 and formic acid (FA).15 Different nanocatalysts in the aforementioned reactions usually exhibit different activities because their activities are highly correlated with their unique structures,16,17 shapes,18 compositions,12 and facets.16,19–22 Conventional techniques, such as UV−vis, usually measure the average result over a large number of molecules or nanoparticles, resulting in missing the highly active nanoparticles with a small population. Searching for these highly active nanoparticles and elucidating the reaction mechanism necessitates the study of the nanocatalysts at the single-nanoparticle level.23–27

Currently, catalysis research on single nanoparticles is mainly based on single-molecule fluorescence,23–26 single-nanoparticle surface plasmon resonance,20 and single-molecule Raman scattering.30 However, studying gas-generating catalysis at the single-nanoparticle level remains difficult because the product gases, such as H₂, CO₂, N₂, and O₂, are difficult to detect by using the aforementioned methods, particularly when the gases are dissolved in solution.31,32 Fortunately, the gases can form nanobubbles at the interface between a solid and a liquid solution.33–40 Compared with the gases dissolved in solution, the nanobubble is substantially easier to detect. Thus far, nanobubbles have been investigated by atomic force microscopy (AFM),53–55 electrochemical techniques,56,57,41 total internal reflection fluorescence microscopy (TIRFM),38 infrared spectroscopy,39 and dark-field microscopy (DFM).40 DFM, in particular, is a convenient method to detect scattered light from nano-objects, such as nanoparticles,42 nanowire,43 and nanobubbles.40 Recently, we have used DFM to study chemical reactions on individual silver nanowires33,44 and silver nanoplates35 in situ and in real time. Research on the light scattering of gas bubbles can be traced back to as early as 1955.46 However, the nanobubbles presented in recent papers are substantially smaller than the gas bubbles in previous works.33–37,41,46,47

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However, gas-generating catalysis at the single-nanoparticle level has rarely been reported, although such research is highly significant in many energy-related research fields. In this paper, we successfully find that nanobubbles can be used to study the gas-generating catalysis, i.e., \( \text{H}_2 \) generation from formic acid (FA) dehydrogenation on a single Pd–Ag nanoparticle via DFM. The methodology and knowledge obtained from this research are applicable to other gas-generating catalysis, such as water splitting,\(^{13-15}\) water electrolysis,\(^1\) and electro-oxidation in fuel cells.\(^{13-15}\)

**RESULTS AND DISCUSSION**

**Track Gas-Generating Catalysis by Nanobubble.** In this research, Pd–Ag (\( n_{\text{Pd}}:n_{\text{Ag}} = 1:1 \)) nanoparticle catalysts have an edge length of 20–230 nm and a thickness of \( \approx 6.2 \) nm were used as a nanocatalyst for FA dehydrogenation to \( \text{H}_2 \) and \( \text{CO}_2 \) (Figure 1a and Figure S1).\(^{48}\) The results of physical characterization by X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS) show that the sample contained well-alloyed Pd–Ag nanoparticles (Figures S2–S4).\(^{48}\) The Pd–Ag nanoparticles were immobilized on a glass slide by direct dropping of a monodispersion and drying in air (Figure 1b and Figure S5).\(^{53}\) A reaction solution with a certain concentration of FA was dropped onto the glass slide with immobilized Pd–Ag nanoparticles and immediately covered with a coverslip. The depth of the microfluidic reactor was 4.2 \( \mu \text{m} \) (Figure S5). The glass slide was then installed onto a dark-field microscope\(^{43}\) (Figure 1b) to detect the gas nanobubble generated via FA dehydrogenation through the reaction as

\[
\text{HCOOH} + \text{Pd–Ag nanoplate} \rightarrow \text{Pd–Ag nanoplate} + \text{H}_2 + \text{CO}_2
\]

Figure 1e shows that the scattering intensity on a single Pd–Ag nanoplate will jump from a low state (\( S_{\text{low}} \)) to a high state (\( S_{\text{high}} \)) when a nanobubble is generated. On the other hand, the scattering intensity will drop from \( S_{\text{high}} \) to \( S_{\text{low}} \) when the nanobubble dissolves (Figure 1e). The jumping time from \( S_{\text{low}} \) to \( S_{\text{high}} \) and the dropping time from \( S_{\text{high}} \) to \( S_{\text{low}} \) are both very short (Figure 1e and Figure S7a). Most of the transitions between \( S_{\text{low}} \) and \( S_{\text{high}} \) only have a single point (pointed to by a red arrow in Figure S7a), and only very few transitions have
two points (pointed to by a green arrow in Figure S7a). Therefore, both the formation and dissolving time of nanobubble are usually too short to be resolved by our EMCCD camera with a 50 ms time resolution. These observations agree with the literature result that the formation time of nanobubbles is less than 1 ms.51

**Waiting Time, Nucleation Time, and Scattering Intensity of Nanobubble.** With FA dehydrogenation on a single Pd–Ag nanocatalyst, many nanobubbles continuously generated and were detected by DFM. Consequently, many transformations between $S_{\text{high}}$ and $S_{\text{low}}$ were observed in the scattering intensity versus time trajectory from the evolution of nanobubbles on a single Pd–Ag nanoplate (Figure 1e). Some important parameters, such as the waiting time of the low state ($\tau_{\text{low}}$), the waiting time of the high state ($\tau_{\text{high}}$), and the nucleation time for one nanobubble ($\tau_{\text{nucleation}}$), can be extracted from the scattering intensity trajectory (Figure 1e).

The waiting time of the low state ($\tau_{\text{low}}$) is the period between the dissolving moment of a former nanobubble and the forming moment of a latter nanobubble (Figure 1e). During the waiting time of the low state ($\tau_{\text{low}}$), gas is continuously generated from reaction 1, and the gas concentration around the single Pd–Ag nanocatalyst can be basically kept at a constant value. Because the reaction rate is fast enough to keep the gas concentration at a supersaturation state,56,50 nanobubbles will generate on the single Pd–Ag nanocatalyst. It should be particularly mentioned that not all gas from reaction 1 blows the nanobubbles, but only a part of the gas does. The other part will directly dissolve to a nearby solution, and play an important role in keeping a relatively high gas concentration around the single Pd–Ag nanocatalyst. Therefore, $\tau_{\text{low}}$ is the nucleation time of a nanobubble ($\tau_{\text{nucleation}}$), i.e.,

\[ \tau_{\text{low}} \equiv \tau_{\text{nucleation}} \]  

The nucleation rate of nanobubbles on a single Pd–Ag nanocatalyst can be calculated by

\[ J = \langle \tau_{\text{nucleation}} \rangle^{-1} \]  

where $J$ (s$^{-1}$) is the nucleation rate of nanobubbles and $\langle \tau_{\text{nucleation}} \rangle$ is from many nanobubbles on an individual Pd–Ag nanoplate with index $i$ (the notation $\langle \rangle$ means “average in an individual nanoparticle”). The nucleation rate of nanobubbles is proportional to the reaction rate on a single Pd–Ag nanocatalyst.

The waiting time of the high state ($\tau_{\text{high}}$) is the lifetime of a nanobubble, which is proportional to the stability of the nanobubble (Figure 1e). A longer $\tau_{\text{high}}$ means a stabler nanobubble. Figure S12 shows the variation in the average waiting time of the high state ($\langle \tau_{\text{high}} \rangle$), which is from many nanobubbles and multiple Pd–Ag nanoplates; the notation $\langle \rangle$ means “average of many particles” for different FA concentrations during the FA dehydrogenation reaction. The value of $\langle \tau_{\text{high}} \rangle$ is less than 3 s, which is much shorter than the lifetimes of nanobubbles reported in the literature (up to hours).33,34,51,52 Such a short lifetime in this research may be due to an unstable condition. The solution around the nanoplate catalyst is strongly disturbed by the continuously generated gas from the reaction. The hydrophilic surface of the slide may be another reason for the short lifetime.33,54

During $\tau_{\text{high}}$, the generated nanobubble can cover the single Pd–Ag nanocatalyst, block the mass transfer of reactant, and decrease the reaction rate. Then, the gas-generating rate has a slight decrease, and so does the gas concentration around the single Pd–Ag nanocatalyst. However, the decrease of gas concentration is not large because $\tau_{\text{high}}$ is always much shorter than $\tau_{\text{low}}$, and the block of the nanobubble is not rigorous due to the small size of the nanobubble. After the nanobubble dissolves, the reactant solution will immerse the single Pd–Ag...
nanocatalyst immediately, and the gas-generating rate will quickly recover. Then, the concentration of dissolved gas will quickly return to a constant value. Because the vibration of gas concentration is very weak, we can take it as a quasi-steady state. When the nanobubble dissolves, the scattering intensity will drop from the high state to the low state.

Figure 1e shows that the scattering intensity of a nanobubble almost retains the same value during the high state, indicating the size of the nanobubble does not change much during \( \tau_{\text{high}} \). The literature also showed that nanobubbles on the interface can retain their size for a few minutes or even days.\(^{55,58}\) Therefore, our observation is consistent with that in the literature.

**Nucleation Rate of Nanobubbles and Activity of a Single Nanocatalyst.** Figure 2a shows the temporal nucleation rate of the nanobubbles on three examples of individual Pd–Ag nanoplates in the presence of 1.67 M FA. From Figure 2a, three characteristic phenomena were observed for the reaction on a single Pd–Ag nanoplate catalyst. First, the temporal nucleation rates of all of the nanoplates exhibit an overall decreasing trend with time. Irrespective of the nucleation rate at the beginning of the reaction, it will decay to zero by the end of the reaction. Second, the temporal nucleation rate on most of the nanoplates usually exhibits large variations with time, indicating dynamic activity fluctuations of individual Pd–Ag nanoplates. This feature is typical of single-nanoparticle catalysis.\(^{54}\) Third, the temporal nucleation rate on different nanoplates exhibits a large heterogeneity from one nanoplate to another. The highest nucleation rate is 10 times greater than the lowest one, which will be discussed in the last section. Therefore, this methodology can be used to identify the highly active catalysts in gas-generating reactions.

To track the variation in activity of the Pd–Ag nanoplates, Figure 2b–f shows the histogram of the nucleation rate for 417 nanobubbles at different times in the presence of 1.67 M FA. At the initial stage of the reaction, the heterogeneity of the activity is very large (Figure 2b). Many highly active nanoplates with a high nucleation rate of nanobubbles are presented in Figure 2b. As the reaction proceeds, the number of highly active nanoplates decreases sharply and the number of less active nanoplates increases (Figure 2c–f). Former research showed that the nucleation of bubbles has a strong relationship with the curvature of the surface,\(^{56}\) which is possible to be induced by different sizes of nanoplates. To avoid the effect of nanoplate size on the nucleation of nanobubbles, we chose only nanoplates with a narrow size of 100–140 nm for the analysis of the nucleation rate (Figure 1d and Figure S5).

Researchers in the catalysis field are widely interested in understanding the catalytic behavior of a single nanocatalyst during gas-generating catalytic reactions.\(^ {1–4,13–21}\) To this end, the quantitative relationship between the activity in an ensemble experiment and the nucleation rate of nanobubbles (\( \langle n_{\text{nucleation}} \rangle^{-1} \)) in a single nanoparticle experiment needs to be elucidated. In this work, great effort is devoted to uncovering this quantitative relationship.

First, Figure 2g shows the average activity per Pd–Ag nanoplate (\( r \)) measured via the ensemble experiment (refer to SL1 in the Supporting Information for experimental details). Here, \( r \) is the average number of dehydrogenation reactions per second that occur on a single Pd–Ag nanoplate in the ensemble experiment (SI1 in the Supporting Information for the details of the calculation). Figure 2g shows that \( r \) gradually decreases with time during the FA decomposition reaction, irrespective of the FA concentration.\(^ {12,57}\) Because the decrease of FA concentration after the reaction is always less than 6.2% in the ensemble experiment (Table S1), the decay of the reaction rate cannot be attributed to the decrease of FA concentration. The deactivation of the catalyst is mainly due to the formation of poisonous intermediates like \( \text{CO}_{\text{ad}} \) on the surface of the catalyst.\(^ {58}\)

Second, Figure 2h shows that the average nucleation rate of a nanobubble (\( \langle n_{\text{nucleation}} \rangle^{-1} \)) on single nanoplates also gradually decreases with time. The decay of \( \langle n_{\text{nucleation}} \rangle^{-1} \) cannot be attributed to the decrease of FA concentration because the decrease of FA concentration after the reaction is estimated to be less than 0.11% in the single nanoparticle experiment (SL1 in the Supporting Information). Therefore, the trend of \( \langle n_{\text{nucleation}} \rangle^{-1} \) agrees well with that of \( r \) in Figure 2g. In particular, both parts g and h of Figure 2 show an activation process in the initial 500 s using 0.50 M FA. Therefore, \( \langle n_{\text{nucleation}} \rangle^{-1} \) also always decays to zero after a certain reaction time (Figure 2h); however, the reaction rates in the ensemble experiment do not (Figure 2g). This difference indicates that the generation of a nanobubble needs an onset value of supersaturation of gas around the single Pd–Ag nanoplate. Only when the supersaturation is higher than the onset value will a remarkable number of nanobubbles be generated on a single nanoplate. The onset value can only be reached using a highly active single nanoplate, as will be shown in the following discussion.

Figure 2i shows the effect of FA concentration on the initial ensemble activity (\( r_{\text{initial}} \)) and the initial nucleation rate of single Pd–Ag nanoplates (\( \langle n_{\text{nucleation}} \rangle^{-1}_{\text{initial}} \)). Both \( r_{\text{initial}} \) and \( \langle n_{\text{nucleation}} \rangle^{-1}_{\text{initial}} \) have a volcano shape with the peak found at a concentration of 1.67 M FA (Figure 2i).\(^ {59,60}\) Furthermore, the volcano shape of \( \langle n_{\text{nucleation}} \rangle^{-1}_{\text{initial}} \) matches the trend of \( r_{\text{initial}} \) very well, indicating a fine consistency between the ensemble and single nanoparticle experiments.

Third, we built a mathematical model to quantitatively describe the relationship between the ensemble activity (\( r \)) and the \( \langle n_{\text{nucleation}} \rangle^{-1} \) of the nanobubbles according to the previous literature (refer to SI2 in the Supporting Information for the formula derivation process); it is described as follows\(^ {36,60} \)

\[
\langle n_{\text{nucleation}} \rangle^{-1} = A \exp \left( \frac{-P_1}{k_r c_s^2} \right).
\]

\[
P_1 = \frac{16 \gamma^3 \Phi(\theta) c_s^2}{3 kTP^2}
\]

(4)

where \( A \) (s\(^{-1}\)) can be treated as a constant, \( \gamma \) (N m\(^{-1}\)) is the liquid surface tension, \( \Phi \) is a function of the contact angle (refer to SI2 in the Supporting Information for its expression), \( \theta \) is the contact angle equaling macroscopic contact angle of solution,\(^ {61} \) \( \sigma \) is the supersaturation of the gas in the liquid, \( c_s \) is the saturation concentration of the gas at a given pressure, and \( P^* \) is the applied pressure at which nucleation occurs. \( \text{Equation 4} \) provides a method to determine the activity of a single nanocatalyst through the measurement of the nucleation rate of the nanobubbles generated on it. In future research, this method may also be applied to measure the activity of a single nanoparticle in other gas-generating catalysis reactions, such as water splitting,\(^ {1–5} \) water electrolysis,\(^ {9} \) and the electro-oxidation of small organic molecules.\(^ {13–15} \)
Figure 3a shows that eq 4 fits the data of average activity per nanoplate (r) versus the nucleation rate (τnucleation) very well. Only the parameters A and k2 vary during the fitting, whereas the other parameters were determined by experimental measurement (SI.1 and SI.13–14 in the Supporting Information). From the fitting, the values of the parameters A and k3 were obtained (Figure 3b). The plot of A versus FA concentration shows a volcano shape with a peak at HCOOH = 1.67 M. A higher A implies a greater ability to generate nanobubbles. Therefore, the nucleation rate of nanobubbles at HCOOH = 1.67 M is faster than that at the other investigated FA concentrations. We attribute the variation of the pre-exponential term A to the concentration change of formic acid and formate, which affects the interface between glass and reaction solution. Figure 3b also shows that the parameter k3 always increases with increasing FA concentration. Equation S7 in the Supporting Information reveals that a higher k2 results in a higher supersaturation of the gas in the liquid for the same reaction rate, which implies that FA influences the supersaturation of hydrogen in solution. Therefore, greater supersaturations of the gas will be reached at higher FA concentrations.

Both parts a and c of Figure 3 show that each curve has a long low stage of nucleation rate of nanobubbles (τnucleation) at the low activity (r). For example, Figure 3c shows that τnucleation is always close to zero when r is less than 7000 s−1. However, the value of τnucleation will exhibit a clear increase if the activity of the Pd–Ag nanoplate exceeds a certain value. We name this value as the onset activity for the Pd–Ag nanoplate (ronset) to massively generate nanobubbles. In this paper, we define the intercept on the horizontal axis of the tangent lines at the inflection point (i.e., the point at maximum slope) as the onset activity (r_onset) (Figure 3c). We define the onset activity by analogy with the onset potential in electrochemistry.26,65 We derive the expression of r_onset from eq 4 as

\[ r_{\text{onset}} = \frac{1}{k_2} \left( c_i + \left( \frac{2}{3} \right)^{1.5} P_i \right) \]

The physical meaning of the onset activity can be defined as the boundary between the appearances of nanobubbles in small and large numbers. Combining eqs 4 and S5, we find that the nucleation rate of nanobubbles is always slower than 3.42% of the maximum rate when the activity is lower than r_onset. When the activity is higher than the onset activity, the nucleation rate of the nanobubble will increase fast.

The black dots and curve in Figure 3d show the onset value of activity (r_onset) for different FA concentrations. The r_onset shows a volcano shape with the peak at HCOOH = 1.67 M. The peak value of r_onset (9130 s−1) at HCOOH = 1.67 M is much higher than the lowest value (5970 s−1) at HCOOH = 3.00 M, indicating that nanobubbles start to massively appear at higher activity at HCOOH = 1.67 M. The model can also provide the onset value of supersaturation for the generation of nanobubbles:

\[ \sigma_{\text{onset}} = \left( \frac{2}{3} \right)^{1.5} \frac{P_i}{c_i} \]

The red curve with square symbols in Figure 3d shows the onset value of supersaturation for the generation of nanobubbles (σ_onset) at different FA concentrations. The value of σ_onset reaches approximately 8 at HCOOH = 1.67 M. If the gas supersaturation around a nanocatalyst is lower than σ_onset, few nanobubbles will appear on the nanocatalyst. This is the reason for the decay of (τnucleation)−1 to zero in Figure 2h. In addition, the dissolved gas in bulk solution has a very weak effect on the formation rate of a nanobubble, because the concentration of H2 in the bulk solution is low, and is usually much lower than that near Pd–Ag nanoplates.

In future research, it is necessary to discover some ways to decrease r_onset, enabling this method to detect slower gas-generating reactions. From eq S5, we know that the onset value of activity (r_onset) is proportional to the square root of p1. Equation 4 shows that p1 is calculated using γ, θ, T, and P′, indicating that r_onset can be decreased by modifying these parameters.

Relationship between Nucleation Rate of Nanobubbles and the Size of Single Pd–Ag Nanocatalysts. Figure 4 shows the time dependent nucleation rate of nanobubbles on different sizes of Pd–Ag nanoplates. To facilitate the analysis, the sizes of Pd–Ag nanoplates are roughly divided into three groups, i.e., small (L < 112 nm), middle (112 nm ≤ L ≤ 126 nm), and large (L > 126 nm). Figure 4a shows that the size of Pd–Ag nanoplates and the nucleation rate of nanobubbles show a relatively strong correlation (ρ = 0.30). Therefore, a Pd–Ag nanoplate with larger size usually has a higher activity. The highest activity appears at a size of about 130 nm in a large-sized group (pointed to by a red arrow). However, the activity of some large Pd–Ag nanoplates is still very low even at the beginning of the reaction in Figure 4a. Moreover, Figure 4a also shows that highly active Pd–Ag nanoplates can appear in each group, indicating the size of the Pd–Ag nanoplate is not the only key factor to affect the activity. Other factors, such as the content of Pd12,65 facet,48 and structure,14 also can strongly affect the activity of the
Figure 4. Time dependent nucleation rate of nanobubbles on different sizes of Pd–Ag nanoplates at 1.67 M FA. (a) $t_s = 0$ s. (b) $t_s = 800$ s. (c) $t_s = 1600$ s. (d) $t_s = 2400$ s. (e) $t_s = 3200$ s. The sizes of Pd–Ag nanoplates are divided into three groups, i.e., small ($L < 112$ nm), middle ($112$ nm $\leq L \leq 126$ nm), and large ($L > 126$ nm). The $L$ is the size of the Pd–Ag nanoplate, i.e., the edge length of a Pd–Ag nanoplate. The red numbers on the top of each plot are the counts of Pd–Ag nanoplates, whose nucleation rate is faster than 1 s$^{-1}$. Pearson’s correlation coefficient ($\rho$) for different time is shown in the top right of each plot.

Pd–Ag catalyst for the FA dehydrogenation. Therefore, the reactivity variation by a factor of 10 is mainly due to these factors for the Pd–Ag nanoplates with similar size.

With the reaction processing, the activity of Pd–Ag nanoplates decreases (Figure 4b–e). For the small Pd–Ag nanoplates, a sharp decrease occurs after 800 s, while a sharp decrease occurs after 1600 s for the middle and large ones. Interestingly, the number of Pd–Ag nanoplates with high activity (>1 s$^{-1}$) in the small-sized group has a weak increase from 22 to 25, indicating an activation process for small Pd–Ag nanoplates. For the middle Pd–Ag nanoplates, there are still four active ones at $t_s = 2400$ s, indicating a better stability. The higher stability may be due to the optimum content of Pd in the middle-sized Pd–Ag nanoplates. Our previous research clearly shows that the synthesis procedure is different for the Ag nanoplates with different sizes at the single nanoparticle level.45 For the middle-sized Ag nanoplates, the deposition of high potential metal occurs in a proper rate at both the edge and the mid part of the nanoplate.55 Therefore, the middle-sized Pd–Ag nanoplates are easier to obtain an optimum content of Pd during the synthesis.

Relationship between Nucleation Rate of Nanobubbles and the Pd Content of Single Pd–Ag Nanocatalysts. Figure 5a shows that the initial activity of Pd–Ag nanoplates increases with the increase of Pd content in an ensemble experiment. However, Figure S20 shows that the activity of Pd–Ag nanoplates after reacting 1500 s has an optimum value at $\sim$50% Pd content. Previous studies also show that an activity peak appears at the optimum Pd content ($\sim$50%) in the Pd–Ag alloy nanocatalyst for FA dehydrogenation.13,64 Therefore, the trend of activity can change with reaction time. In this research, we usually compare the initial activity of Pd–Ag nanoplates for ensemble and single nanoparticle experiments.

According to the trend in Figure 5a, we suppose the Pd content could play a key role in the catalysis at the single nanoparticle level. To prove the hypothesis, it is needed to measure the Pd content in single nanoparticles, which finish their single nanoparticle catalysis research. In this research, we used energy dispersive X-ray spectroscopy (EDX, EDAX APOLLO 105DD) coupled with field emission scanning electron microscopy (FE-SEM, QUANTA FEG 250) to measure the Pd and Ag contents in single nanoparticles. Figure Sb shows that the activity and Pd content (i.e., $n_{\text{Pd}}/(n_{\text{Pd}} + n_{\text{Ag}}))$ can be measured for the same set of single nanoparticles. For the nanoplate in Figure Sb, the Pd content is 50.7%, and the activity, i.e., the nucleation rate of nanobubbles, is 2.88 s$^{-1}$. To find more Pd–Ag nanoplates, we did not wash the slide after the single nanoparticle research. We just dried the slide in air, and then did EDX measurement. Thus, there are usually some dirty dots, which are SDS or sodium formate, that surround the single Pd–Ag nanoplates (SEM image in Figure Sb). However, these dirty dots did not affect the detection of Pd and Ag contents in an ensemble experiment. However, Figure S20 shows that the activity of Pd–Ag nanoplates after reacting 1500 s has an optimum value at $\sim$50% Pd content. Previous studies also show that an activity peak appears at the optimum Pd content ($\sim$50%) in the Pd–Ag alloy nanocatalyst for FA dehydrogenation.13,64 Therefore, the trend of activity can change with reaction time. In this research, we usually compare the initial activity of Pd–Ag nanoplates for ensemble and single nanoparticle experiments.

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contents, because they only contain some light elements including C, H, O, and S.

In order to study the effect of Pd content on the activity of single Pd–Ag nanoplates, we measured the activity and Pd content for many single nanoplates (Figure 5c). The gray dots in Figure 5c are for the single nanoparticles, and the red dots are for the average value in a certain range of Pd content. Figure 5c clearly shows that the activity of Pd–Ag nanoplates increases with the increase of Pd content for both the single Pd–Ag nanoplates and the average activity. The trend in single nanoparticle research is consistent with that in an ensemble experiment, as shown in Figure 5a. Therefore, the Pd content is the key factor for the activity of single Pd–Ag nanoplates with similar size. Moreover, this research successfully demonstrates that the key factor for the highly active nanocatalyst can be uncovered by the careful study on the physical properties, such as nanostructure, size, composition, spectroscopy, etc., after single nanoparticle catalysis research.

**CONCLUSION**

In summary, we successfully studied the gas-generating catalysis, i.e., FA dehydrogenation to H2 and CO2 on single Pd–Ag nanoplate catalysts, by monitoring nanobubbles using DFM. The gas-generating catalysis was studied at a high spatial resolution (single nanoparticle) and at a high time resolution (50 ms). The nanobubble evolution process was successfully proved to involve the nucleation time and lifetime. The nucleation rate of the nanobubbles was found to be proportional to the catalytic activity of the individual nanocatalyst. A mathematic model was built to quantitatively describe the relationship between the catalytic activity and the nucleation rate. The model revealed that an onset reaction rate exists for a single Pd–Ag nanoplate \( r_{\text{onset}} \) to generate nanobubbles. A remarkable number of nanobubbles will be generated on a single nanoplate only when the reaction rate of a single Pd–Ag nanoplate is higher than the onset rate. The value of \( r_{\text{onset}} \) is as high as 9130 s\(^{-1}\) at 1.67 M FA and is as low as 5970 s\(^{-1}\) at 3.00 M FA. The research also reveals that the size of Pd–Ag nanoplates and the nucleation rate of nanobubbles show a relatively strong correlation (\( \rho = 0.30 \)). The middle-sized Pd–Ag nanoplates usually have both high activity and high stability due to the optimum Pd content. However, the size of the Pd–Ag nanoplate is not the only key factor to affect the activity. Further research shows that the Pd content of single Pd–Ag nanocatalysts has a strong effect on the nucleation rate of nanobubbles, indicating that the Pd content is the key factor for the activity of single Pd–Ag nanoplates with similar size. Because the gas-generating catalysis on a single nanocatalyst is difficult to do, this research becomes significant in providing an effective way to find the highly active nanocatalyst and study the mechanism of the nanocatalyst for gas-generating reaction at the single-nanoparticle level, enabling further investigation in many other energy-related fields, such as water splitting and the electro-oxidation of small organic molecules.

**ASSOCIATED CONTENT**

1. Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b08523.

Additional experimental details, materials characterization, figures, and model development (PDF)