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# Single Molecule Investigation of Nanoconfinement Hydrophobicity in Heterogeneous Catalysis

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**ABSTRACT:** Nanoconfinement imposes physical constraints and chemical effects on reactivity in nanoporous catalyst systems. In the present study, we lay the groundwork for quantitative single-molecule measurements of the effects of chemical environment on heterogeneous catalysis in nanoconfinement. Choosing hydrophobicity as an exemplary chemical environmental factor, we compared a range of essential parameters for an oxidation reaction on platinum nanoparticles (NPs) confined in hydropholic and hydrophobic nanopores. Single-molecule experimental measurements at the single particle level showed higher catalytic activity, stronger adsorption strength, and higher activation energy in hydrophobic nanopores than those in hydrophilic nanopores. Interestingly, different dissociation kinetic behaviors of the product molecules in the two types of nanopores were deduced from the single-molecule imaging data.

Over the last decades, chemists have developed numerous synthetic strategies for confining reaction centers in nanoscale space to improve the performance of heterogeneous catalysts supported on zeolites, metalorganic frameworks (MOFs), covalent-organic frameworks (COFs), mesoporous silica particles, carbon nanotubes, and other porous materials.<sup>1-6</sup> The nanoscale space creates unique local environments for completing chemical processes more efficiently compared to the bulk, which is mainly attributable to changes in the chemical nature of spatially confined molecules and moieties.<sup>7-8</sup> A limited mechanistic understanding of chemical processes in nanoconfinement has been obtained through either theoretical calculations<sup>9-12</sup> or ensemble measurements over many catalysts.<sup>13-16</sup>

To fill the still large gaps between theoretical and realistic catalytic systems with a molecular-level understanding of chemical processes in nanoconfinement under reaction conditions, we have recently developed a single-molecule approach for in situ studies of catalytic reactions and molecular transport inside nanopores with the specially designed multilayer core-shell model nanocatalysts.<sup>17-19</sup> Our previous experiments revealed the physical constraints of nanoconfinement on molecular orientation and enrichment of reaction intermediates.<sup>20</sup> In the present work, we report new efforts on understanding the critical roles of chemical environments of nanoconfinement in altering catalytic reaction kinetics.

The noncovalent interactions between confining environment with its guest substrate molecules are essential for selectivity, activity, and stability in catalysis. Synthetic strategies such as introducing distal hydrogen bond donors,<sup>21</sup> hydrophobic binding cavities,<sup>22-23</sup> as well as tailoring physical dimensions<sup>20</sup> and geometries<sup>24</sup> are commonly adapted. In this study, we synthesized the multilayer core-shell nanocatalysts with hydrophilic or





hydrophobic post-functionalized nanopores. Reaction rates, molecular adsorption strength, and product molecule dissociation kinetics are experimentally quantified at the single-molecule level for a mechanistic understanding of catalytic reaction behaviors in hydrophilic and hydrophobic nanopores.

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The core-shell nanoparticle (NP) composes of a spherical SiO<sub>2</sub> core with 100 nm diameter and a 120 nm thick mesoporous shell with  $\sim$  3 nm pore structure (Figure 1a, Figure S1). Pt NPs of 5 nm diameter, which serve as active centers for the catalytic reaction, are loaded atop of the SiO<sub>2</sub> core and at the bottom of nanopores. The pores are subsequently functionalized with -SO<sub>3</sub>H or -CF<sub>3</sub>, creating hydrophilic or hydrophobic environments, respectively (Figure 1a. Supporting Information). The transmission electron microscopy (TEM) images (Figure S3) and N<sub>2</sub> physisorption analysis (Figure S4, Table S1) demonstrated that the functionalized core-shell nanocatalysts have intact and well-aligned pore structure. The presence of surface functional groups was further confirmed by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and quantified by <sup>29</sup>Si solid-state nuclear magnetic resonance (SSNMR) analysis (Figure S5). Using Xrav photoelectron spectroscopy (XPS), we further confirmed the oxidation of -SH to -SO<sub>3</sub>H by H2O2, where the binding energy of S2<sub>P</sub> peak shifts from 164.0 eV to 168.8 eV (Figure S6).<sup>25-27</sup> Detailed synthesis procedures and characterization information are included in the Supporting Information.

The core-shell nanocatalysts were dispersed in ultrapure methanol, drop-casted, and dried on quartz slides at low density (Figure S7). A continuous flow of reactantcontaining solution was introduced to nanocatalysts using a syringe pump. The reaction chosen for our single-molecule



Figure 2. Reaction kinetics quantified at single particle single-molecule level. (a) Catalytic reaction rates at different reactant concentrations in hydrophilic (black) and hydrophobic (violet) nanopores. Fitting the kinetic data (solid lines) directly using DLH equation gives adsorption equilibrium constant  $K_{AR}$  of 3.6 ± 1.3 and 5.1 ± 2.2  $\mu$ M<sup>-1</sup> and reaction rate constant  $k_{\text{eff}}$  of  $0.27 \pm 0.04$  and  $0.37 \pm 0.04$  s<sup>-1</sup> particle<sup>-1</sup> in hydrophilic and hvdrophobic nanopores, respectively. Alternatively, histogram distribution of  $K_{AR}$  (b) and  $k_{eff}$ (c) from fitting kinetic data on single nanocatalyst are also determined. Gaussian fitting the histogram distribution (solid lines) of  $K_{AR}$  and  $k_{eff}$  gives center values of 2.9  $\pm$  0.6 and 4.5  $\pm$  1.5  $\mu$ M<sup>-1</sup> (t(48) = 5.1, P < 0.05) and reaction rate constants  $k_{\rm eff}$  of 0.29 ± 0.04 and  $0.39 \pm 0.05 \text{ s}^{-1}$  particle<sup>-1</sup> (t(47) = 9.3, P < 0.05) in hydrophilic and hydrophobic nanopores, respectively.

study was fluorogenic oxidation of non-fluorescent Amplex red (AR, Figure 1a). The highly fluorescent product molecule, resorufin (Re), was imaged using prism-type total internal reflection fluorescence microscope (Figure S8) equipped with a high numerical aperture water immersion objective and a highly sensitive electron multiplying chargecoupled device camera. The individual catalytic events were captured as fluorescent bursts, such as those shown in Figure 1b. Catalytic reaction rate on a single core-shell nanocatalyst  $v_r$ , defined as  $\langle \tau_{off} \rangle^{-1}$ , could be determined from these fluorescence bursts with turn-over resolution (Figure S9-10). In Figure 2a, the catalytic activities in hydrophilic and hydrophobic nanopores are quantitatively compared as a function of AR concentration. Fitting results of reaction kinetics (Figure 2b, c) using diffusion-limited Langmuir-Hinshelwood (DLH) model<sup>18</sup> reveal that the adsorption equilibrium constant  $K_{AR}$  and the reaction rate constant  $k_{\rm eff}$  measured in hydrophobic nanopores are larger than those measured in hydrophilic nanopores with statistical significance. Ensemble results (Figure S11) also suggest higher catalytic activities of core-shell nanocatalysts with hydrophobic nanopores. Moreover, the reaction kinetics in nonfunctionalized nanopores (-OH),<sup>20</sup> which is also hydrophilic, are very similar to that in -SO<sub>3</sub>H functionalized nanopores.

Both theoretical studies and experimental measurements suggested that aromatic molecules tend to adsorb in a flat conformation on the metal surfaces by forming  $\pi$ -bonds with the metal surface.<sup>28-32</sup> On the other hand, planar molecules such as AR confined in nanopores are usually oriented with its long molecular axis parallel to the pore direction (Figure S12), namely standing orientation with respect to the Pt surface,<sup>33-37</sup> therefore, causing weaker adsorption strength.<sup>18</sup> Such standing molecular orientation of AR inside nanopores would increase the proximity between the phenol group of AR and chemisorbed oxygen on the Pt surface (Pt(0)),<sup>38</sup> thereby facilitating the oxidation reaction (Figure S13) and reducing the activation energy.<sup>20</sup> Stronger adsorption strength of AR on Pt NPs in hydrophobic nanopores suggests that AR molecules have a lower probability of approaching Pt NPs with the standing orientation in hydrophobic nanopores in comparison to that in hydrophilic nanopores, therefore its corresponding higher apparent activation energy  $E_a$  (Figure S14) is higher.

Our previous work has shown that confinement effects in nanopores can boost the catalytic activities through enhancing the local concentrations of intermediate species<sup>20</sup> like AR radicals<sup>39-40</sup> (Figure S13), which is the key explanation of the seemingly inconsistent correlation between high reaction rate and high activation energy. In the current study, lower mass transport rates of Re in the hydrophobic nanopores compared to that in the hydrophilic nanopores was revealed from single molecule tracking experiment (Figure S15-17). Even though AR radicals could not be imaged directly due to lack of fluorescence signals, their structural similarities to Re suggest that their mass transport in hydrophobic nanopores should also be slower. As a result, the local enrichment of the intermediate AR radicals in the hydrophobic nanopores is more significant therefore promoting higher activity than that in the hydrophilic nanopores. Moreover, control experiments of imaging single particles incubated with Re molecules also 1

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showed that the hydrophobic nanopores present stronger trapping capabilities (Figure S18).

We also studied the dissociation of Re from the core-shell nanocatalysts, i.e., Re escaping the confining nanopores. With turn-over resolution, the dissociation rates  $v_d$ , defined as  $\langle \tau_{on} \rangle^{-1}$ , in hydrophilic and hydrophobic nanopores were quantitatively measured at the single-NP, single-molecule level (Figure S9-10). We also notice that Re may stay on the



Figure 3. Dissociation kinetics quantified at single particle single-molecule level. (a) Dissociation model with direct  $(k_3)$  and reactant-assisted  $(k_1, k_{.1}, k_2)$  dissociation pathways. (b) Dissociation rates are quantified at different reactant concentrations in hydrophilic (black) and hydrophobic (violet) nanopores. Solid line are fitting results of the kinetic data using dissociation equation.

shell surface near the pore entrance after it diffuses out of the pore (Figure S16d). Though we cannot completely rule out such possibility, Re diffusion on the core-shell particle surface is very short lived in the presence of the solution flow in our experiments, which makes it reasonable to use  $<\tau_{on}>$  as Re residence time in nanopores. As shown in Figure 3, a distinctively different dependence of  $v_d$  on reactant concentration is observed in the two types of nanopores. In the hydrophilic nanopores,  $v_d$  varies at different reactant concentrations, showing no clear trend. In the hydrophobic nanopores, however,  $v_d$  increases with the increasing reactant concentration and eventually saturates at  $\sim 9 \text{ s}^{-1}$ particle<sup>-1</sup>. The distinct dissociation kinetics of Re indicate different dissociation mechanisms in hydrophilic and hydrophobic nanopores.

There are two possible dissociation pathways (Figure 40 3a): the reactant assisted dissociation pathway  $(k_1, k_2, k_2)$ 41 and the direct dissociation  $(k_3)$  pathway. The kinetics model 42 of Re dissociation can be deduced accordingly as  $v_d =$ 43  $\frac{k_2 K[\text{AR}] + k_3}{(1 + K[\text{AR}])} \text{ where } K = \frac{k_1}{(k_{-1} + k_2)}.^{41} \text{ In the dissociation kinetics}$ 44 45 equation, the term  $k_2 K$ [AR] represents the reactant assisted 46 dissociation pathway, and  $k_3$  stands for the direct 47 dissociation pathway. Three types of kinetics behavior in 48 the Re dissociation process can be predicted depending on 49 the relative magnitude of kinetic parameters  $\{k_2, k_3, \text{ and } K\}$ : 50 (1) type I,  $k_2 > k_3$ ,  $v_d$  increases and saturates when reactant concentration increases, (2) type II,  $k_2 < k_3$ ,  $v_d$  decreases and 51 flattens when reactant concentration increases, (3) type III, 52  $k_2 = k_3$  or K = 0,  $v_d$  is independent of reactant concentration. 53 Fitting the kinetics data for the hydrophilic nanopores in 54 Figure 3 (black square) using the dissociation equation 55 above gives the dissociation rate constants  $k_2$ ,  $k_3$  of  $3.2 \pm 1.1$ , 56 5.4  $\pm$  0.9 s-1 particle-1, respectively, and K of 0.56  $\pm$  1.1  $\mu$ M-57

1, suggesting that the dissociation of Re in the hydrophilic nanopores follows the type II model. The determined dissociation rate constants  $k_2$ ,  $k_3$  of 9.8 ± 0.2 and 4.1 ± 0.4 s<sup>-1</sup> particle<sup>-1</sup>, respectively, and *K* of 9.2 ± 2.5  $\mu$ M<sup>-1</sup> suggests the type I model for the hydrophobic nanopores (Figure 3, violet square).

At low [AR], the direct dissociation pathway dominates, and the dissociation rate equals to  $k_3$ . The smaller  $k_3$  in the hydrophobic nanopores suggests stronger confinement effects on trapping Re, which is consistent with the smaller mass transport rate (Figure S17). At high [AR], the dominant dissociation pathway shifts to the reactant assisted dissociation mechanism, and the dissociation rate approximates  $k_2$ . Larger  $k_2$  in the hydrophobic nanopores could also facilitate the catalytic reactions since removing Re from the confining nanopores opens the catalytic active site for the next cycle of chemical conversion.

In summary, we investigated the effects of nanopore hydrophobicity on confined catalytic reaction kinetics at the single-particle single-molecule level. Experimental results reveal faster chemical reaction rate and stronger adsorption strength for the oxidation of AR by Pt NPs in hydrophobic nanopores than that in hydrophilic nanopores. On the other hand, higher activation energy was also obtained in hydrophobic nanopores. The seeming contradiction between faster reaction rates and higher activation energy in hydrophobic nanopores is due to the confinement effects on trapping intermediate species. Furthermore, the dissociation kinetics of product molecule Re is measured at the single-molecule level. Different dissociation mechanisms in the two types of nanopores are uncovered. This work exemplifies the potential of our single-molecule approach to systematically study physical and chemical nanoconfinement effects, as well as their interplay at the molecular level, and provides guidance for tuning a wide variety of nanopore properties to optimize catalytic reactions kinetics, molecular adsorption strength, reaction activation energy, and product molecule dissociation pathways.

#### ASSOCIATED CONTENT

#### **Supporting Information**

Experimental details, additional results, discussion, and supporting figures are available free of charge via the Internet at http://pubs.acs.org.

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#### Author Contributions

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#### Notes

The authors declare no competing financial interest.

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#### REFERENCES

- 1. Xiao, J.; Pan, X.; Guo, S.; Ren, P.; Bao, X. Toward Fundamentals of Confined Catalysis in Carbon Nanotubes. J. Am. Chem. Soc. 2015, 137 (1), 477.
- Liu, H.; Yu, H.; Xiong, C.; Zhou, S. Architecture controlled PtNi@mSiO2 and Pt-NiO@mSiO2 mesoporous core-shell nanocatalysts for enhanced p-chloronitrobenzene hydrogenation selectivity. RSC Adv. 2015, 5 (26), 20238.
- Qiao, Z.-A.; Zhang, P.; Chai, S.-H.; Chi, M.; Veith, G. M.; Gallego, N. C.; Kidder, M.; Dai, S. Lab-in-a-Shell: Encapsulating Metal Clusters for Size Sieving Catalysis. J. Am. Chem. Soc. 2014, 136 (32), 11260.
- 4. Zhao, M.; Ou, S.; Wu, C.-D. Porous Metal–Organic Frameworks for Heterogeneous Biomimetic Catalysis. Acc. Chem. Res. 2014, 47 (4), 1199.
- 5. Dusselier, M.; Davis, M. E. Small-Pore Zeolites: Synthesis and Catalysis. Chem. Rev. 2018, 118 (11), 5265.
- Sharma, R. K.; Yadav, P.; Yadav, M.; Gupta, R.; Rana, P.; Srivastava, A.; Zbořil, R.; Varma, R. S.; Antonietti, M.; Gawande, M. B. Recent development of covalent organic frameworks (COFs): synthesis and catalytic (organicelectro-photo) applications. Mater. Horiz. 2020, 7 (2), 411.
- Petrosko, S. H.; Johnson, R.; White, H.; Mirkin, C. A. Nanoreactors: Small Spaces, Big Implications in Chemistry. J. Am. Chem. Soc. 2016, 138 (24), 7443.
- 8. Tagliazucchi, M.; Szleifer, I. How Does Confinement Change Ligand–Receptor Binding Equilibrium? Protein Binding in Nanopores and Nanochannels. J. Am. Chem. Soc. 2015, 137 (39), 12539.
- 9. Lísal, M.; Brennan, J. K.; Smith, W. R. Chemical reaction equilibrium in nanoporous materials: NO dimerization reaction in carbon slit nanopores. J. Chem. Phys. 2006, 124 (6), 064712.
- 10. Jakobtorweihen, S.; Hansen, N.; Keil, F. J. Combining reactive and configurational-bias Monte Carlo: Confinement influence on the propene metathesis reaction system in various zeolites. J. Chem. Phys. 2006, 125 (22), 224709.
- Malijevský, A.; Lísal, M. Density functional study of chemical reaction equilibrium for dimerization reactions in slit and cylindrical nanopores. J. Chem. Phys. 2009, 130 (16), 164713.
- Hansen, N.; Jakobtorweihen, S.; Keil, F. J. Reactive Monte Carlo and grand-canonical Monte Carlo simulations of the propene metathesis reaction system. J. Chem. Phys. 2005, 122 (16), 164705.
  - Bi, H.; Qiao, L.; Busnel, J.-M.; Liu, B.; Girault, H. H. Kinetics of Proteolytic Reactions in Nanoporous Materials. J. Proteome Res. 2009, 8 (10), 4685.
- Li, G.; Fu, C.; Oviedo, M. B.; Chen, M.; Tian, X.; Bekyarova, E.; Itkis, M. E.; Wong, B. M.; Guo, J.; Haddon, R. C. Giant Raman Response to the Encapsulation of Sulfur in Narrow Diameter Single-Walled Carbon Nanotubes. J. Am. Chem. Soc. 2016, 138 (1), 40.
- 15. Zhao, H.; Sen, S.; UdayabhaskararaoT; Sawczyk, M.; Kučanda, K.; Manna, D.; Kundu, P. K.; Lee, J.-W.; Král, P.; Klajn, R. Reversible trapping and reaction acceleration within dynamically self-assembling nanoflasks. Nat. Nanotechnol. 2016, 11 (1), 82.
  - Suwarno; Ngene, P.; Nale, A.; Eggenhuisen, T. M.; Oschatz, M.; Embs, J. P.; Remhof, A.; de Jongh, P. E. Confinement Effects for Lithium Borohydride: Comparing Silica and Carbon Scaffolds. J. Phys. Chem. C 2017, 121 (8), 4197.
  - 17. Chen, T.; Dong, B.; Chen, K.; Zhao, F.; Cheng, X.; Ma, C.; Lee, S.; Zhang, P.; Kang, S. H.; Ha, J. W.; Xu, W.; Fang, N. Optical

Super-Resolution Imaging of Surface Reactions. Chem. Rev. 2017, 117 (11), 7510.

- Dong, B.; Pei, Y.; Zhao, F.; Goh, T. W.; Qi, Z.; Xiao, C.; Chen, K.; Huang, W.; Fang, N. In situ quantitative singlemolecule study of dynamic catalytic processes in nanoconfinement. Nat. Catal. 2018, 1 (2), 135.
- Han, R.; Ha, J. W.; Xiao, C.; Pei, Y.; Qi, Z.; Dong, B.; Bormann, N. L.; Huang, W.; Fang, N. Geometry-Assisted Three-Dimensional Superlocalization Imaging of Single-Molecule Catalysis on Modular Multilayer Nanocatalysts. Angew. Chem. Int. Ed. 2014, 53 (47), 12865.
- 20. Dong, B.; Pei, Y.; Mansour, N.; Lu, X.; Yang, K.; Huang, W.; Fang, N. Deciphering nanoconfinement effects on molecular orientation and reaction intermediate by single molecule imaging. Nat. Commun. 2019, 10 (1), 4815.
- 21. Borovik, A. S. Bioinspired Hydrogen Bond Motifs in Ligand Design: The Role of Noncovalent Interactions in Metal Ion Mediated Activation of Dioxygen. Acc. Chem. Res. 2005, 38 (1), 54.
- 22. Murakami, Y.; Kikuchi, J.-i.; Hisaeda, Y.; Hayashida, O. Artificial Enzymes. Chem. Rev. 1996, 96 (2), 721.
- Breslow, R.; Dong, S. D. Biomimetic Reactions Catalyzed by Cyclodextrins and Their Derivatives. Chem. Rev. 1998, 98 (5), 1997.
- 24. Corma, A. State of the art and future challenges of zeolites as catalysts. J. Catal. 2003, 216 (1), 298.
- Rodella, C. B.; Barrett, D. H.; Moya, S. F.; Figueroa, S. J. A.; Pimenta, M. T. B.; Curvelo, A. A. S.; Teixeira da Silva, V. Physical and chemical studies of tungsten carbide catalysts: effects of Ni promotion and sulphonated carbon. RSC Adv. 2015, 5 (30), 23874.
- Zou, X.; Nie, X.; Tan, Z.; Shi, K.; Wang, C.; Wang, Y.; Zhao, X. Synthesis of Sulfonic Acid-Functionalized Zirconium Poly(Styrene-Phenylvinyl-Phosphonate)-Phosphate for Heterogeneous Epoxidation of Soybean Oil. Catalysts 2019, 9 (9).
- 27. Ravi, S.; Roshan, R.; Tharun, J.; Kathalikkattil, A. C.; Park, D. W. Sulfonic acid functionalized mesoporous SBA-15 as catalyst for styrene carbonate synthesis from CO2 and styrene oxide at moderate reaction conditions. Journal of CO2 Utilization 2015, 10, 88.
- 28. Favot, F.; Corso, A. D.; Baldereschi, A. Adsorption geometry of benzene on Pd(110): Results of first-principles calculations. EPL 2000, 52 (6), 698.
- 29. Mittendorfer, F.; Hafner, J. Density-functional study of the adsorption of benzene on the (111), (100) and (110) surfaces of nickel. Surf. Sci. 2001, 472 (1), 133.
- 30. Gland, J. L.; Somorjai, G. A. Low-energy electron diffraction and work function studies of adsorbed organic monolayers on the (100) and (111) crystal faces of platinum. Adv. Coll. Int. Sci. 1976, 5 (3), 205.
- Castillejos, E.; Debouttière, P. J.; Roiban, L.; Solhy, A.; Martinez, V.; Kihn, Y.; Ersen, O.; Philippot, K.; Chaudret, B.; Serp, P. An Efficient Strategy to Drive Nanoparticles into Carbon Nanotubes and the Remarkable Effect of Confinement on Their Catalytic Performance. Angew. Chem. Int. Ed. 2009, 48 (14), 2529.
- 32. Jenkins, S. J. Aromatic adsorption on metals via firstprinciples density functional theory. Proc. R. Soc. A 2009, 465 (2110), 2949.
- 33. Kumarasinghe, R.; Higgins, E. D.; Ito, T.; Higgins, D. A. Spectroscopic and Polarization-Dependent Single-Molecule Tracking Reveal the One-Dimensional Diffusion Pathways in Surfactant-Templated Mesoporous Silica. J. Phys. Chem. C 2016, 120 (1), 715.
- Jung, C.; Kirstein, J.; Platschek, B.; Bein, T.; Budde, M.; Frank, I.; Müllen, K.; Michaelis, J.; Bräuchle, C. Diffusion of Oriented Single Molecules with Switchable Mobility in

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57

58 59

Networks of Long Unidimensional Nanochannels. J. Am. Chem. Soc. 2008, 130 (5), 1638.

- Feil, F.; Jung, C.; Kirstein, J.; Michaelis, J.; Li, C.; Nolde, F.; Müllen, K.; Bräuchle, C. Diffusional and Orientational Dynamics of Various Single Terylene Diimide Conjugates in Mesoporous Materials. Micropor. Mesopor. Mater. 2009, 125 (1–2), 70.
- Higgins, D. A.; Park, S. C.; Tran-Ba, K.-H.; Ito, T. Single-Molecule Investigations of Morphology and Mass Transport Dynamics in Nanostructured Materials. Annu. Rev. Anal. Chem. 2015, 8 (1), 193.
  - 37. Pramanik, R.; Ito, T.; Higgins, D. A. Molecular Length Dependence of Single Molecule Wobbling within Surfactant- and Solvent-Filled Silica Mesopores. J. Phys. Chem. C 2013, 117 (29), 15438.
  - Serra-Maia, R.; Bellier, M.; Chastka, S.; Tranhuu, K.;
    Subowo, A.; Rimstidt, J. D.; Usov, P. M.; Morris, A. J.;
    Michel, F. M. Mechanism and Kinetics of Hydrogen

Peroxide Decomposition on Platinum Nanocatalysts. ACS Appl. Mater. Interfaces 2018, 10 (25), 21224.

- Dębski, D.; Smulik, R.; Zielonka, J.; Michałowski, B.; Jakubowska, M.; Dębowska, K.; Adamus, J.; Marcinek, A.; Kalyanaraman, B.; Sikora, A. Mechanism of oxidative conversion of Amplex<sup>®</sup> Red to resorufin: Pulse radiolysis and enzymatic studies. Free Radic. Biol. Med. 2016, 95, 323.
- Gorris, H. H.; Walt, D. R. Mechanistic Aspects of Horseradish Peroxidase Elucidated through Single-Molecule Studies. J. Am. Chem. Soc. 2009, 131 (17), 6277.
- 41. Xu, W.; Kong, J. S.; Yeh, Y.-T. E.; Chen, P. Single-Molecule Nanocatalysis Reveals Heterogeneous Reaction Pathways and Catalytic Dynamics. Nat. Mater. 2008, 7 (12), 992.

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