

Facet-controlled Single Atom Catalysts for Efficient CO Oxidation

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CO oxidation has been extensively investigated in heterogeneous catalysis due to its importance in both industrial applications and fundamental catalytic studies [1]. Single atom catalysts (SACs), which are composed of atomically dispersed metal sites on proper supports, have emerged as an effective CO oxidation material, owing to their high atom utilization efficiency and unique electronic and physical features [2-3]. In SACs, single metal atoms with an average size of ~0.1 nm have the maximum surface energy, which tend to aggregate into clusters/nanoparticles easily. Hence, building proper chemical bonding with supports combined with accurate local structural analysis is of importance to stabilize single atoms and control catalytic performance. Currently, X-ray absorption spectroscopy (XAS) is the most frequently used characterization technique for probing the aforementioned local coordination; however it requires signal modelling of a theoretical structure under the assumption of homogeneity of said structure, which only provides average information of the coordination number and oxidation states of single metal species [4]. However, single atoms are generally dispersed randomly on the support surface, and the average model predicted by XAS may not be the real structure of active sites during the catalytic process. Thus, SACs with specific coordination environments need to be designed and a more intuitive technique, scanning transmission electron microscopy combined with electron energy loss spectroscopy (STEM/EELS), needs to be applied simultaneously for a more detailed analysis on the local structure at an atomic scale. Meanwhile, STEM/EELS during *in situ* heating can offer direct structural change visualization and chemical coordination analysis of SACs, which is also important for understanding the local coordination stability during the catalytic process.

Herein, a series of Pt single atoms with optimized local coordination structures was synthesized on the facet-controlled anatase TiO₂ supports (named as Pt SA/TiO₂), as shown in Figure 1 [5]. The TiO₂ in the shape of nanosheet, nanowire and truncated bipyramid expose corresponding facets of (001), (100) and (101), respectively. On the different TiO₂ facets, the Pt single atom should form disparate coordination structures with different chemical states, consequently showing various CO oxidation properties and stabilities. To further observe the dynamic behavior of Pt single atoms during the catalytic process, *in situ* heating was performed on a Protochips heating E-chip under vacuum from room temperature (RT) to 450 °C. Small probe currents and minimal acquisition time have been selected during experiments to minimize beam effects on the single metal atoms. The *in situ* imaging of the Pt SACs revealed that the Pt single atom can remain at the same location on the TiO₂ nanosheet support when the temperature is below 200 °C (Figure 2a-2d). After the temperature was kept at 200 °C for 5 mins, the Pt atom moved 0.48 nm without the formation of a Pt cluster (Figure 2e), and then stayed at the same place when the temperature further increased to 400 °C (Figure 2f-2h). Following 10 mins at 400-450 °C, the TiO₂ nanosheet support started to decompose with loss of visible lattice fringes and main structures. Through the aforementioned imaging and spectroscopic techniques, we are able to acquire a comprehensive understanding on the thermal stability and catalytic activity in relation to the Pt local coordination

supported on the different support facets.

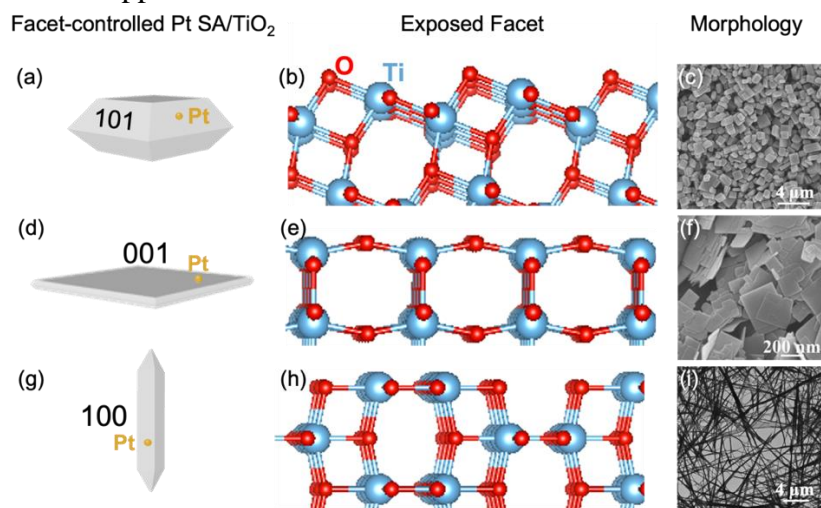


Figure 1. Different structures of anatase TiO_2 support with specific exposed facet and shape for Pt single atoms incorporation. (a-c) Truncated bipyramid with exposed facet of (101), (d-f) nanosheet with exposed facet of (001), (g-i) nanowire with exposed facet of (100).

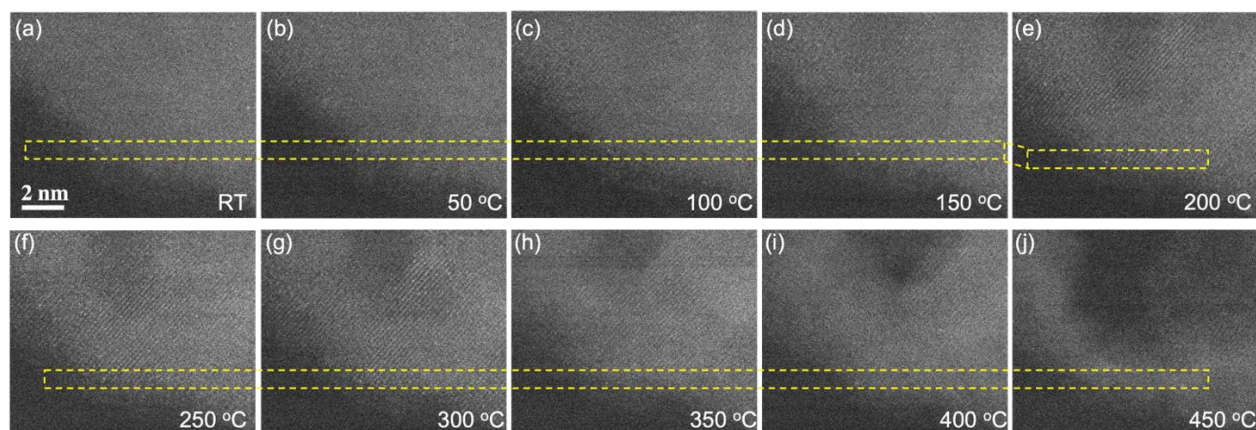


Figure 2. In situ aberration-corrected STEM characterization of Pt SA/ TiO_2 nanosheet at different annealing temperatures from room temperature (RT) to 450 °C for 5 mins, respectively. The inset yellow box indicates both position and movement of Pt single atoms.

References:

- [1] B. Qiao, A. Wang, X. Yang, L. F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li, T. Zhang, *Nat. Chem.* **3** (2011), p. 634-641.
- [2] A. Wang, J. Li, T. Zhang, *Nat. Rev. Chem.* **2**(2018), p. 65-81.
- [3] L. Nie, D. Mei, H. Xiong, B. Peng, Z. Ren, X. I. P. Hernandez, A. DeLaRiva, M. Wang, M. H. Engelhard, L. Kovarik, A. K. Datye, Y. Wang, *Science* **358** (2017), p.1419-1423.
- [4] X. Li, X. Yang, J. Zhang, Y. Huang, B. Liu, *ACS Catal.* **9** (2019), p. 2521-2531.
- [5] This work was supported by the National Science Foundation (NSF) awards under grant No. CBET-2031494 and CHE-1955786. The authors acknowledge Mr. Peikui Wang, Dr. Jaeha Lee, and Prof. Phillip Christopher for providing the shape-controlled Pt/ TiO_2 SACs sample, and the use of facilities and instrumentation at the UC Irvine Materials Research Institute (IMRI) supported in part by the NSF through the MRSEC program (DMR-2011967).