Single Atoms at Crystal Ladder Steps

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Abstract:

In this Chem issue, Wu reported a freestanding ladder-like ZnO surface with abundant unsaturated step sites offering an attractive platform for selectively anchoring single-Au atom (Au_1) with one-dimensional assembly. This opens a new strategy for the synthesis of single-atom sites with tunable arrangements for ultrasensitive sensing and highly active catalysis.

Main text: Structures with singly dispersed heteroatoms on the substrate have attracted considerable recent interest for the future generation of catalysis, sensor, and transistors. However, the efficient production of single-atom sites is often plagued by undesired diffusion and aggregation of single-atoms. Fundamentally limited by the nature of high entropy and high surface energy of the single-atom sites, the synthesis and maintenance of the single-atom sites are intrinsically difficult to achieve. A common strategy to overcome this obstacle is to design and synthesize substrates with abundant unsaturated defects and vacancies that can selectively trap, chelate, and stabilize single atoms.[1] Dispersion of single atoms on different types of substrates such as metals, metal oxides, metal dichalcogenides, and graphitized carbon materials have shown considerable success.[1-3] However, because of the difficulty to precisely manipulate and control such defects, these single-atom sites are often randomly distributed on the surface without any selectivity control of the deposition location. Although techniques, such as atomic layer deposition,[4] optical tweezers,[5] and scanning tunneling microscopy combined with hydrogen-resist lithography,[6] can precisely deposit atoms on the target position or even manipulate the movement of the atoms, these approaches typically require costly equipment, sophisticated operation protocols, and often with low yield. Therefore, researchers are looking for new -strategies that can selectively distribute the single-atom sites on the desired position on a large scale. In 2016, Dvořák *et al.* discovered that the monoatomic step edges of CeO_2 could effectively promote the immobilization of Pt single atoms while the terrace sites only lead to the Pt clusters.[7] Thus, using traditional wet-chemistry synthesis to create step-site rich nanostructures with different topology would offer an effective strategy for selectively dispersing the single atoms.

Taking advantage of the traditional wet-chemistry synthesis, by tailoring the surface morphology and defect level of the ZnO substrate, a group of researchers led by Yuen Wu, achieved the selective deposition of single Au atoms on the step sties of ZnO ladder structures (Figure 1), as reported in this issue of *Chem.*[8] The authors synthesized a novel ZnO ladder structure with four lamellar layers stacked along the horizontal direction. It was found that the deposited single Au atoms tend to reside along the step region where the under-coordinated step sites provide sufficient oxygen vacancies to trap and stabilize the individual Au atoms. Interestingly, these single Au sites maintain one-dimensional geometry along the lattice steps.

The authors found that the growth of the ladder-like ZnO structure follows a layer stacking process, in which the step region was formed when the nucleation and growth of a new hexagonal ZnO layer started over an existed ZnO layer. The ZnO was grown in the lateral plane to form the hexagonal nanolayer in the supersaturated precursor solution, and subsequently, the new nucleation sites were found to form on the original layer surface and initiate a new-layer expansion. This new-layer expansion process could thus lead to a layer-stacking ladder structure until the termination of the crystal growth (Figure 1, upper panel). Taking advantage of the abundant under-coordinated step sites on the ladder ZnO structure, the authors successfully prepared the singly dispersed Au atoms at the step sites on the ZnO surface (Au_1-ZnO). With a unique electronic structure, the Au_1-ZnO surface that exhibits a highly specific charge transfer NO_2 adsorbates, allowing to create highly sensitive and selective gas sensors for NO_2 detection.

This work opens the possibility of manipulating the position of the deposited single atoms by using the wet-chemistry synthesis to precisely tailor the surface configuration of the substrate. Previous works in this field focused more on how to enhance the metal mass loading on the substrate while avoiding aggregation, with little attention to the exact location of such atomic sites. The reported single-atom structures typically show a statistically random dispersion of single-atom sites.[1] In contrast, by tailoring the surface topography and selective adsorption, the distinct coordination environment of the step sites drives the single atoms to selectively deposit on the step sites, allowing to rationally control of the density and more notably the spatial arrangement of the single

Au atoms, including isolated atoms, dual metal sites, one-dimensional atomic arrays, two-dimensional atomic networks, or even three-dimensional atomic spirals by using stepped spiral substrates (Figure 1, lower panel).[9] This could thus promise a new generation of atomic-scale materials with unprecedented controllability in terms of composition, structure, and reactivity. Such a wet-chemistry based arrangement of single atoms may not be as accurate as those of the optical tweezers but offers a pathway to high through production.

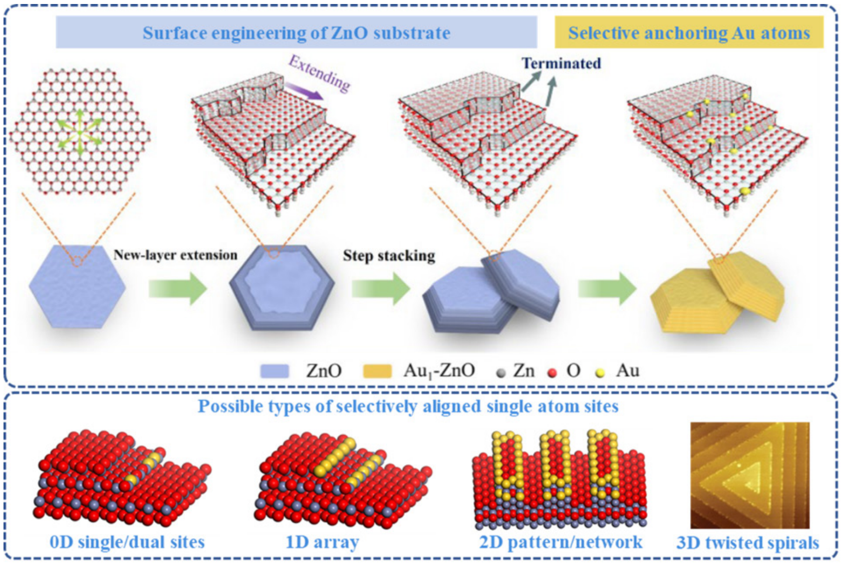

Figure 1. The surface morphology engineering of ZnO for selectively single-atom trapping and the possible types of aligned single atoms. The upper panel is adapted from Ref. 8, and the right image in the lower panel is adapted from Ref. 9.

Beyond gas sensing, such designable single-atom sites may offer significant potential for heterogeneous catalysis, particularly for reactions that require some specific arrangement of the metal sites to guide the specific reaction pathway and control product selectivity, such as water gas shift reaction, hydrogenation reaction, photochemical/electrochemical water spitting, aerobic oxidation reaction, CO_2 reduction, and even NH_3. For example, although the Au single atoms on perfect CeO_2 surface are inactive for CO oxidation, Liu *et al.* find that the Au single atoms at step sites of ceria support are highly active towards CO oxidation, signifying the significance of single-atom site arrangements in catalysis.[10] Similar strategies may be readily applicable to other oxide substrates FeO_x, MgO, or CeO_2 or other single metal atoms (Au, Pd, Pt or Ni, Co, etc.). Apart from the dispersion of monocomponent single metal atoms, dispersion of single atoms sites with multiple components is critical for exploring the synergetic effect of different atoms for enhancing catalytic activity, selectivity, or enabling cascading tandem reactions (et., Pt/Ni pair, Ni/Fe pair, *etc.*).

Together, taking advantage of the wet-chemistry synthesis on a large-scale, the authors had successfully prepared a ZnO nano-ladder structure with rich step sites that can then coordinate with single Au atoms for NO_2 sensing. This work explored the critical role of substrate surface topography in selectively anchoring the single-atoms with tunable spatial arrangements. This could help develop a new generation of atomic-scale materials with unprecedented flexibility in terms of composition, structure, and reactivity.

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