Photoinduction of palladium single atoms supported on defect-containing γ-AlOOH nanoleaf for efficient trans-stilbene epoxidation

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ABSTRACT
Exploring the interaction between metal and support is of great importance in enhancing the catalytic performance and deepening the mechanistic understanding of single atom catalysis. Here we describe a photoinduction method to construct atomically dispersed palladium atoms supported over defect-containing boehmite (γ-AlOOH) nanoleaf with a palladium loading of 0.32 wt%. The existence of singly dispersed palladium atoms is confirmed by spherical aberration correction electron microscopy, extended X-ray absorption fine structure measurement, and CO-absorbed diffuse reflectance infrared Fourier transform spectroscopy. This catalyst shows excellent catalytic efficiency in trans-stilbene epoxidation to yield trans-stilbene oxide (TOF: 416 h⁻¹; conversion: 84 %; selectivity: 99 %). In addition, various aromatic olefins were successfully transformed into the corresponding epoxides with high selectivity and scalability. DFT study further reveals that the high catalytic activity originates from under-coordinated single palladium atoms in the defect-containing γ-AlOOH in a unique coordination environment. This lays the foundation for the facile creation of single atom catalysts and sheds light on the possibility for scale-up production.

1. Introduction
Epoxidation, oxygenation of olefins to yield cyclic epoxides, is an important reaction in chemical industry and the epoxides constitute valuable building blocks for the production of fine chemicals [1,2]. Trans-stilbene, one typical type of alkenes, has been commonly used as a probe molecule to evaluate the catalyst’s activity [3–6]. But the use of expensive oxidants (organic peroxides and peracids) or co-reagents is typically required [3]. To solve this issue, several catalytic systems (heterogeneous and homogeneous) have been developed, allowing the use of O₂ as the oxidant, with no co-reagents being needed. Noble metal-based nanocatalysts, such as Au and Ag, have been employed in this reaction due to their high catalytic efficiency [2,7–9]. But the metals’ high cost and high tendency to aggregate on the supports generally lead to low atom utilization. Beller et al. fabricated a cobalt oxide catalyst to be applied in trans-stilbene epoxidation with tert-butyl hydroperoxide for 20 h to get the corresponding epoxide with 99 % conversion and 97 % yield [3]. Yang et al. described cobalt substituted TUD-1 mesoporous materials for trans-stilbene epoxidation under high O₂ pressure of 2.76 MPa to afford trans-stilbene oxide with conversion of 93 % and selectivity of 91 % [6]. Wang and co-workers created a Fe₂ cluster catalyst for the reaction, and 93 % selectivity along with 91 % conversion were obtained with a reaction time up to 24 h [10]. In this context, effective catalyst systems with high activity and selectivity that require lower O₂ pressure, shorter reaction time, and lower temperature are still sought.

Single atom catalysts (SACs) have gained a great deal of interest worldwide because they can offer advantages in both heterogeneous and homogeneous catalysis, showing extraordinary catalytic activity in a wide scope of industrially important reactions [11–14]. SACs contain singly dispersed metal atoms over the supports, with unique electronic and geometric properties, endowing maximum atom efficiency and significantly reducing the usage of noble metals [15–20]. To date, a
variety of approaches to constructing SACs have been reported, but the search for general methods that can facilitate construct SACs with high activity and stability is still challenging [21–24]. Moreover, detachment and aggregation of the metal species, burying of the metal species by the support or cocking, and blocking of active sites by strong binding of foreign species are the potential causes for catalyst life reduction [25–28]. Therefore, strong metal-support interactions are key to achieving exceptional catalytic activity and stability [11,21,29,30]. Zheng et al. described a photochemical route to create a palladium single atom catalyst, over titanium oxide nanosheets by reduction of palladium ions with ultraviolet light and ethylene glycol, with excellent hydrogenating activity [22]. Boehmite (γ-AlO(OH)) has been the most important precursor or intermediate for the synthesis of alumina and alumina-derived nanomaterials for use as adsorbents, catalysts, and catalyst supports [31–35]. It has a lamellar structure with orthorhombic symmetry and the Al\textsuperscript{3+} ions lie in distorted and edge-sharing octahedral arrays of oxide ions [31,33]. Due to the presence of –OH groups on the surface of γ-AlO(OH), it is favorable to interact with foreign molecules and potentially as ideal support for single atom catalysis.

Herein, we report a photoinduction strategy to create atomically dispersed palladium atoms supported over defect-containing γ-AlO(OH) nanoflakes. Briefly, γ-AlO(OH) was initially synthesized by solvent-thermal method before it was treated by defect engineering to give defective γ-AlO(OH). Studies have shown the unique and favorable role of the oxygen vacancy in adsorption and activation of O\textsubscript{2} [36,37]. Then, a photoinduction reduction process was carried out by irradiation with ultraviolet light (UV) to yield atomically dispersed palladium sites anchored on defective γ-AlO(OH). This UV treatment is a critical step since it facilitates the removal of Cl ions on the original Pd salt and stabilizes the Pd atoms by forming Pd-O bonds over the γ-AlO(OH) support. This catalyst delivered high efficiency in alkene epoxidation, along with excellent recyclability and scalability. A DFT study reveals that the enhanced catalytic activity originates from the under-coordinated palladium atoms in the defective γ-AlO(OH). Moreover, the strong metal-support interaction contributes to the modulation of the electronic state and effectively prevents the agglomeration of palladium species, contributing to the sustained catalytic activity. To the best of our knowledge, this is the first report employing γ-AlO(OH) as support for directly constructing SACs. Our findings may provide an opportunity for facile synthesis of SACs on various oxyhydroxide under mild conditions. The promising extension of these results to other catalytic reactions might set the stage for other applications of the SACs described herein.

2. Experimental sections

2.1. Chemicals

All chemicals were used as received without further purification. Aluminum nitrate nonahydrate, polyvinyl pyrrolidone (PVP), Na\textsubscript{2}PdCl\textsubscript{4}, PdCl\textsubscript{2}, acetic acid, sodium borohydride, zinc nitrate hexahydrate, methanol, 2-methylimidazole, urea, ethanol, trans-stilbene, acetonitrile, N,N-dimethylformamide (DMF), 1-octane, toluene, cis-stilbene, 1-(12Z)-2-(phenylethynyl)-3-methylbenzene, N,N-dimethylacetamide (DMAC), 1,1′-(12Z)-1,2-ethenediyliis[4(methyl)benzene], trans-alpha-methyl-stilbene, triphenylethylene, 1-(1,1-dimethyllythyl)4-[2-[4-(1-methyl ethyl)phenyl]ethenyl]-benzene, 1,1′-(12Z)-1,2-ethenediyliis[2-(1-methylthyl)-benzene], 1,1′-(12Z)-1,2-ethenediyliis[3-(1-methylthyl)benzene], 1,1′-(12Z)-1,2-ethenediyliis[4-(1(E)-2-phenylethynyl)benzene], 1,1′-(12Z)-1,2-ethenediyliis[2-(1,1-dimethylthyl)benzene], (E)-1,2-Bis(4-bromophenyl)ethene, N-methyl pyrrolidone (NMP) were purchased from Aladdin. Commercial carbon-supported Pd (Pd/C, 5 wt% Pd) was from Aldrich. Deionized water from Milli-Q System was used in all experiments.

2.2. Synthesis of the catalysts

Synthesis of defective γ-AlO(OH): γ-AlO(OH) was prepared by a solvent thermal method. Specially, 260 mg of Al(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O and 260 mg of PVP were introduced into a mixed solvent containing 10.0 mL of C\textsubscript{6}H\textsubscript{12}O\textsubscript{6}, 10.0 mL of H\textsubscript{2}O, and 5.0 mL of C\textsubscript{2}H\textsubscript{6}O. The above mixture was sonicated for 0.5 h before it was transferred to a Teflon-lined autoclave and then heated at 180 °C for 24 h. The white precipitate was washed with ethanol and dried in a vacuum oven at 80 °C for 12 h to give γ-AlO(OH).

Next, 200 mg of white γ-AlO(OH) was evenly spread at the bottom of the porcelain boat and thermally treated in a stream of 5% H\textsubscript{2}/Ar mixed gas at 180 °C for 2 h to create defective γ-AlO(OH) with oxygen vacancies.

Synthesis of Pd\textsubscript{1}/γ-AlO(OH): Pd\textsubscript{1}/γ-AlO(OH) was synthesized via a photoinduction UV treatment. This was carried out on a Xenon-lamp source (Beijing Perfectlight Technology Co. Ltd., PLS-SXE300D/300DUV) equipped with an optical filter that only allows the transmission of 365 nm UV. The UV treatment was operated at an operating current of 15 A. The power density of the UV light was measured to be 20.7 mW/cm\textsuperscript{2} by a PM-2000 photoradiometer (Beijing Perfectlight Technology Co. Ltd.). The vertical distance between the suspension surface and the light source was 12 cm. The diameter of the beaker was 4 cm, which is smaller than the light spot diameter (6 cm) of Xenon-lamp source. Typically, 200 mg of defective γ-AlO(OH) powder was dispersed in 35 mL of deionized water in a beaker under sonication for 1 h before addition of 80 μL of Na\textsubscript{2}PdCl\textsubscript{4} (10 mg/mL) aqueous solution. Then, the dispersion was kept stirring and irradiated by the UV light for 1 h. Finally, the dispersion was centrifuged, washed with ethanol, and dried in a vacuum oven to give Pd\textsubscript{1}/γ-AlO(OH). The Pd loading of the sample was measured to be 0.32 wt% based on ICP-AES result.

Synthesis of Pd\textsubscript{NPs}/γ-AlO(OH): Pd NPs/γ-AlO(OH) was prepared by a reduction method. 200 mg of defective γ-AlO(OH) was added to 50 mL of deionized water and sonicated for 1 h before addition of 120 μL of Na\textsubscript{2}PdCl\textsubscript{4} solution (100 mg mL\textsuperscript{-1}). The suspension was then stirred vigorously for 2 h at room temperature. 1 mL of NaBH\textsubscript{4} (0.1 mol L\textsuperscript{-1}) aqueous solution was added and the mixture was further stirred for another 2 h. Finally, the precipitate was washed and dried in a vacuum oven at 80 °C. The Pd loading of the sample was measured to be 4.2 wt% based on ICP-AES result.

Synthesis of Pd\textsubscript{NPs}/N-C: ZIF-8 was synthesized by a previously reported method and Pd\textsubscript{NPs}/γ-AlO(OH) was fabricated by an impregnation method followed by a pyrolysis treatment [19]. In a typical synthesis, 0.558 g of Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O was dissolved in 15 mL of methanol and subsequently added to 15 mL of methanol with 0.616 g of 2-methylimidazolide under sonication. Then, the mixture was left under static at room temperature for 12 h. Finally, the precipitate was centrifuged and vacuum dried in a vacuum oven at 80 °C for 24 h to give ZIF-8. Next, 200 mg of ZIF-8 powder was thermally treated at 950 °C for 2 h in a stream of Ar with a ramping rate of 3 °C min\textsuperscript{-1} to give black N-doped carbon. 100 mg of the resulting N-doped carbon powder was dispersed in 10 mL of ethanol and sonicated for 1 h to form a homogeneous dispersion before addition of 50 μL H\textsubscript{2}PdCl\textsubscript{4} (20 mg mL\textsuperscript{-1}) aqueous solution. The precipitate was stirred vigorously for 6 h at room temperature before it was centrifuged and vacuum-dried at 80 °C. Finally, the product was calcined at 300 °C in a stream of 5 % H\textsubscript{2}/Ar with a ramping rate of 5 °C min\textsuperscript{-1} for 2 h. The Pd loading of the catalyst was measured to be 0.675 wt% based on ICP-AES result.

Synthesis of Pd\textsubscript{NPs}/C\textsubscript{B/C\textsubscript{N4}}: Pd\textsubscript{NPs}/C\textsubscript{B/C\textsubscript{N4}} was prepared by a previously reported method [38]. The Pd loading of the sample was measured to be 0.16 wt% based on ICP-AES result.

2.3. Characterisation

Scanning electron microscope (SEM) images were acquired on an FEI Quanta450 microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) images were obtained on an FEI Tecnai G2 F20 microscope. High-angle annular dark-field scanning
transmission electron microscopy (HAADF-STEM) images were taken on a Titan Themis G2 TEM microscope (Thermo Scientific, USA) under 300 kV with probe and image spherical aberration correctors, and the Energy-Dispersive X-ray spectrometry (EDX) spectra and mappings were acquired by using the equipped Super-X detector system. X-ray diffraction (XRD) measurements were conducted on a D/max-2200PC diffractometer (Rigaku) using Cu Kα radiation operated at 40 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on Thermo Kalpha using a monochromated Al Kα radiation (1486.6 eV). Electron paramagnetic resonance (EPR) measurements were performed on a Bruker EMX plus model spectrometer operating at the X-band frequency at 298 K, with an operating frequency of 9.85 GHz and a microwave power of 2 mW. Thermogravimetric analysis (TGA) was performed on TG-Q50 (TA, USA) thermal analyzer heating from room temperature to 900 °C at the rate of 10 °C min⁻¹. Elemental analysis of Pd in samples was tested by inductively coupled plasma atomic emission spectrometry (ICP-AES) on an Optimisa 7300 DV.

Fourier transform infrared (FTIR) spectra were acquired on a Nicolet iS50 (Thermo Scientific) spectrometer. CO titration experiments were performed on the Micromeritics AutoChem II 2920 apparatus with a TCD detector. 100 of the sample was initially treated under argon at 200 °C for 1 h before it was cooled down to 50 °C. Then, pulse injection of CO was conducted on the pre-treated sample. The metal dispersion was calculated assuming a stoichiometry of one CO molecule per surface metal atom. Diffuse reflectance infrared Fourier transform (DRIFT) spectra of chemisorbed CO were recorded in an in-situ diffuse reflectance cell on a Nicolet iS50 spectrometer (Thermo Scientific). Each spectrum was collected for 60 scans at a resolution of 5 cm⁻¹. The sample (100 mg) was pretreated in the cell with a flowing He gas (50 mL/min) at 200 °C for 1 h. The temperature was then cooled down to room temperature for CO chemisorption. After collecting a background spectrum of the sample under the He gas, the cell was switched to 1 vol% CO/He (50 mL/min) mixed gas for CO adsorption for 1 h, followed by purging with the He gas. The collected spectra were subtracted from the sample background spectra in He gas to obtain the spectra for chemisorbed CO. Adsorption of organic substrates on samples was tested on a Shimadzu UV-VIS UV-2600 spectrometer. Brunauer-Emmett-Teller (BET) measurements were performed on micromeritics ASAP2460 analyzer and the samples were degassed at 573 K for 6 h before the measurement.

XAS measurements for the Pd K-edge were performed on beamline 20-BM-B at the Advanced Photon Source at Argonne National Laboratory. Measurements were carried out in fluorescence mode with electron energy of 7 GeV and an average current of 100 mA. The obtained XAFS data was processed in Athena (version 0.9.26) for background, pre-edge line and post-edge line calibrations. Then Fourier transformed fitting was carried out in Artemis (version 0.9.26). The k² weighting, k-range of 3–12 Å⁻¹ and R range of 1–3 Å were used for the fitting Pd foil and PdO; k-range of 2–10 Å⁻¹ and R range of 1–3 Å was used for the fitting of Pd samples. The four parameters, coordination number, bond length, Debye-Waller factor and Edge shift (CN, R, σ², ΔEds) were fitted without anyone parameter being fixed, constrained, or correlated. For Wavelet Transform analysis, the χ(k) exported from Athena was imported into the Hama Fortran code. The parameters were listed as follow: R range, 1–4 Å, k range, 0–13 Å⁻¹; k weight, 2; and Morlet function with k = 10, σ = 1 was used as the mother wavelet to provide the overall distribution. For Wavelet Transform analysis, the χ(k) exported from Athena was imported into the Hama Fortran code. The parameters were listed as follow: R range, 1–4 Å, k range, 0–13 Å⁻¹; k weight, 2; and Morlet function with k = 10, σ = 1 was used as the mother wavelet to provide the overall distribution.

### 2.4. Catalytic evaluation

The catalytic reaction was operated using 25 mL of Schlenk glass vessel tubes under 1 atm O₂ atmosphere. For epoxidation of trans-stilbene, 100 μmol of trans-stilbene and 0.05 μmol of catalyst (a molar ratio of 2000:1 for trans-stilbene: Pd) were dispersed in 5 mL of N, N-dimethylethamide in a vessel tube and the reaction was performed at 120 °C with a stirring speed of 1000 rpm. An O₂ balloon was employed to blow about 1 atm O₂. Over the course of the reaction, the liquid product was separated by filtration for analysis by gas chromatography (Techcomp GC-7980) with an HP-5 capillary column (30 m × 0.32 mm i. d. × 0.25 μm film thickness) equipped with a flame ionization detector (FID). Each catalytic reaction was performed three times. The error bars represent the standard deviation and the corresponding relative standard deviation is within 5%. The turnover frequency (TOF) values of the samples were obtained at 10 % conversion of the substrate and based on the total Pd loading in the catalyst [23,39,40].

For the hot filtration test, the catalytic reactions studied in the present work were stopped after the conversion ratios were in the range between 20 % and 30 %. The catalyst was then removed by filtration and the supernatant in each catalytic system was allowed to stir under reaction conditions and the conversion was checked by GC after a certain period. For recovering and reusing the catalyst, the reaction mixture was centrifuged and the solid catalyst was separated and washed with ethanol before vacuum dried at 80 °C. Then, the spent catalyst was collected for the next catalytic cycle with a fresh substrate. Kinetic studies for the reaction on Pd₁/γ-Al₂O₃ and γ-Al₂O₃ in the temperature range of 393 to 423 K were performed in a kinetically controlled regime. The reaction rate (k) was calculated by dividing the number of the reacted trans-stilbene by the reaction time. By plotting lnk as a function of 1/T, an Arrhenius plot was achieved. With the slope and intercept of the Arrhenius plot, the apparent activation barrier (Ea) can be obtained.

### 2.5. Density-functional theory calculations

Density-functional theory (DFT) calculations were performed using the Dmol³ software package based on the linear combination of atomic orbitals (LCAO) method [41,42]. Electron-ion interactions were described using the DFT Semi-core Pseudopotentials (DSSP) pseudopotentials. A double numerical (DND) basis set was applied to expand the wave functions with an orbital cutoff of 3.1 Å for H, 3.3 Å for O, 3.7 Å for C, 4.8 Å for Al, 4.5 Å for Pd, respectively. For the electron-electron exchange and correlation interactions, the functional parametrized by Perdew-Burke-Ernzerhof (PBE) [43], a form of the general gradient approximation (GGA), was employed. The van der Waals interaction was described using the DFT-D2 method proposed by Grimme [44].

The surface of γ-Al₂O₃ (1 1 1) plane was simulated with the slab model and a sufficiently large vacuum region of 15 Å was applied to separate the periodic images. For the geometry optimizations, the bottom atoms were fixed at the bulk position. The Brillouin-zone integrations were conducted using Monkhorst-Pack (MP) grids of special points. A K-point sets with a separation of 0.07 Å⁻¹ was used for all the model surface cells. The convergence criterion for the electronic self-consistent field (SCF) loop was set to 10⁻⁵. The atomic structures were optimized until the residual forces below 0.003 Ha Å⁻¹. The transition state was located via the quadratic synchronous transit (QST) method with a tolerance of 0.003 Ha Å⁻¹.

The adsorption energies, E_{ads}, were calculated using the following equation:

\[
E_{\text{ads}} = E_{\text{adsorbate-surface}} - E_{\text{adsorbate}} - E_{\text{surface}}
\]

where \(E_{\text{adsorbate-surface}}\) is the total energy of surface covered with adsorbates, \(E_{\text{adsorbate}}\) is the energy of adsorbate, and \(E_{\text{surface}}\) is the energy of clean surface. A negative value of \(E_{\text{ads}}\) corresponds to a release of energy, i.e. adsorption on the surface is energetically favorable.
3. Results and discussions

3.1. Synthesis and characterizations of the singly dispersed Pd catalysts

In a typical synthesis (Fig. 1a and S1 in Supporting Information), γ-AlOOH was synthesized by a solvent-thermal method (Fig. S2). Subsequently, it was treated by defect engineering to yield defective γ-AlOOH (Fig. S3). Then, a photochemical reduction approach was conducted by irradiation with UV to give atomically dispersed palladium over defective γ-AlOOH support (Pd₁/γ-AlOOH) with Pd loading up to 0.32 wt%. In Fig. 1b and c, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images show the leaf-like morphology of Pd₁/γ-AlOOH. Atomic force microscope (AFM) image shows a thickness of 3.2 nm (Fig. 1c, inset). The lattice spacing of 0.28 nm in high-resolution transmission electron microscopy (HR-TEM) image is assigned to the (1 0 0) lattice planes of γ-AlOOH (Fig. 1d). Aberration-corrected high-angle annular dark-field scanning transmission electron microscope (AC HAADF-STEM) analysis (Fig. 1e) confirms that the singly dispersed palladium atoms are distinguished as bright dots evenly dispersed over the support, without the presence of any visible metallic nanoclusters. In addition, the intensity profiles in different areas further verified the existence of isolated palladium atoms. The energy-dispersive X-ray elemental mapping results demonstrate that the O, Al, and Pd elements are homogeneously distributed over the support (Fig. 1f). The dispersion of Pd atoms in Pd₁/γ-AlOOH was tested by CO titration and the results were calculated to be nearly 97 % (Table S1), implying the vast majority of palladium atoms are atomically dispersed [23,29].

X-ray diffraction (XRD) patterns show typical peaks that can be indexed to γ-AlOOH (JCPDS No. 21-1307), as shown in Fig. 2a. The small peak at 18.5° is assigned to an Al(OH)₃ impurity [45]. Typical metallic palladium peaks are noticed on Pd NPs/γ-AlOOH and can also be found in TEM and HAADF-STEM images (Fig. S4). But no reflections associated with metallic palladium peak were observed on Pd₁/γ-AlOOH, excluding the presence of large Pd nanoparticles. X-ray photoelectron spectroscopy (XPS) measurements were performed and the results show the presence of C, O, Al, and Pd elements in Pd₁/γ-AlOOH (Fig. S5a). In the C 1s spectrum (Fig. S5b), there are three components: 285.0 eV originates was from C–C bonds, 286.3 eV from C–OH species, and the peak at 288.7 eV is associated with C=O groups [45]. For the O1s spectrum (Fig. S5c), three peaks at 530.0, 531.3, and 532.6 eV are ascribed to lattice oxygen, oxygen vacancy, and hydroxyl species, respectively. Fig S5d shows the Al 2p peak at 74.2 eV. For Pd 3d spectrum (Fig. S5e): the Pd₅/₂ peak of Pd₁/γ-AlOOH was observed at a binding energy of 336.3 eV, implying the palladium in the catalyst carried a positive charge and the valence state of the Pd was between Pd⁰ and Pd²⁺ [46–48]. No Cl 2p signal is observed by XPS measurement (Fig. S5f), suggesting the removal of Cl⁻ on Pd under UV treatment.

To verify the atomic dispersion of palladium atoms over the defective γ-AlOOH support, X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements were conducted (Fig. 2b-f). The XANES spectra in Fig. 2b show the energy absorption threshold of Pd₁/γ-AlOOH situated between Pd foil and PdO, implying the valence of the Pd atom in the catalyst is positively charged.
and between Pd$^0$ and Pd$^{2+}$ [38,49]. This agrees well with the XPS results. In Fig. 2c, the EXAFS (without phase correction) curve of Pd foil displays a notable peak at 2.48 Å that can be attributed to Pd–Pd coordination. For PdO, it exhibits two main peaks at 1.56 Å and 2.98 Å that can be assigned to Pd–O and Pd–Pd in the first and second coordination shells, respectively. Pd$_1$/$\gamma$-AlOOH only shows one dominant peak at 1.52 Å associated with Pd–O shell of PdO reference without Pd–Pd coordination, confirming the presence of predominantly singly dispersed Pd atoms over the defective $\gamma$-AlOOH. This is in good agreement with the STEM and CO chemisorption results. Additionally, no observable Pd–Cl coordination was found around 1.84 Å [48,50], in line with the XPS results. EXAFS fitting was conducted to obtain the structural configuration of palladium atom in Pd$_1$/$\gamma$-AlOOH (Fig. 2d and Table S2). The coordination number of palladium atom with its surrounding oxygen atoms was calculated to be 4.0 ± 0.7, implying one palladium atom was coordinated to four oxygen atoms. The mean Pd-O bond length was approximately 2.03 Å (Table S2). Wavelet transform extended X-ray absorption fine structure (WT-EXAFS) analysis was further conducted to identify the dispersion of palladium species (Fig. 2e). Pd$_1$/$\gamma$-AlOOH exhibits a single intensity maximum at around 5.3 Å$^{-1}$ that can be assigned to the Pd–O contribution of the first nearest-neighbor coordination shell. In addition, no detectable Pd–Pd signals are found compared with that of Pd foil and PdO references. This indicates the isolated nature of palladium atoms anchored on the defective $\gamma$-AlOOH through Pd–O bonding. The oxidation state of Pd in Pd$_1$/$\gamma$-AlOOH was fitted and the average valence state is approximately +1.17 (Fig. 2f), meaning an oxidized state of the single palladium atom.

CO-absorbed diffuse reflectance infrared Fourier transform spectroscopy (CO-DRIFTS) was performed to further confirm the atomic dispersion of palladium atoms on the catalyst (Fig. 2g) [51,52]. We observe only one sharp peak at 2115 cm$^{-1}$ in the DRIFT spectrum of Pd$_1$/$\gamma$-AlOOH, which can be ascribed to the stretching frequency of linear-adsorbed CO on the isolated Pd sites in a top configuration [53]. For Pd NPs/$\gamma$-AlOOH, it exhibits one broad peak at 2056 cm$^{-1}$ which is associated with the bridge-adsorbed CO on Pd clusters [22]. An electron paramagnetic resonance (EPR) measurement was performed to detect any unpaired electrons in the samples (Fig. 2h). Compared with defective $\gamma$-AlOOH and Pd NPs/$\gamma$-AlOOH, a sharp signal at a g value of 2.003 was observed. This means that, compared to other control samples, there is a larger amount of unpaired electrons in Pd$_1$/$\gamma$-AlOOH [48,54,55]. Taken together, the above characterization results unambiguously confirmed the atomically dispersed palladium atoms have successfully deposited over the defective $\gamma$-AlOOH.

Fourier transform infrared (FT-IR) spectra of the catalysts are shown in Fig. S6. A broad band at 3320 cm$^{-1}$ in all the samples is associated with the –OH stretching mode, implying a large number of hydroxyl groups on the sample surfaces [56]. A shoulder peak at 3100 cm$^{-1}$ and a sharp peak at 1067 cm$^{-1}$ can be assigned to the stretching and bending modes of Al–OH [57]. The peak at 1430 cm$^{-1}$ is related to the vibration overtone of the –OH groups on the sample surfaces [57]. Two bands at 749 and 633 cm$^{-1}$ show the vibration mode of AlO$_6$ [56]. These results confirmed that the lattice framework of $\gamma$-AlOOH support remained unchanged following doping by palladium. The results of N$_2$ adsorption/desorption isotherms and pore size distributions are shown in Fig. S7.
Thermogravimetric analysis (TGA) was conducted and the weight loss consists of three similar phases for γ-AlOOH and Pd1/γ-AlOOH (Fig. S8). Specifically, the first phase between room temperature and 150 °C is attributed to the removal of physically adsorbed water. The second phase between 150 and 500 °C is associated with the transformation of boehmite to transition γ-Al2O3. The third phase in the range 500 to 900 °C is caused by the elimination of residual hydroxyl groups.

3.2. Investigation of catalytic performance

The catalytic performance of Pd1/γ-AlOOH for epoxidation of trans-stilbene was examined as a model reaction under mild conditions of 1 atm O2 at 120 °C (Fig. 3). The O2 was used as the oxidant and no other additives were introduced into the reaction. Home-made Pd1/C3Na2, Pd1/N-C, and commercial Pd/C (5 wt%) were characterized and used as control samples (Figs. S9–11). The solvent impact was initially investigated and N,N-dimethylacetamide (DMAC) was selected as the appropriate solvent (Fig. 3a and Table S3). We assume that the DMAC might facilitate the adsorption and activation of trans-stilbene for the epoxidation reaction. The γ-AlOOH support was initially tested and low catalytic activity was observed (Table S4). The use of Pd1/γ-AlOOH showed exceptional catalytic activity with a high turnover frequency (TOF) value of 416 h⁻¹, along with a conversion of 84 % and a selectivity of 99 % toward trans-stilbene oxide within 4 h at a molar ratio of 1:2000 (Pd:trans-stilbene), as shown in Fig. 3b,c and S12. Hot filtration and ICP-AES tests confirmed no palladium leaching was occurred (Fig. S13). For PdNPs/γ-AlOOH, it only delivered a TOF value of 137 h⁻¹, with 56 % conversion and 61 % selectivity toward trans-stilbene oxide over the same period.

To better understand the critical role of UV treatment in the synthesis, we deliberately prepared a single atom catalyst by the same method but without UV radiation (Fig. S14). The Pd: Cl molar ratio in this catalyst (here denoted as PdCl2/γ-AlOOH) was measured to be ~1:2 as confirmed by elemental analysis. The catalytic activity of PdCl2/γ-AlOOH was similar to that of γ-AlOOH support (Fig. S12) but much lower than that of Pd1/γ-AlOOH. Next, ICP-AES and Mohr titration methods were used to test the amount of Pd and Cl ions in the reaction solvent, respectively. We found the Pd: Cl molar ratio was approximately 1:1.8. Therefore, we assume that during the catalytic reaction at 120 °C under 1 atm O2, a certain amount of PdCl2 in PdCl2/γ-AlOOH was leached into the reaction solvent. To confirm this point, we tested the recycling ability of PdCl2/γ-AlOOH (Fig. S15) and found obvious activity decay for PdCl2/AlOOH. Moreover, the corresponding catalytic performance was similar to that of γ-AlOOH. Together, the above evidence suggests that the UV treatment facilitates the removal of Cl ions on Pd and stabilizes the Pd atoms by forming Pd-O bonds over the γ-AlOOH support, and the poor catalytic performance of PdCl2/γ-AlOOH can be attributed to the leaching of PdCl2 species.

Other samples showed extremely low catalytic activity to give trace products. For example, H2PdCl4 showed a conversion of 57 % and selectivity of 91 % to trans-stilbene oxide, but with a low TOF of 144 h⁻¹. For the commercial Pd/C, a lower conversion of 47 % and selectivity of...
86% to the target product were accomplished, with a TOF of 131 h⁻¹. No catalytic activity was observed for Pd₁/C₃N₄. We found Pd₁/γ-AlOOH is very active for this reaction, as it required relatively mild conditions and shorter reaction time than those previously reported works (Table S5). Moreover, it has excellent recycling stability (10 cycles) in both conversion and selectivity to yield trans-stilbene oxide (Fig. 3d). Characterization of the recovered Pd₁/γ-AlOOH following the recycling test showed no obvious change (Fig. S16), along with no detectable metal leaching in the reaction solvent.

Kinetic studies of trans-stilbene epoxidation over Pd₁/γ-AlOOH and γ-AlOOH in the temperature ranges of 393 K to 423 K (Fig. 3e and S17) were conducted in kinetically controlled regimes. The Pd₁/γ-AlOOH exhibits a much lower Eₐ of 45.3 kJ mol⁻¹ compared to that of γ-AlOOH (Eₐ = 93.2 kJ mol⁻¹). This indicates that Pd₁/γ-AlOOH was more active and can effectively suppress the activation energy to trigger the reaction. Next, an adsorption test (Fig. 3f) was performed and the results imply the adsorption tendency of trans-stilbene over Pd₁/γ-AlOOH is higher than those of γ-AlOOH and Pd NPs/γ-AlOOH, implying a favorable interaction between trans-stilbene and Pd₁/γ-AlOOH.

Large scale trans-stilbene epoxidation reaction was carried out (scale-up 60-fold). Two batches of reactions on milligram and gram-scales yielded the target products in excellent conversion and selectivity (Fig. 3g). In addition, this catalyst has a satisfactory shelf-life of at least 12 months. Without any activation treatment, the stored catalyst (Fig. 3h). For the above reactions, we may conclude that the singly dispersed Pd atoms with the unique coordination environment over defective γ-AlOOH are responsible for the remarkable catalytic activity.

3.3. Insight into the catalytic behavior

Density functional theory (DFT) calculations were performed to explore detailed insight into the unique catalytic activity of Pd₁/γ-AlOOH. The electron transfer in Pd₁/γ-AlOOH was initially studied and the values of Bader charge were calculated (Fig. 4a). The Pd atom is an electron donor, containing a fewer number of charges than its atomic reference, while O atoms in proximity to the Pd atom are electron acceptors. Quantitatively, the Pd atom is positively charged with 0.92 e, in line with the XPS and XAFS results. The charge density difference analysis also shows that the electrons transfer from the Pd atom to adjacent O atoms (Fig. 4b and Fig. S18). This would result in a favorable interaction between the Pd₁-O₂ and the reactant. The calculated density of states (DOS) of γ-AlOOH and Pd₁/γ-AlOOH was further investigated (Fig. 4c,d). The emerging Pd states are located near 0 eV below the Fermi energy. Additionally, the rise of states at the Fermi energy is reduced by the Pd atom and its surrounding O atoms, which might lead to the enhanced catalytic activity.

The energy profiles for the epoxidation of trans-stilbene over Pd₁/γ-AlOOH and γ-AlOOH were calculated (Fig. 4e and Fig. S19). We found the trans-stilbene initially approaches Pd₁/γ-AlOOH via a non-planar configuration, where van der Waals interactions play an important role in the adsorption step. We first studied the competitive adsorption between O₂ and trans-stilbene over γ-AlOOH and Pd₁/γ-AlOOH, respectively. The adsorption energies of O₂ on γ-AlOOH and Pd₁/γ-AlOOH (Fig. S20) were calculated to be -11.78 and -14.62 eV, respectively, suggesting the O₂ is easier adsorbed on Pd₁/γ-AlOOH and then be activated. The adsorption energies of trans-stilbene on two samples are shown in Fig. S21. The significant difference in adsorption energy suggests that there is almost no competitive adsorption between O₂ and trans-stilbene over the two catalysts. For both catalysts’ surfaces, O₂ molecule adsorption is the first step in both reaction pathways, and trans-stilbene favors to adsorb on Pd₁/γ-AlOOH over γ-AlOOH in the

![Fig. 4. Catalytic mechanism study of Pd₁/γ-AlOOH for trans-stilbene epoxidation. (a) Bader charge. (b) Side view of charge density difference. The yellow and green regions represent the charge depletion and accumulation regions, respectively. The isosurface value is 0.003 e/Å³. The calculated density of states of (c) γ-AlOOH and (d) Pd₁/γ-AlOOH. (e) Reaction pathway and corresponding energy profiles of Pd₁/γ-AlOOH and γ-AlOOH in trans-stilbene epoxidation. The red line refers to the reaction on Pd₁/γ-AlOOH; the black line refers to the reaction on γ-AlOOH. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](attachment://fig4.png)
following step. As shown in Fig. S22, the O–O bond length of the adsorbed O$_2$ species on Pd$_1$/γ-AlOOH was measured to be 1.30 Å, which is in excellent agreement with the reported bond length (~1.32 Å) of superoxide-like (O$_2^-$) species. For γ-AlOOH, the O$_2$ connects one Al atom with an O–O bond length of 1.41 Å.

The oxidation of trans-stilbene begins with an electrophilic attack of the O$_2$ species toward the C–C bond of trans-stilbene. The adsorption energies of trans-stilbene on O$_2$ pre-adsorbed γ-AlOOH and Pd$_1$/γ-AlOOH were investigated (Fig. S23), and the results were calculated to be −0.03 and −0.70 eV, respectively. This implies the trans-stilbene favors to adsorb on O$_2$ pre-adsorbed Pd$_1$/γ-AlOOH. As shown in Fig. S24, the O–O bond elongates from 1.30 Å in adsorbed O$_2$ on Pd$_1$/γ-AlOOH to 1.66 Å following trans-stilbene binding with one O atom. The O–O bond breaks after one O atom interacts with trans-stilbene, affording trans-stilbene oxide and a residual O atom on the bridge site between one Pd atom and one Al atom with bond lengths of 1.90 Å and 1.77 Å, respectively. This type of structure would eventually facilitate the releasing of the O atom in the next catalytic cycle to regenerate the active sites in Pd$_1$/γ-AlOOH. For γ-AlOOH (Fig. S25), the O–O bond elongates from 1.41 Å to 1.43 Å when trans-stilbene binding with one O atom. The O–O bond breaks to give a trans-stilbene oxide and a residual O atom connected with two Al atoms with bond lengths of 1.74 Å and 1.73 Å, respectively. Then, the desorption energies of trans-stilbene oxide on O-adsorbed γ-AlOOH and Pd$_1$/γ-AlOOH (Fig. S26) were calculated to be 4.01 and −0.08 eV, respectively. This means that the trans-stilbene oxide would leave the active sites of Pd$_1$/γ-AlOOH much easier due to weak adsorption energy relative to that of γ-AlOOH.

In both cases, the formations of trans-stilbene oxide are exothermic (Fig. 4e). In the case of Pd$_1$/γ-AlOOH, three energy barriers were calculated to be 0.58, 0.42, and 0.95 eV, respectively. For γ-AlOOH, the corresponding energy barriers were 1.01, 0.35, and 1.14 eV, respectively, most of which are significantly higher than those of Pd$_1$/γ-AlOOH. In good agreement with the experimental results, the Pd$_1$/γ-AlOOH has been demonstrated a favorable role in catalyzing this reaction due to a much lower energy barrier and appropriate adsorption behaviors.

3.4. Substrate scope of the isolated Pd catalysts

We next sought out to evaluate the scope and efficiency of Pd$_1$/γ-AlOOH in the selective epoxidation of a variety of aromatic olefins including substituted cis- and trans-stilbene derivatives (Fig. 5, Table S6). These epoxides are industrially important intermediates for the synthesis of organic molecules. To our delight, epoxidation of substituted cis- and trans-stilbene derivatives afforded the desired products in good to excellent efficiency. Specifically, substituted cis-stilbene derivatives yielded the corresponding products in extremely high conversion (~83%) and selectivity (99%), indicating our catalyst is also efficient in catalyzing cis-stilbene derivatives. Similarly, trans-stilbene derivatives bearing methyl-, phenyl-, isopropyl, tertiary butyl, and bromine substitutes were selectively converted to the corresponding epoxides with satisfactory efficiency (54 to 82% Conv. & 99% Sel.). This implies that a broad range of functional groups were tolerated employing this catalyst in this transformation.
4. Conclusion

In summary, we report a facile and efficient room-temperature photoinduction strategy to construct palladium single atoms over defective γ-AlOOH nanoflake as a bench-stable catalyst. The electronic features of the palladium atoms by the metal-support interactions have been elucidated through advanced characterizations and DFT calculations. We found that the introduction of the oxygen vacancy in γ-AlOOH can effectively anchor and confine palladium atoms at the atomic level. The UV treatment is a critical step for the removal of Cl ions on Pd and photoinduction strategy to construct palladium single atoms over as-prepared Pd stabilization of Pd atoms by forming Pd-O bonds over the features of the palladium atoms by the metal-support interactions have exceptional reduction at the atomic level, which may be applied to the design of other catalyst systems.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References


