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1 General Negative Pressure Annealing Approach for Creating
2 Ultra-high-loading Single Atom Catalyst Libraries

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29 **Abstract**

30 Catalyst systems populated by high-density single atoms are crucial for improving
31 catalytic activity and selectivity, which can potentially maximize the industrial
32 prospects of heterogeneous single-atom catalysts (SACs). However, achieving
33 high-loading SACs with metal contents above 10 wt% remains challenging. Here we
34 describe a general negative pressure annealing strategy to fabricate ultrahigh-loading
35 SACs with metal contents up to 27.3 ~ 44.8 wt% for 13 different metals on a typical
36 carbon nitride matrix. Furthermore, our approach enables the synthesis of
37 high-entropy single-atom catalysts (HESACs) that exhibit the coexistence of multiple
38 metal single atoms with high metal contents. In-situ aberration-corrected
39 HAADF-STEM (AC-STEM) combined with ex-situ X-ray absorption fine structure
40 (XAFS) demonstrate that the negative pressure annealing treatment accelerates the
41 removal of anionic ligand in metal precursors and boosts the bonding of metal species
42 with N defective sites, enabling the formation of dense N-coordinated metal sites.
43 Increasing metal loading on a platinum (Pt) SAC to 41.8 wt% significantly enhances
44 the activity of propane oxidation towards liquid products, including acetone, methanol,
45 and acetic acid *et al.* This work presents a straightforward and universal approach for
46 achieving many low-cost and high-density SACs for efficient catalytic
47 transformations.

48 **Keywords:** single-atom catalysts libraries, ultrahigh metal loading, universal
49 synthesis, negative pressure synthesis

50

51 **Introduction**

52 The development of advanced catalysts must meet the requirements of future
53 sustainable chemistry, but their commercial potential is contingent on high reaction
54 efficiency and maximal atom economy¹. Single atom catalysts (SACs), integrating
55 atomically dispersed metal centers with tunable coordination structures over
56 appropriate supports, exhibit remarkable activity and unique selectivity in
57 electrocatalysis, photocatalysis, and thermal-catalysis²⁻⁷. Moreover, the maximal
58 atom utilization efficiency of this class of catalysts greatly improves the atom
59 economy, especially for noble-metal-based catalysts. Therefore, it is beneficial for
60 sustainable chemistry⁸⁻¹². Given these merits of SACs, tremendous efforts have been
61 devoted to developing a variety of synthesis methods for many technical applications
62¹³⁻¹⁶. Nevertheless, considering their high surface energy, the SACs are generally
63 constructed with low metal loadings to circumvent the aggregation of metal atoms
64 into metal clusters or nanoparticles¹⁷. This results in a low metal areal density. Taking
65 the Pt SACs as a typical example, they display impressive activity and selectivity in
66 the thermal-driven activation of light alkane¹⁸⁻²⁰. A literature analysis shows that the
67 metal contents of most Pt SACs are 2 wt% or below (Figure. 1a and Supplementary
68 Table 1)²¹⁻²⁴, and the Pt areal density of most catalysts are hard to surpass 1.5
69 atoms/nm² (Supplementary Table 1). In this case, the SACs with insufficient areal
70 density of active sites not only limit their overall catalytic performance but also
71 decrease the productivity per unit volume or mass of catalysts. Therefore, the
72 development of a universal synthesis strategy for accessing SACs with high metal
73 loading and sufficient areal density is significant in this field, but challenging²⁵⁻²⁸.

74 Recently, several strategies have been reported to construct ultra-high-loading
75 (UHL, higher than 10 wt%) SACs on different supports²⁹. Wang et al adopted
76 crosslinking carbon quantum dots as supports to provide abundant anchoring sites to
77 favor the formation of high densities of single metal atoms³⁰. Lu reported a two-step
78 annealing strategy to obtain high-loading SACs on distinct carbon and metal oxide
79 supports³¹. This strategy effectively controls the bonding of metal precursors with the
80 carrier and prevents thermal-induced aggregation of metal into nanoparticles. Zou

81 developed a laser planting method to simultaneously create defects and anchor metal
82 atoms, eventually achieving high-loading single metal atoms on carbon, TiO₂, and Cu
83 NPs³². In contrast with these pioneering works, a facile and routine available
84 synthetic strategy without the using of expensive equipments is highly attractive for
85 the practical preparation and application of high-loading SACs.

86 Herein, we report a general negative pressure annealing approach to construct
87 UHL-SACs libraries, consisting of 13 different transition metal SACs supported on
88 polymeric carbon nitride (PCN) with ultra-high metal loading. Based on the XAFS
89 and in-situ aberration-corrected HAADF-STEM (AC HAADF-STEM), the negative
90 pressure and thermal treatment enable fast dispersion of metal atoms over the support
91 rather than aggregation, which are furtherly trapped by nitrogen sites (Figure 1b). As a
92 result, 13 different SACs are successfully prepared on PCN with ultra-high metal
93 loadings of 27.3 ~ 44.8 wt%. Moreover, SACs and high-entropy single atoms (HESAs)
94 composed of multiple metal sites with high metal loadings can be also readily
95 obtained on N-doped carbon (NC). These evidences strongly validate the universality
96 and scalability of the negative pressure annealing strategy for constructing a wide
97 range of low-cost and high-areal-density SACs.

98

99 **2. Results and Discussion**

100 **2.1. Synthesis and structure investigation of Pt UHL-SACs**

101 Given the wide applications of Pt-based catalysts³³, UHL-SACs of Pt are initially
102 investigated. The PCN is used as the substrate firstly, which exhibits characteristic
103 diffraction peaks at 2 θ of 27.6 and 60.0 degrees (Supplementary Figure 1). The C 1s
104 and N 1s XPS spectra provide additional confirmation of the formation of C-N
105 bonding (Supplementary Figure 2) with a N/C atomic ratio of 1.05, establishing ample
106 coordinate nodes for UHL-SAC fabrication. The platinum-based UHL-SACs, denoted
107 as Pt SACs/PCN, were synthesized by impregnating chloroplatinic acid onto PCN and
108 subsequent annealing in a vacuum. To elucidate the crucial role of the negative
109 pressure environment, a reference sample was prepared by annealing in Ar flow at
110 101 KPa (Pt NPs/PCN). The annealing pressure shows negligible impact on the

111 apparent morphology and chemical constitution (Supplementary Figure 3-5) of
112 Pt-based catalysts compared with the PCN substrate. Moreover, the color of these two
113 samples turns black from yellow following Pt deposition (Supplementary Figure 6).
114 Based on ICP analysis, the Pt contents are measured as 41.8 wt% and 40.9 wt% for Pt
115 SACs/PCN and Pt NPs/PCN, respectively (Supplementary Table 2).

116 The TEM image of the Pt NPs/PCN (Figure 1c) illustrates an accumulation of the
117 metal particles with sizes around 10-50 nm. XRD pattern of Pt NPs/PCN (Figure 1d)
118 showcases the distinctive diffraction peaks characteristic of crystalline Pt, revealing
119 the formation of Pt particles during annealing under ambient pressure. On the contrary,
120 an absence of discernible diffraction peaks related to crystalline Pt was observed for
121 Pt SACs/PCN. Additionally, the TEM image of Pt SACs/PCN (Figure 1e and
122 Supplementary Figure 7) reveals no observable Pt particles, underscoring the effective
123 prevention of metal aggregation under vacuum annealing conditions. To delve into the
124 local structure of Pt sites in Pt SACs/PCN, an AC HAADF-STEM measurement was
125 employed. Figures 1f and g reveal dense bright spots assigned to isolated Pt atoms are
126 uniformly distributed over PCN, affirming the atomic dispersion of Pt sites on PCN
127 randomly (Figure 1h). Moreover, the average areal density of isolated Pt is estimated
128 to 6.5 atoms/nm^2 based on the measured BET surface area of the PCN
129 (Supplementary Figure 8-9), similar with the pixel statistics of Figure 1g (5.6
130 atoms/nm^2). These results identify the Pt SACs/PCN as one of the catalysts with the
131 highest density of isolated Pt sites. Furthermore, EDS element mapping (Figure 1i-j)
132 affirm the uniform distribution of Pt, reinforcing the accuracy of these statistical
133 findings. Figure 1k presents the XPS results of Pt SACs/PCN, which reaffirms the
134 ultra-high Pt loading (survey) with a positive oxidation state evidenced by the Pt $4f_{7/2}$
135 binding energy of 72.7 eV. The XANES spectrum of Pt SACs/PCN, positioning the
136 white line intensity between Pt foil and PtO₂, further verifies the partially positive
137 oxidation state of Pt (Figure 1l). The FT EXAFS spectra (Figure 1m) are exploited to
138 elucidate the coordination environment of Pt sites. The Pt SACs/PCN exhibits a
139 dominant peak assigned to Pt-N coordination at 1.6 Å, with the absence of Pt-Pt
140 coordination at 2.5 Å. This result aligns seamlessly with wavelet transformation

141 results (Figure 1n), identifying the N-coordinated single-atom Pt sites in Pt
142 SACs/PCN. These findings serve as conclusive evidence for successfully fabricating
143 ultra-high loading single-atom catalysts via the negative pressure annealing approach.

144 To shed light on the formation of Pt SACs/PCN, the structure evolution of Pt
145 species during the annealing process was investigated by temperature-dependent
146 in-situ AC HAADF-STEM, ex-situ XAFS, and XPS, in vacuum and Ar condition
147 respectively. The temperature-dependent in-situ AC HAADF-STEM images in
148 vacuum conditions are shown in Figure 2a and Supplementary Figure 10. Dense
149 bright spots are observed at 20 °C, revealing the uniform distribution of Pt precursor
150 on the substrate. Moreover, no clusters and particles are generated along the
151 temperature increasing from 20 to 400 °C, even after the sample is kept at 400 °C for
152 359 s. On the contrary, when annealing in the Ar flow, the atomic Pt can only be
153 stabled below 300 °C (Figure 2b). Observable Pt particles are generated when the
154 temperature reaches to 300 °C. These particles grow bigger when the temperature is
155 further increased to 400 °C. The corresponding EDS element measurements at
156 different temperatures show a faster increase of Pt/Cl atomic ratio in vacuum than in
157 Ar (Supplementary Table 3), demonstrating the accelerated Cl removal from Pt
158 precursor in negative pressure conditions.

159 The coordination changes are investigated by XAFS. Figure 2c shows the Pt *L*-edge
160 FT EXAFS spectra in vacuum conditions at different temperatures. Pt-Cl coordination
161 is detected at 200 °C, which transfers to Pt-N coordination at 300 °C. Moreover, no
162 Pt-Pt coordination is detected even at 400 °C, excluding the formation of Pt-Pt
163 bonding. For samples annealed under Ar environment (Figure 2d), the dominant Pt-Cl
164 coordination at 200 °C is significantly decreased at 300 °C, companying with the
165 formation of Pt-Pt coordination, which further takes the predominance at 400 °C. The
166 FT EXAFS results are in good agreement with the in-situ AC HAADF-STEM and
167 EDS results, demonstrating the different transformation pathways of Pt precursor in
168 vacuum and Ar environment. The oxidation states of Pt under different annealing
169 pressures show down-hill tendencies along the increasing temperature (Figure 2e-f),
170 which may due to the loss of Pt-Cl bonding and the formation of Pt-N or Pt-Pt

171 coordination. However, for the sample annealed in Ar, the Pt oxidation state is lower
172 than that annealed in vacuum (Figure 2g). This can be attributed to the weaker
173 electronegativity of Pt than N. These results illustrate the evolution of Pt UHL-SACs,
174 that is Pt-Cl coordination rapidly dissociates at relatively low temperatures to generate
175 active Pt species, and the vacuum condition greatly suppresses the metal aggregation
176 via promoting the Pt-N coordination at relatively high temperatures, thus enables the
177 formation of high-density Pt SACs.

178 **2.2. Universally Preparing Metal UHL-SACs**

179 To reveal the generality of the negative pressure annealing approach, this synthetic
180 process is extended to 12 other single-atom metal sites on PCN (M SACs/PCN, M=V,
181 Cr, Mn, Fe, Co, Ni, Cu, Zn, Nb, Mo, Ir and Au, Figure 3a). The metal loadings of all
182 these catalysts are measured between 27.3 wt% to 44.8 wt%, and the metal areal
183 density are confirmed at a high level (Figure 3b, Supplementary Table 2, and
184 Supplementary Figure 9). The white-line intensities from the XANES spectra indicate
185 the positive oxidation state of the metal sites in M SACs/PCN (Supplementary Figure
186 11). The AC HAADF-STEM (Figure 3c) and FT-EXAFS spectra (Figure 3d) identify
187 the N-coordinated single-atom metal sites, and the absence of the metal-metal
188 coordination excludes the formation of the metal clusters. The characterizations of
189 XRD, TEM, EDS mapping, and XPS are shown in Supplementary Figure 12-24,
190 which further indicate the uniform distribution of the positive-charged isolated metal
191 sites on the PCN substrate, and no aggregation of the metal is detected.

192 The adaptability of the negative pressure annealing approach on different substrates
193 is also investigated. The NC obtained via the pyrolysis of guanine is used instead of
194 PCN to prepare UHL-SACs (M SACs/NC, M=Pt, Fe, Co, Ni, and Cu). The XRD of
195 the NC substrate reveals the structure of graphitic carbon (Supplementary Figure 25).
196 The XPS results confirm the doping of N on carbon (Supplementary Figure 26). The
197 characterizations, including AC HAADF-STEM, FT-EXAFS, EDS element mapping,
198 XANES, XRD, and XPS (Figure 4a-e and Supplementary Figure 27-34), identify the
199 N-coordinated single-atom metal sites with positive oxidation states in these M
200 SACs/NC. The metal contents are measured as high as 34.1 wt% (Pt), 21.5 wt% (Fe),

201 19.6 wt% (Co), 17.7 wt% (Ni), and 29.8 wt% (Cu) (Supplementary Table 2),
202 demonstrating the obtain of UHL-SACs with high metal areal density on NC substrate
203 (Supplementary Figure 35-36). Moreover, high-entropy single atoms (HESACs)
204 containing Pt, Fe, Co, Ni, and Cu are also prepared on the NC. As shown in Figure 4
205 f-g and Supplementary Figure 37, all five metals distribute uniformly on the NC as
206 N-coordinated isolate metal sites. The metal contents are 15.6, 3.1, 4.1, 2.3, and 7.3
207 wt% for Pt, Fe, Co, Ni, and Cu, respectively, resulting in an overall metal content of
208 32.4 wt% (Figure 4h, Supplementary Table 2). The positive oxidation states of the
209 metal sites are confirmed (Supplementary Figure 38-39). Furthermore, no condensed
210 matter of any metal is detected (Figure 4i and Supplementary Figure 40-41). Although
211 a limited number of metals were tested on NC, we speculate that the formation of
212 SACs on NC follows the same evolution pathway as that on PCN, demonstrating the
213 versatility of this synthetic method on different N-containing carbon substrates for
214 preparing SACs with multiple metals. Together, this work provides a universal
215 synthetic strategy to fabricate various UHL-SACs and even HESACs.

216

217 **2.3. Catalytic Evaluation of Pt SACs/PCN**

218 The partial oxidation of propane to valuable liquid oxygenates represents a novel
219 strategy to utilize this class of light alkane³⁴. Among the several current strategies,
220 such as electrocatalysis³⁵, photocatalysis³⁶⁻³⁷, thermal-derived homogeneous³⁸, and
221 thermal-derived heterogeneous catalysis, the exploitation of heterogeneous catalyst
222 shows the greatest application potential³⁹⁻⁴¹. However, the consumption of costly
223 oxidants poses an obstacle to it. To address this issue, a catalytic process that can
224 transfer propane to oxygenates with low-cost oxidants is urgently needed. Inspired by
225 the molecular oxygen activation capacity of isolated Pt sites², Pt SACs/PCN is
226 evaluated in the oxidation of propane with oxygen in this work.

227 The reaction is performed at 175 °C in a 240 mL autoclave, with propane (5 bar) as
228 reactant, oxygen (6 bar) as oxidant, and acetonitrile (70 ml) as solvent (Figure 5a).
229 The decreased pressure and the gas chromatography (GC) results indicate the
230 consumption of propane, and the gas production is identified as CO (Supplementary

231 Figure 42). Interestingly, liquid productions are detected in acetonitrile, which is
232 dominated by oxygenates (acetone, acetic, and methanol, *et al*), revealing the capacity
233 of Pt SACs/PCN in transforming propane into valuable liquid productions (Figure 5
234 b-c and Supplementary Figure 43). These liquid productions are further quantitatively
235 analyzed via the external standard method (Supplementary Figure 44-45). As shown
236 in Figure 5d, the liquid product is confirmed as 37.1 mmol/g_{cat} at 3h, which increases
237 with the reaction time, and reaches 71.9 and 107.6 mmol/g_{cat} at 6 and 9 h, surpassing
238 the low-loading Pt SACs/PCN, Pt nanoparticles (Pt NPs/PCN) and commercial Pt/C
239 catalyst (Figure 5e). To reveal the intrinsic activity of Pt SACs/PCN, the turnover
240 frequency (TOF) and mass-specific activity are confirmed as 1.6×10^{-3}
241 mol_{pro}·mol_{Pt}⁻¹·s⁻¹ and 12.0 mmol/g_{cat}/h (Figure 5f-g and Supplementary Table 4),
242 well-placed among select prior reports of propane activation performance with
243 oxygen. Interestingly, among the catalysts working with oxygen, only Pt SACs/PCN
244 selects the pathway toward oxygenates (Figure 5g). This may be the first observation
245 of heterogeneously catalytic oxidation of propane to oxygenates with oxygen, which
246 provides a strategy to utilize propane for harvesting valuable liquid productions.
247 Moreover, the catalytic performance of Pt SACs/PCN shows insignificant decay after
248 be reused five times (Figure 5h), and the used catalyst maintains the dense isolated Pt
249 sites (Supplementary Figure 46), confirming its stability. To clarify the effect of the
250 substrates, Pt SACs on NC were also evaluated in the propane oxidation (Figure 5e).
251 Following a similar trend with Pt SACs/PCN, Pt SACs/NC with higher Pt loading
252 shows better activity than those with lower Pt loading and Pt particles, and the
253 productions are dominated by oxygenates. These catalyst evaluations demonstrate the
254 potential application of high-loading Pt SACs in activating light alkanes.

255 In conclusion, we report a general negative pressure annealing strategy to fabricate
256 ultrahigh-loading single-atom catalysts across a broad range of transition metals.
257 Besides monometallic SACs, high-entropy single-atom catalysts that contain multiple
258 metal single atoms with high metal contents can also be obtained, proving the general
259 applicability of the pressure annealing method. In-situ microscopic studies combined
260 with ex-situ XAFS reveal the pivotal role of the vacuum annealing condition in

261 suppressing the aggregation of metal species, enabling the formation of dense
262 N-coordinated Pt sites. Furthermore, UHL Pt SACs/PCN exhibits superior catalytic
263 performance in the oxidation of propane towards valuable liquid production. These
264 findings provide valuable guidance for preparing a wide range of high-density SACs
265 and show great potential use in efficient catalytic transformations.

266

267 **Methods**

268 **Materials.** Guanine, melamine, vanadyl sulfate, chromic nitrate, manganous nitrate,
269 ferric nitrate, cobaltous nitrate, nickel nitrate, cupric nitrate, zinc nitrate, niobium
270 oxalate were purchased from Sinopharm Chemical Reagent Co.. Molybdenum
271 pentachloride, chloro-iridic acid, chloroplatinic acid, tetrachloro-auric acid were
272 purchased from Aladdin. All solutions were prepared using deionized water. All the
273 chemicals were used without further purification.

274 **Synthesis of PCN.** The mixture of melamine and dicyandiamide (molar ratio=7:3)
275 was pyrolyzed in a tube furnace at 600 °C for 1.5 h (Ar flow, 100 sccm). The obtained
276 powder (3 g) was treated in 65wt% HNO₃ (50 ml) at 80 °C for 6 h, followed by an
277 ultrasonic treatment for 1h. The suspension was centrifuged and washed with
278 deionized water to gain yellow powder, which was labelled as polymeric carbon
279 nitride (PCN).

280 **Synthesis of NC.** Guanine was pyrolyzed in a tube furnace at 600 °C for 1.5 h (Ar
281 flow, 100 sccm). The obtained black powder was labeled as N-doped carbon (NC).

282 **Synthesis of Pt SACs/PCN, Pt NPs/PCN, and Pt SACs/NC.** Pt SACs/PCN were
283 prepared via the impregnation-vacuum pyrolysis method. 20 ml chloroplatinic acid
284 solution (0.075 mol/L) was added in 1 g PCN. The obtained suspension was
285 ultrasonic treated for 15 min, aged at room temperature for 2 h, and dried at 80 °C for
286 8 h. The obtained powder was placed in a tube furnace. The tube furnace was firstly
287 purged by 100 sccm Ar flow for 15 min. Then, the outlet was connected to an
288 operating mechanical pump (limiting pressure 6×10^{-2} Pa), and the inlet was closed.
289 After 1 h of pyrolysis under vacuum conditions at 400 °C, the black powder Pt
290 SACs/PCN was obtained. Pt/NPs/PCN was prepared via the same procedure, except

291 for the pyrolysis process, which was carried out in Ar flow (atmospheric pressure). Pt
292 SACs/NC was prepared by the impregnation-vacuum pyrolysis method, using 0.035
293 mol/L chloroplatinic acid solution and NC substrate.

294 Synthesis of M SACs/PCN and M SACs/NC. M SACs/PCN (M=V, Cr, Mn, Fe, Co,
295 Ni, Cu, Zn, Nb, Mo, Ir and Au) was synthesized via the same method with Pt
296 SACs/PCN, using vanadyl sulfate, chromic nitrate, manganous nitrate, ferric nitrate,
297 cobaltous nitrate, nickel nitrate, cupric nitrate, zinc nitrate, niobium oxalate,
298 molybdenum pentachloride, chloro-iridic acid, and tetrachloro-auric acid as the metal
299 precursor, respectively. The concentration of metal precursor solution was 0.17 mol/L
300 for V, Cr, Mn, 0.2 mol/L for Fe, Co, Ni, Cu, and Zn, 0.12 mol/L for Nb and Mo, 0.075
301 mol/L for Ir, and 0.045 mol/L for Au. The vacuum pyrolysis temperature for V, Cr,
302 Mn, Fe, Co, Ni, Cu, and Zn SACs/PCN was 500 °C. M SACs/NC (M= Fe, Co, Ni, Cu)
303 were prepared according to the method of M SACs/PCN. The concentration of the
304 metal precursor solution was 0.07-0.1 mol/L.

305 Synthesis of HESACs. HESACs were prepared according to the method of M
306 SACs/NC. The metal precursor solution was a mixture of ferric nitrate, cobaltous
307 nitrate, nickel nitrate, cupric nitrate, and chloroplatinic acid. Their concentration in the
308 solution was 0.015, 0.015, 0.01, 0.03, and 0.02 mol/L, respectively.

309 Characterization. The transmission electron microscopy (TEM) images and the
310 corresponding element mapping were recorded on a JEOL-2100F FETEM. The
311 electron acceleration energy was 200 kV. The morphologies of the samples were
312 measured on Thermo-Fisher Apreo S scanning electron microscope. HAADF-STEM
313 images were recorded on the JEOL JEMARM200F TEM/STEM system. The in-situ
314 heating aberration-corrected high-angle annular dark field scanning transmission
315 electron microscope (Cs-HAADF-STEM) experiments were conducted on a
316 double-spherical aberration corrected FEI Titan Themis Z scanning transmission
317 electron microscope with an accelerating voltage of 300 kV combined with the in-situ
318 heating holder provided by FEI company. The prepared precursor was dispersed onto
319 the in-situ heating chip purchased from FEI company. Before STEM imaging, beam
320 shower was carried out for 15 min. A probe size of 9 was used to image. The heating

321 rate was set as 10 °C/min. To exclude the influence of e-beam irradiation, the images
322 of control areas were collected only at each temperature point. The crystallographic
323 phase of the as-synthesized materials was characterized by X-ray powder
324 diffractometer (XRD, Bruker D8 Advance, $\lambda = 1.5418 \text{ \AA}$). Raman spectroscopy
325 (WITec alpha300R, 532 nm laser) was used to study the structure and disorder of the
326 catalysts. X-ray photoelectron spectroscopy (XPS) measurements were performed on
327 a PHI 5000 VersaProbe III X-ray photoelectron spectrometer using an Al K α X-ray
328 source. The power is 12.5W, the bandpass energy of the full spectrum test is 280 eV,
329 and the bandpass energy of the fine spectrum test is 112 eV. The spectra are calibrated
330 by C1s (284.8eV), and the spectral analysis is performed by Avantage software.
331 Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was employed
332 with PerKinElmer Optima 2100DV to detect the loading content of metal on catalysts.
333 X-ray Absorption Fine Structure Spectroscopy (XAFS) were collected at beamline
334 1W1B of Beijing Synchrotron radiation Facility and beamline BL14W1 of Shanghai
335 Synchrotron Radiation Facility. The acquired XAFS data were analyzed by Athena
336 and Artemis software modules in IFEFFIT software package.

337 Catalytic performance test. The catalyzed oxidation of propane with molecular
338 oxygen was carried out in a 240 mL autoclave reactor. In a typical run, 70 ml
339 acetonitrile solvent and 100 mg catalyst were added in the reactor. And, 5 bar propane
340 and 6 bar oxygen was then added in the reactor According to the ideal gas equation,
341 the added propane was about 35.4 mmol. The reaction was carried out at 175 °C. After
342 the reaction, the reactor was cooled to room temperature. The liquid phase was flited
343 and analyzed by a gas chromatograph-mass spectrometer (Agilent 8890-5977B). The
344 qualitative analysis was performed on a HP-5 MS capillary column (inner diameter
345 $0.25\mu\text{m}$, length 30 m), and the quantitative analysis was performed with FID detector
346 (as shown in Supplementary Figure 43-44), using HP-5 capillary column ($0.25 \mu\text{m}$, 30
347 m) and calculated by the external standard method (Supplementary Figure 45). The
348 gas phase was collected and analyzed by a Panna A60 gas chromatography. The yield
349 of liquid oxy-compounds after 9 h reaction over Pt SACs/PCN is calculated by the
350 moles of carbon in liquid oxy-compounds (23.19 mmol carbon) and the carbon inlet

351 (35.4 mmol propane, 106.2 mmol carbon).

352

353 **Data availability**

354 The data that support the findings of this study are available within the article and
355 its Supplementary Information files. All other relevant data supporting the findings of
356 this study are available from the corresponding authors upon request.

357

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503

504 **Author Contributions Statement**

505 Y. W.[†], C. L.[†], and X. H.[†] contribute to this work equally. Y. W. designed the basic
506 principle and arranged the experiment. C. L. experimented. Y. Q. and K. L. worked
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508 and C. H. performed the XAFS measurement. X. H. and Y. L. performed the in-situ
509 aberration-corrected HAADF-STEM. Jintao. B., Z. Li. and X. W. revised the writing
510 work.

511

512 **Competing interests Statement**

513 The authors declare no competing interests.

514

515 **Figure 1. Structure investigation of the Pt UHL-SACs (Pt SACs/PCN).** (a) Metal
516 contents of the most reported Pt SACs. (b) Schematic illustration for preparing
517 UHL-SACs. (c) TEM image of 40.9 wt% Pt NP/PCN. (d) XRD patterns of 40.9 wt%
518 Pt NP/PCN and 41.8 wt% Pt SACs/PCN. (e-n) Structure characterization of 41.8 wt%
519 Pt SACs/PCN: (e) TEM image, (f-h) Aberration-corrected HAADF-STEM image and
520 the corresponding intensity profiles in the (g) yellow square and (h) red square, (i-j)
521 EDS element mapping, (k) XPS results of 41.8 wt% Pt SACs/PCN. (l) Pt *L*-edge
522 XANES spectra, (m) Pt *L*-edge FT EXAFS spectra, and (n) the corresponding wavelet
523 transformation results.

524

525 **Figure 2. Insight of the Pt species transformation during the generation of Pt**
526 **SACs/PCN and Pt NPs/PCN.** Temperature-dependent in-situ aberration-corrected
527 HAADF-STEM images of (a) Pt SACs/PCN and (b) Pt NPs/PCN, the scale bar
528 represents 5 nm. (c, d) Pt *L*-edge FT EXAFS spectra and (e, f) XANES spectra of
529 samples annealed at different temperatures in (c, e) vacuum and (d, f) Ar. (g) Pt 4f
530 XPS spectra of samples annealed at different temperatures in vacuum and Ar.

531

532 **Figure 3. The universal preparation of UHL-SACs on PCN (M SACs/PCN).** (a)
533 The metal elements used for fabricating M SACs/PCN. (b) The metal content in the
534 as-prepared catalysts. (c) Aberration-corrected HAADF-STEM and (d) FT-EXAFS
535 spectra of various M SACs/PCN.

536

537 **Figure 4. Fabricating UHL-SACs on N-doped Carbon (NC) substrate.** The
538 aberration-corrected HAADF-STEM images and FT-EXAFS spectra of NC supported
539 UHL-SACs with (a) Pt, (b) Fe, (c) Co, (d) Ni, and (e) Cu. (f) TEM and (g)
540 Aberration-corrected HAADF-STEM images of the UHL HESACs. (h) The metal
541 content in the HESACs. (i) FT-EXAFS spectra for the metals in HESACs.

542

543 **Figure 5. Catalytic evaluation of Pt SACs/PCN in propane oxidation.** (a)
544 Illustration of the reaction condition. (b) Gas chromatographic profile and (c) mass
545 spectra of the liquid productions measured by GC-MS. (d) Catalytic performance of
546 Pt SACs/PCN over reaction time. (e) Catalytic performance of various catalysts at 6h.
547 (f) TOF value of the catalyst used in this work. (g) Comparison of the propane
548 oxidation performance with previous reports. (h) Stability test. The maximum
549 measurement error for (d) and (e) is $\pm 3.8\%$, which represent the standard deviation of
550 3 replicates at least.

551