A sulfur-tethering synthesis strategy toward high-loading atomically dispersed noble metal catalysts

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INTRODUCTION
Maximizing the atom utilization efficiency of noble metal–based heterogeneous catalysts by downsizing them into nanoscale and even atomic scale is of great significance for catalysis, as only the exposed metal atoms are involved directly in the catalytic process. The limitation of increasing the metal utilization efficiency is the atomic dispersion of metals on porous supports, which presents a hot research topic in the past few years (1–5). A wide variety of atomically dispersed metal catalysts with unprecedented catalytic activities have been reported recently for catalyzing CO oxidation (6), C–H activation (7), hydrogenation (5, 8), methane oxidation (9), electrocatalytic hydrogen evolution (10), and oxygen reduction (11). On the other hand, the electronic properties of the atomically dispersed metals are quite different from their bulk counterparts, endowing the metals with unexpected catalytic selectivity (12) and steady poison-resistant properties (13) in various reactions. In addition, the atomically dispersed catalysts bridge the gap between heterogeneous and homogeneous catalysis and offer a fundamental platform for understanding the catalytic mechanism of heterogeneous catalysts at the molecular level (5, 14).

The synthetic challenge of atomically dispersed catalysts lies in the difficult-to-stabilize ligand-free separated atoms on solid supports, since metal atoms tend to aggregate into larger particles owing to the sharply increased surface free energy with the decrease of particle size. Some emerging synthetic strategies have been proposed to obtain such a distinctive class of catalysts, such as a mass-selected soft-landing technique (15), a precursor-preselected method (16), a photochemical strategy (5), an iced photochemical reduction (17), an atomic layer deposition method (10), and a thermal transformation of metal nanoparticles (4, 18). These methods, however, still face a few challenging problems for practical applications, such as the complicated equipment, high-cost metal precursors used for synthesis, and very low metal loading. Another efficient strategy toward atomically dispersed catalysts is to use high–surface area supports that can supply numerous anchor sites for fixing large-content metal atoms, typically including metal oxide nanoparticles (4, 5), zeolite (19), mesoporous graphitic carbon nitride (20), covalent triazine frameworks (21), and surface-functionalized porous carbons (22). In particular, Zeng and co-workers achieved a very high loading of 7.5 wt % for atomically dispersed Pt supported on monolayered MoS2 (23); Kim and co-workers reported a 5 wt % atomically dispersed Pt on a microporous sulfur-doped carbon (micro S-C) support that was prepared by template-templating zeolite and using toxic H2S gas as sulfur source (12). Although these great progresses have been made, fabricating stable atomically dispersed catalysts with metal loading higher than 2.0 wt % through a general approach remains a formidable challenge.

In this work, we demonstrate a general and scalable synthesis approach to a family of atomically dispersed metal catalysts with high metal loading of up to 10 wt %, including Ru, Rh, Pd, Ir, and Pt, by using mesoporous sulfur-doped carbons (meso S-C) as supports (Fig. 1). The meso S-C supports with high sulfur content (>10 wt %) and large surface area (>1000 m2 g−1) can effectively prevent metal atoms from aggregating when removing the ligands from metal precursors by the thermal reduction process at 200°C to 300°C owing to the strong chemical metal-sulfur interactions. The prepared atomically dispersed catalysts display much enhanced catalytic performance for formic acid oxidation reaction (FAOR) and quinoline hydrogenation compared to commercial catalysts.

RESULTS
Synthesis and characterization of the catalysts
The meso S-C supports were prepared by a cobalt-assisted carbonization of molecular precursors with SiO2 nanoparticles as hard templates at 800°C, followed by NaOH and H2SO4 etching steps to remove the SiO2 template and cobalt, respectively (see the details in Materials and Methods). The as-prepared meso S-C support had a large Brunauer-Emmet-Teller (BET) surface area of >1000 m2 g−1 and a pore volume of >2.0 cm3 g−1, as well as a high sulfur content of >10 wt % (see table S1). Inductively coupled plasma atomic emission spectrometry measurement showed a negligible cobalt species (lower than 0.2 wt %) left in the meso S-C supports.

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To demonstrate the capability of meso_S-C for supporting atomically dispersed metals, we first synthesized the xPt/meso_S-C catalysts (x represents the percentage content of Pt) via the wet impregnation of a H₂PtCl₆ precursor and thermal reduction by 5 vol % H₂/Ar at 250°C for 2 hours (Fig. 1). The reduction ability of H₂ for H₂PtCl₆ on meso_S-C at 250°C was confirmed by H₂ temperature-programmed reduction (H₂-TPR) analysis (fig. S1A). After H₂ reduction, no Cl signal could be detected in the Pt/meso_S-C catalyst by x-ray photoelectron spectroscopy (XPS) measurement (fig. S1F), suggesting the complete removal of the Cl ligand.

Atomic-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was then performed to analyze the morphologies of Pt species at the atomic scale for the catalysts with gradually increased Pt loading from 5 to 30 wt %. For the catalysts with Pt loading of less than 20 wt %, we observed numerous separated Pt atoms along with some loose Pt aggregations consisting of a few randomly dispersed Pt atoms (Fig. 2, A to C, and fig. S2, A to F). No Pt crystalline lattice or larger particles could be found throughout the meso_S-C support for these catalysts. With the increase of Pt loading to 30 wt %, clear Pt crystal lattice appeared in the HAADF-STEM image of the 30Pt/meso_S-C catalyst (Fig. 2D and fig. S2, G and H). X-ray diffraction (XRD) pattern analyses verified the emergence of a crystalline Pt phase for 30Pt/meso_S-C (Fig. 2E). XPS was carried out to study the electronic state change of the Pt species during the catalysis synthesis (fig. S1K). The binding energy (BE) of Pt negatively shifted from 74.1 eV for H₂PtCl₆ to 72.4 eV for H₂PtCl₆/meso_S-C, indicating that the Pt (IV) component in H₂PtCl₆ was already reduced to Pt (II) during the wet impregnation and drying process. A similar phenomenon was also reported on other carbon supports (24). After H₂ reduction, the BE of Pt species in the 5Pt/meso_S-C catalyst exhibited a further negative shift of 0.2 eV but was still higher than that of bulk Pt (BE = ~71.0 eV).

X-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) were measured to further characterize the electronic and coordination structures of Pt species in the Pt/meso_S-C catalysts. The intensity of the white line of Pt species in Pt/meso_S-C was much lower than that of H₂PtCl₆ precursor but higher than that of metallic Pt foil (Fig. 2F and fig. S2J), indicating that the Pt species in Pt/meso_S-C were partially oxidized, which was well consistent with the XPS results. The Fourier-transformed k²-weighted
EXAFS spectra of the Pt/meso_S-C catalysts are presented in Fig. 2G and fig. S2J. The Pt/meso_S-C catalysts with the Pt loading of 5 to 20 wt % presented a prominent peak at ca. 1.9 Å in EXAFS, which could be ascribed to the Pt-S coordination (note that Pt-O coordination was located at a much lower R value in the PtO2 sample) (12, 22, 25), and no peak of Pt-Pt coordination could be observed at the position of around 2.5 to 2.8 Å. Differently, Pt-Pt coordination appeared in addition to the Pt-S coordination when the Pt loading increased to 30 wt %.

Fitting of EXAFS was then carried out to obtain the quantitative chemical configurations of Pt species, and the results are summarized in Table 1. The coordination number (CN) of Pt-S in 5Pt/meso_S-C was equal to that in 10Pt/meso_S-C (ca. 3.6), and no Pt-Pt contribution was observed, suggesting that the Pt species in these two catalysts were in the same isolated environment. Considering that the sulfur species are mainly in the form of C-S-C as revealed by high-resolution XPS (fig. S2K), we therefore presume that, in these atomically dispersed catalysts, four thiophenic S moieties coordinated with one Pt atom to form the Pt-S4 mononuclear complex-like structure (fig. S2L), which typically endowed the heterogeneous Pt species with homogeneous catalyst properties (12). Similar single-atom metal-N4 structures were frequently reported in the metal-N-C catalyst system (12, 26). When the Pt loading reached 20 wt %, the component of Pt-S decreased with the average CN down to 2.8 and the Pt-Pt contribution emerged. With further increase of Pt loading to 30 wt %, we found much lower Pt-S CN (ca. 2.2) and higher Pt-Pt CN (ca. 4.4). Note that the Pt-Pt distance (ca. 2.717 Å) in 20Pt/meso_S-C was much shorter than that in Pt foil (ca. 2.763 Å). The contraction of the Pt-Pt bond might come from the decreasing electron density in the disordered ultrasmall nanocluster (25). Increased Pt-Pt distance (ca. 2.734 Å) was measured in 30Pt/meso_S-C catalyst compared to 20Pt/meso_S-C, suggesting that the Pt atoms were aggregating from disorder to order phase with the increase of Pt loading.

Overall, the absence of a Pt-Pt contribution in 5Pt/meso_S-C and 10Pt/meso_S-C catalysts revealed by EXAFS analyses definitely proved the atomic dispersion of Pt on the meso_S-C supports with high Pt loading of up to 10%, which exceeds the loading of recently reported ligand-free noble metal catalysts with atomic dispersion (12, 23). The randomly packed Pt atom aggregations observed by HAADF-STEM in 5Pt/meso_S-C and 10 Pt/meso_S-C should come from the overlapping of Pt atoms in 3D meso_S-C structures or the loose packing with a monolayer of Pt atoms on carbon surface. Moreover, the strong chemical interaction between metal and the meso_S-C supports was also strongly verified by the EXAFS analyses.

To identify the pivotal structural parameters of meso_S-C for the synthesis of high-loading atomically dispersed metal catalysts, we carried out several control syntheses. First, meso_S-C with low sulfur content (LS-meso_S-C) was prepared by heat treatment of pristine meso_S-C under flowing 5 vol % H2/Ar at 900°C for 2 hours and also used as support for loading Pt by the same process. The sulfur content markedly decreased from 14.3 to 1.2 wt % upon the second heat treatment in the reducing atmosphere, while the BET surface area remained nearly unchanged (see table S1). Many crystalline Pt particles were clearly present in HAADF-STEM images of the LS-meso_S-C–supported 5 wt % Pt (fig. S3A). In addition, we also synthesized a microporous S-doped carbon (micro_S-C) support by carbonizing a thiophene-containing conjugated microporous polymer to study the influence of a porous structure for loading Pt atoms. The sulfur content (13.8 wt %) of the micro_S-C support was almost the same as that of meso_S-C, while the BET surface area (666 m2 g−1) and pore volume (0.39 cm3 g−1) were much less than those of meso_S-C. HAADF-STEM observations revealed that individual Pt atoms, clusters, and particles bigger than 2.5 nm coexisted in the micro_S-C–supported 5 wt % Pt (fig. S3B). Similarly, the maximum loading for atomically dispersed Pt on zeolite-templated micro_S-C that has a very high BET surface area (2400 to 2800 m2 g−1) and a high sulfur content (17 wt % S) was also limited to 5 wt % (12). We therefore conclude from these results that the high sulfur content, large surface area, and mesoporous structure would enable the meso_S-C supports with abundant and easily accessible sulfur-containing sites for strongly anchoring Pt atoms with high mass percentage.

| Sample          | Shell | N    | R (Å)            | σ² (10⁻³ Å²) | ΔEg (eV)   | r factor |
|-----------------|-------|------|------------------|-------------|------------|----------|
| Pt foil         | Pt-Pt| 12   | 2.763 ± 0.003    | 4.5 ± 0.4   | 6.90 ± 0.43| 0.002    |
| PtO2            | Pt-O | 6 (fixed) | 1.987 ± 0.009 | 4.1 ± 0.7   | 8.1 ± 1.2  | 0.024    |
| Pt-S            | 6 (fixed) | 3.102 ± 0.007 | 2.9 ± 0.5 | 9.9 ± 0.2  |
| 5Pt/meso_S-C    | Pt-S  | 3.6 ± 0.3 | 2.270 ± 0.007 | 3.4 ± 0.7   | 3.06 ± 0.46| 0.007    |
| 10Pt/meso_S-C   | Pt-S  | 3.6 ± 0.3 | 2.264 ± 0.007 | 3.4 ± 0.7   | 3.06 ± 0.46| 0.004    |
| 20Pt/meso_S-C   | Pt-S  | 2.8 ± 0.3 | 2.261 ± 0.008 | 5.2 ± 0.9   | 3.06 ± 0.46| 0.002    |
| Pt-Pt           | 2.3 ± 0.7 | 2.717 ± 0.036 | 9.3 ± 2.4 | 6.90 ± 0.43|
| 30Pt/meso_S-C   | Pt-S  | 2.2 ± 0.2 | 2.267 ± 0.007 | 6.1 ± 0.8   | 3.06 ± 0.46| 0.003    |
| Pt-Pt           | 4.4 ± 0.6 | 2.734 ± 0.005 | 8.8 ± 0.9 | 6.90 ± 0.43|

For further comparison, several commercially available and home-made carbons were also examined as supports for loading Pt, including Vulcan XC-72R (XC-72R), carbon nanotubes (CNTs), reduced graphene oxide (RGO), mesoporous nitrogen-doped carbon (meso_N-C), and...
mesoporous oxygen-doped carbon (meso-O-C). For all these carbon supports, we failed to prepare atomically dispersed Pt catalysts for the loading of 5 wt %, as indicated by the HAADF-STEM results (fig. S3, C to H). Note that although meso-N-C and meso-O-C also had a mesoporous structure and a large BET surface area (table S1), they could not effectively suppress the Pt atom agglomeration when removing the ligands by thermal reduction with H2. The heteroatoms in meso-N-C (4.7 wt % N) and meso-O-C (23.4 wt % O) and some defects in the commercial carbon black may also provide anchor sites for binding Pt atoms (28–30), but these kinds of interactions seem to be much weaker than those in meso-S-C. With the strong affinity of sulfur to noble metals as a result of the soft acid–soft base interaction (25, 31), aggregation of Pt atoms could be notably suppressed on the meso-S-C support.

To extend the applicable scope of our synthetic strategy, we additionally prepared another four atomically dispersed noble metal catalysts, including Ir, Pd, Ru, and Rh. H2-TPR profiles confirmed that the metal precursors of IrCl3, PdCl2, RuCl3, and RhCl3 could be reduced by H2 at 250°C (fig. S1, B to E). XPS results indicated that the Cl ligand could be thoroughly removed from Pd, Ru, and Rh precursors on meso-S-C under 5 vol % H2/Ar at 250°C (figs. S1, H to J). In the case of Ir/meso-S-C, the thermal reduction in pure Ar at 500°C was proven to be more efficient to remove the Cl ligands without Ir atom aggregation than the H2 reduction at 250°C (fig. S1G). The BE of all the metals showed a negative shift compared to corresponding precursors, indicating a decreased oxidation state after thermal reduction at an evaluated temperature (figs. S1, L to O). We did not find obvious Ir atom agglomeration by HAADF-STEM for the Ir/meso-S-C catalysts when the Ir loading was below 10 wt % (Fig. 3A and fig. S4A). EXAFS analyses confirmed the exclusive presence of an Ir-S bond with CN of ca. 3.8 for both 5Ir/meso-S-C and 10Ir/meso-S-C samples (Fig. 3E, fig. S4C, and table S2). When the Ir loading was further increased to 15 wt %, a large number of Ir particles appeared in the HAADF-STEM image, and an Ir-Ir bond was observed in the EXAFS spectra (fig. S4, B and C). By similar loading-dependent synthesis experiments, we identified that the maximum metal loading for atomically dispersed Pd, Rh, and Ru on the meso-S-C supports was 5, 5, and 3 wt %, respectively (Fig. 3, B to D and F to H, and fig. S5).

**Catalytic performance for FAOR**

We first studied the catalytic performance of atomically Pt/meso-S-C catalysts for FAOR, which were tested in an aqueous solution of 0.5 M H2SO4 and 0.5 M HCOOH under room temperature by the rotating disk electrode technique. A commercial Pt/C catalyst (20 wt %; Johnson Matthey) was also tested under the same conditions. We observed two obvious peaks in the anodic sweep for the FAOR on Pt/C (Fig. 4A). The first peak at ~0.6 V comes from the direct oxidation route that involves a dehydrogenation process, while the secondary peak at ~1.0 V arises from the electrochemical oxidation of adsorbed CO molecules (COads) through the indirect pathway (32, 33). The FAOR on Pt/C mainly goes through the indirect route, in which the Pt surface is easily poisoned by the reaction intermediate COads. Differently, the FAOR anodic sweep voltammograms of the atomically Pt/meso-S-C catalysts show a prominent peak at ~0.85 V, indicating that the oxidation of formic acid is dominant in a direct pathway owing to the isolated Pt sites in 10Pt/meso-S-C (33). An additional peak at ~1.0 V gradually rose with the increase of the Pt loading on meso-S-C from 10 to 30 wt %, which is probably associated with the emergence of Pt clusters in 20Pt/meso-S-C and 30Pt/meso-S-C.

We then compared the catalytic activity of the catalysts by normalizing the current at ~0.6 V versus reversible hydrogen electrode. As shown in Fig. 4B, the atomically dispersed 10Pt/meso-S-C catalyst exhibited a high FAOR activity of 2.38 A mgPt⁻¹, which is 31 times
higher than that of Pt/C (0.074 A mg⁻¹ Pt). Although the activity of 20Pt/meso_S-C and 30Pt/meso_S-C decreased with the increase of Pt loading, the activity of these two catalysts was still much higher than that of commercial Pt/C because of the high dispersion of Pt atoms on meso_S-C. We attribute the much enhanced FAOR activity on Pt/meso_S-C to the improved intrinsic activity induced by the isolated single-atom Pt sites and high Pt atom utilization (33). The stability of the Pt/meso_S-C and Pt/C catalysts was then investigated by chronopotentiometry (CA) at 0.4 V (fig. S6). The current decay was observed with the testing time for all catalysts as reported in the literatures (32, 34), but the stable current for the FAOR on 10Pt/meso_S-C was still significantly higher than that on Pt/C after 7200 s.

Catalytic hydrogenation of quinoline

We then studied the partial hydrogenation of quinoline on the prepared 5Ir/meso_S-C catalyst to further demonstrate the utility of this class of atomically dispersed catalysts. The tetrahydroquinoline ring system plays a significant role in pharmaceutical synthesis and has been studied extensively in recent years (35). Ir complexes with various ligands were proved to be effective for quinoline hydrogenation (36), yet the homogeneous catalysis processes always require extremely complicated separation processes and sometimes need harsh added I₂. With 0.1 mol% of 5Ir/meso_S-C catalyst, full conversion of the substrate was achieved in ethanol at 100°C under 2 MPa of hydrogen pressure for 2 hours. No by-products, such as 5,6,7,8-tetrahydroquinoline and decahydroquinoline, were detected. For comparison, Ir/XC-72R, Ir/CNT, and Ir/RGO catalysts with 5 wt % Ir loading were also prepared on the corresponding supports and tested for catalyzing quinolone hydrogenation under the same conditions. Less than 20% conversions of quinolone were obtained for all these reference materials (Fig. 4C). To further evaluate the activity of the atomically dispersed Ir catalysts, we calculated turnover frequencies (TOFs) under the quinoline conversion in 15 to 25% of all cases to ensure that the reaction remained under kinetic control. TOF for quinoline hydrogenation over 5Ir/meso_S-C and 10Ir/meso_S-C was as high as 1292 and 1149 hour⁻¹, respectively, giving an around 20-fold enhancement compared to the commercial Ir/C catalyst (57 hour⁻¹). The catalytic performance of the atomically dispersed Ir/meso_S-C catalysts was better than the single Ru site catalyst (37), Cu@Ru nanocrystals (38), Rh particles (39), and even the homogeneous iridium complexes catalyst (36), revealing the superior advantage of the atomically dispersed metal catalyst. When single Ir atoms and Ir clusters coexisted in 15Ir/meso_S-C (see fig. S4B), the TOF value sharply decreased to 604 hour⁻¹ under the same condition. Besides

Fig. 4. Catalytic performance of atomically dispersed noble metal catalysts. (A) FAOR anodic sweep voltammograms of the atomically Pt/meso_S-C and reference catalysts, as normalized by the Pt mass. The inset shows the magnified curve of Pt/C. Test conditions: sweep rate, 10 mV s⁻¹; 0.5 M H₂SO₄ 0.5 M HCOOH; and Pt loading, 10.2 μg cm⁻² for all samples. (B) Comparison of the mass activity of the catalysts for FAOR at 0.6 V. (C) Catalytic performance of quinoline hydrogenation over 5Ir/meso_S-C and reference catalysts. (D) Recycle of 10Ir/meso_S-C for catalytic hydrogenation of quinoline.
the high Ir atom utilization, the electronic interaction between Ir and S may also positively affect the quinoline hydrogenation. XANES spectra revealed that the Ir in 5Ir/meso_S-C and 10Ir/meso_S-C had a higher oxidation state than bulk Ir (fig. S4D), implying an electron transfer process between Ir and meso_S-C. The electron-deficient Ir sites may tend to the preferential adsorption of N-containing rings, leading to the regioselective hydrogenation of the heterocyclic ring (8). Moreover, H$_2$ might undergo a heterolytic dissociation route during the $H_2$ activation process owing to the non-availability of M-M pairs in the atomically dispersed metal catalysts for homolytic dissociation of H$_2$ (5). Then, the H$^{+}$/H$^-$ pair preferentially transfers to the unsaturated bond, which in turn enhances the catalytic performance (40).

In addition, the 10Ir/meso_S-C catalyst sustained its initial activity and selectivity after five recycling tests (Fig. 4D). No agglomeration of Ir atoms was observed by HAADF-STEM after recycling (fig. S7), and selectivity after five recycling tests (Fig. 4D). No agglomeration from much harsher reaction conditions.

DISCUSSION
To summarize, we have demonstrated a sulfur-tethering strategy for the scalable synthesis of a family of atomically dispersed catalysts with high noble metal loading by using meso_S-C as supports. The meso_S-C supports with high porosity and sulfur content offered numerous accessible sulfur sites for immobilizing noble metal atoms based on the strong chemical metal-sulfur interactions. The prepared atomically dispersed catalysts exhibited much enhanced performance for catalyzing FAOR and quinoline hydrogenation compared to the commercial carbon–supported nanoparticle catalysts. Our work may open a new gate for fabricating high-loading atomically dispersed metal catalysts by an easy scale-up route for practical industrial use.

MATERIALS AND METHODS
Materials
SiO$_2$ fumed powder (7 nm, 99%; S5130) was purchased from Sigma-Aldrich. 2,2'-Bithiophene (98%) was obtained from J&K Scientific Ltd. Commercial Pt/C was purchased from Johnson Matthey Chemicals Ltd. All other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd., China. All the chemicals were used as received without further purification.

Synthesis of the meso_S-C support
Meso_S-C was prepared through cobalt-assisted carbonization of molecular precursor according to our previous works (41, 42). In a typical synthesis, 2 g of 2,2-bithiophene, 2.0 g of SiO$_2$, and 1.0 g of Co(NO$_3$)$_2$·6H$_2$O were added into 150 ml of tetrahydrofuran and stirred for 6 hours under room temperature to form a homogeneous mixture. The solvent was then removed by rotary evaporation. The dried powder was ground in an agate mortar and then carbonized under flowing N$_2$ for 2 hours at 800°C with a heating rate of 5°C min$^{-1}$. Afterward, the carbonized product underwent alkaline etching with 2.0 M NaOH for 3 days and acidic etching with 0.5 M H$_2$SO$_4$ for 6 hours at 90°C successively. After drying the product overnight at 85°C, the meso_S-C support was finally yielded. The meso_N-C and meso_O-C supports were prepared by the same process with 1,10-phenanthroline and glucose as precursor, respectively. Meso_S-C supports with low sulfur content were obtained by thermal treatment of the pristine meso_S-C supports under N$_2$ at 900°C for 2 hours.

The micro_S-C support was prepared by the carbonization of thiophene-containing conjugated microporous polymer, which was synthesized via a FeCl$_3$-catalyzing polymerization process (43). Briefly, 166 mg of 2,2-bithiophene and 1.30 g of FeCl$_3$ were dissolved in 30 and 20 ml of anhydrous CHCl$_3$, respectively. Then, the 2,2-bithiophene solution was dropwise added into the FeCl$_3$ solution under nitrogen atmosphere, then stirred for 24 hours, and followed by adding 100 ml of methanol. The obtained precipitate was collected by filtration and washed with methanol and 2 M HCl solution, then extracted in a Soxhlet extractor with tetrahydrofuran for 24 hours, and dried in vacuum at 80°C for 24 hours to get the polymer. The as-prepared polymer was further carbonized at 800°C under flowing N$_2$ for 2 hours to get the micro_S-C.

Synthesis of the atomically dispersed noble metal catalysts
For 5Pt/meso_S-C synthesis, 95 mg of meso_S-C was firstly dispersed in 20 ml of deionized water before a certain amount of H$_2$PtCl$_6$ aqueous solution (1.5 mg ml$^{-1}$ Pt) was added. After ultrasonic mixing for 1 hour, the suspension was stirred vigorously for 12 hours, and the water was

Table 2. Hydrogenation of various quinoline derivatives on the 5Ir/meso_S-C catalyst. Reaction condition: $T$ = 100°C, $P$ = 2 MPa, 2 hours, Ir/substrate = 0.1 at %, 0.5 mmol substrate, 1 ml ethanol as solvent, o-xylene as standard.

| Entry | Reactant | Product | Conv. (%) | Sel. |
|-------|---------|---------|-----------|------|
| 1     | ![Image](image1) | ![Image](image2) | 98.7$^*$ | >99.9 |
| 2     | ![Image](image3) | ![Image](image4) | 95.1 | >99.9 |
| 3     | ![Image](image5) | ![Image](image6) | 99.9 | >99.9 |
| 4     | ![Image](image7) | ![Image](image8) | 97.8$^*$ | >99.9 |
| 5     | ![Image](image9) | ![Image](image10) | 97.7$^*$ | >99.9 |
| 6     | ![Image](image11) | ![Image](image12) | 99.9 | >99.9 |
| 7     | ![Image](image13) | ![Image](image14) | 96.4$^+$ | >99.9 |
| 8     | ![Image](image15) | ![Image](image16) | 99.9 | >99.9 |
| 9     | ![Image](image17) | ![Image](image18) | 96.8$^+$ | >99.9 |
| 10    | ![Image](image19) | ![Image](image20) | 95.9$^+$ | >99.9 |

*$T$ = 120°C. $^+$ $T$ = 120°C, 3 hours.
removed by rotary evaporation. Last, the precursor was treated with 5 vol % H\textsubscript{2}/Ar for 2 hours at 250°C with a heating rate of 5°C min\textsuperscript{-1}. The preparation process of 5Rh/meso\textsubscript{-}S-C, 5Pd/meso\textsubscript{-}S-C, and 3Ru/meso\textsubscript{-}S-C was similar to that of Pt/meso\textsubscript{-}S-C. For the 5Ir/meso\textsubscript{-}S-C synthesis, the final reduction step was performed in flowing Ar at 500°C. Ir/CNT, Ir/RGO, and Ir/XC-72R were prepared under the same conditions.

Physicochemical characterizations
HAADF-STEM images were performed on JEM-ARM 200F with an accelerating voltage of 200 kV. XRD analysis was performed on a Philips X'Pert PRO SUPER X-ray diffractometer with Cu K\alpha radiation (\(\lambda = 1.54056 \) Å). The surface chemical state of the supported metal was analyzed by XPS conducted on an Emeso_S-CAL MKII with an excitation source of Mg K\alpha radiation (1253.6 eV). The BET surface areas and pore size distribution of the supports were measured by N\textsubscript{2} sorption isotherms (77 K) and the Barrett-Joyner-Halenda model with ASAP 2020. The H\textsubscript{2}-TPR was performed on Autosorb-iQ (Quantachrome Instruments, USA) in a U-type quartz tube. First, the sample was heat-treated in He flow (50 ml min\textsuperscript{-1}) for 1 hour at 300°C with a heating rate of 10°C min\textsuperscript{-1} and then the sample was cooled to 25°C. Subsequently, the sample was heated from 25° to 800°C with a heating rate of 5°C min\textsuperscript{-1} under 10% H\textsubscript{2}/Ar flow (50 ml min\textsuperscript{-1}) after reaching the stable baseline (ca. 0.5 hours). The desorbed gas was detected by a thermal conductivity detector.

The XAFS spectra at the Pt L-edge, Ir L-edge, and Ru K-edge were measured in transmission or fluorescence mode at the beamline 1W1B station of the Beijing Synchrotron Radiation Facility operated at 2.5 GeV and 250 mA. Pd and Rh K-edge were tested in transmission mode at the BL14W1 station of Shanghai Synchrotron Radiation Facility (SSRF) operated at 3.5 GeV and 220 mA. The x-ray energy was tuned by a fix-exit Si (111) double-crystal monochromator and calibrated using Pt/Rh/Pd foil or Ir/Ru metal powder before the experiments. All samples were pelleted as disks with a diameter of 8 mm and a thickness of 1 mm. The XAFS data were processed using the IFEFFIT package (44). The raw data were background-subtracted, normalized, and Fourier-transformed by the ATHENA program. Least-squares curve fit analysis of the EXAFS data was carried out using the ARTEMIS program. The many-body amplitude-reduction factor S\textsuperscript{2} was determined from the fitting of the standard Pt foil and then set for all other Pt samples. The k range for Fourier transformation was from 2.5 to 12.4 Å\textsuperscript{-1}, and the fitted R range was from 1.1 to 3.2 Å. The fitting methods of multiple k-weight and multiple datasets were exploited to get better and reasonable parameters, such as setting the same energy shifts for all the Pt-S shell and all the Pt-Pt shell, respectively.

FAOR catalytic performance
Formic acid electrochemical oxidation measurements were performed using a CHI-760e electrochemical workstation (CH Instruments Inc., Shanghai, China) by using a three-electrode electrochemical cell at room temperature. A glassy carbon disk (5 mm in diameter), a platinum wire, and a saturated calomel electrode were used as working, counter, and reference electrodes, respectively. For the preparation of catalyst ink, 2 mg of the 10Pt/meso\textsubscript{-}S-C was homogenously dispersed in 2 ml of the isopropanol/NAFION solution, followed by stirring and ultrasonication. A certain amount of the catalyst ink was placed uniformly on the glassy carbon disk working electrode with a Pt loading of 10.2 µg cm\textsuperscript{-2} for all catalysts. The electrocatalytic performance of Pt/meso\textsubscript{-}S-C for the FAOR was estimated by cyclic voltammetry (CV) and CA in a mixture of 0.5 M HCOOH and 0.5 M H\textsubscript{2}SO\textsubscript{4} solution. All CV profiles were obtained in the range of +0.05 to +1.2 V with a sweep rate of 50 mV s\textsuperscript{-1}.

Hydrogenation of quinoline
In a typical catalysis experiment, 58.8 µl of quinoline (0.5 mmol), a certain amount of 5Ir/meso\textsubscript{-}S-C catalyst, and 1 ml of ethanol were added into a glass reaction vessel. Next, the reaction vessel was placed into an autoclave reactor, subsequently purged with H\textsubscript{2} five times at 1 MPa, and pressurized to 2 MPa H\textsubscript{2}. The reactor was preheated at 100°C and then stirred at 1000 rpm for 2 hours. After the reaction was completed, the autoclave was placed in ice water. Orthoxylene (70 µl) was then added in the reaction system as an internal standard, and the solution was diluted with 10 ml of ethyl acetate. Last, the reaction products were analyzed using a Shimadzu gas chromatograph with a flame ionization detector and with high-purity nitrogen as the carrier gas. The TOF value was calculated by keeping the quinoline conversion about 20% based on the total Ir loading in the catalyst. For the recycling experiments, 1 mmol of quinoline and 1.9 mg of 10Ir/meso\textsubscript{-}S-C and 1 mmol of ethanol were added into a glass reaction vessel and reacted for 1 hour in accordance with the above steps; then, the catalyst was separated by centrifugation, washed with ethanol and ethyl acetate for several times, and then dried under vacuum condition at 60°C overnight.

**SUPPLEMENTARY MATERIALS**
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/10/eaa6322/DC1

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A sulfur-tethering synthesis strategy toward high-loading atomically dispersed noble metal catalysts
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