Bottom-Up Construction of Metal—Organic Framework Loricae on Metal Nanoclusters with Consecutive Single Nonmetal Atom Tuning for Tailored Catalysis

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their structures (compositions) and properties. However, surface single nonmetal atom doping is challenging and rarely reported. For the first time, we have developed synthetic methods, realizing "surgery"-like, successive surface single nonmetal atom doping, replacement, and addition for ultrasmall metal nanoparticles (metal nanoclusters, NCs), and successfully synthesized and characterized three novel bcc metal NCs $Au_{38}I(S-Adm)_{19}$, $Au_{38}S(S-Adm)_{20}$, and $Au_{38}IS(S-Adm)_{19}$ (S-Adm: 1-adamantanethiolate). The influences of single nonmetal atom replacement and addition on the NC structure and optical properties (including absorption and photoluminescence) were carefully investigated, providing insights into the structure



(composition)-property correlation. Furthermore, a bottom-up method was employed to construct a metal-organic framework (MOF) on the NC surface, which did not essentially alter the metal NC structure but led to the partial release of surface ligands and stimulated metal NC activity for catalyzing *p*-nitrophenol reduction. Furthermore, surface MOF construction enhanced NC stability and water solubility, providing another dimension for tunning NC catalytic activity by modifying MOF functional groups.

INTRODUCTION

Metal nanoclusters (NCs, ultrasmall metal nanoparticles) have attracted increasing interest in recent years partly due to their tunability with atomic precision.¹⁻⁶ Metal atom doping has been widely employed for tailoring the physicochemical properties of metal NCs and enabling the composition (structure)-property correlation.⁷⁻¹⁴ However, surface nonmetal atom introduction, especially "surgery"-like single nonmetal atom doping, replacement, or addition, is challenging owing to the control difficulties.¹⁵⁻²³ To the best of our knowledge, surface single nonmetal atom replacement, not to mention successive surface single nonmetal atom doping, replacement, and addition, has not been previously reported. Unlike thiols and phosphines, single nonmetal atoms such as sulfur and halogen can provide more room for access by the substrates and thus facilitate catalytic reactions;²⁴⁻²⁸ nevertheless, single nonmetal atoms might not protect NCs from attack as well as thiols or phosphines. To counteract the negative effect of surface single nonmetal atom occupation on NC stability, one strategy is to construct loricae for enhanced protection of the metal NCs. As such, metal-organic frameworks (MOFs) are ideal candidates since they have well-defined and tunable pore structures,^{29–31} which not only protect metal NCs from attack but also leave room for reaction, providing pathways for substance transport, and so

forth.³²⁻³⁸ Notably, MOF introduction can also alter the hydrophilicity of metal NCs, as we previously reported, which enables hydrophobic metal NCs to catalyze reactions in the aqueous phase.³⁹ The introduction of MOF loricae on metal NCs has been reported and generally conducted by mixing MOFs with metal NCs.³⁹⁻⁴³ In this complex strategy, the size match between the MOF cavity and the metal NC should be considered, or else the encapsulation can not be well conducted. An alternative complexing strategy is the bottomup construction of a MOF lorica on a template-like metal NC surface based on the self-adaptation of metal NCs and MOF loricae.^{41,44-50} However, such a complexing mode has rarely been reported, and calcination of the resulting composites is generally adopted before their use as catalysts. 41,44,45,47,48 Under this circumstance, it remains unclear whether there are some modifications on the metal NCs surface during MOF lorica formation. This study was inspired by these interesting

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Figure 1. Synthesis (a) and crystallographic arrangement (b) of $Au_{38}I$, $Au_{38}S$, and $Au_{38}IS$. Note that, all C and H atoms are omitted in (b) for clarity.

issues, including the aforementioned challenging single nonmetal atom "surgery". Our strategy is detailed below.

RESULTS AND DISCUSSION

Syntheses and Structural Analyses of Three Au_{38} NCs. Gold NCs were selected as the investigated NCs due to their relative stability compared to silver and other metal NCs. 1-Adamantanethiol (Adm-SH) was selected as the protecting ligand for its bulkiness and rigidity, which may leave room for single atom coating on the surface of gold NCs and also produce single sulfur atoms well after thermal cracking.^{17,51,52} Iodine (I) and sulfur (S) were selected as the incoming single nonmetal atoms, given that they have good affinity with gold and can be easily provided by salt and thiol, respectively. Specifically, KI and Adm-SH were employed as the precursors of I and S, respectively. Interestingly, it was found that the addition of Cd^{2+} could accelerate the production of S, thus $Cd(NO_3)_2$ ·4H₂O was added during the synthesis of S-enclosed gold NCs. Considering that Au-thiol interaction is generally stronger than Au-S complexing,^{20,21,53,54} we conjectured that acid addition might weaken the Au-thiol interaction and facilitate controlled S occupation, which was confirmed experimentally. Therefore, nitric acid was added as a mediator in all of the syntheses. As shown in Figure 1a, the single I-doped gold NC Au₃₈I(S-Adm)₁₉ (Au₃₈I for short) was synthesized by a typical two-step synthesis method with the addition of KI and some parameter modifications. Subsequently, the single S-doped gold NC Au₃₈S(S-Adm)₂₀ (Au₃₈S for short) was synthesized by replacing KI with Cd(NO₃)₂·4H₂O (see the Methods for the experimental



Figure 2. Au_{30} and Au_{29} kernels of the three Au_{38} NCs. (a) Quasi-octahedral Au_6 unit; (b) pyramidal Au_5 unit; (c) hourglass-like Au_6 unit; (d) AuS(S-Adm) "staple"; (e) Au_{18} unit of Au_{38} I NCs; (f) Au_{30} kernel of Au_{38} I NCs; (g) side view of Au_{30} kernel; (h) ideal bcc Au_{30} kernel; (i) Au_{17} unit of Au_{38} S and Au_{38} IS NCs; (j) Au_{29} kernel of Au_{38} S and Au_{38} IS NCs; (k) Au(a)-Au(b); and Au(a)-Au(c) distances of Au_{38} S and Au_{38} IS. For clarity, all C and H atoms are omitted. Yellow and purple denote S, gray denotes C, and the other colors denote Au.

details). Finally, the single S-adduct Au₃₈IS(S-Adm)₁₉ (Au₃₈IS for short) was synthesized by the additional introduction of $Cd(NO_3)_2 \cdot 4H_2O$. The molecular composition of $Au_{38}I$ was identified by electrospray ionization mass spectrometry (ESI-MS) and further confirmed by single-crystal X-ray crystallography (SCXC). As shown in Figure S1a, one dominant ion peak at m/z 5527.67 was readily assigned to $[Au_{38}I(S-Adm)_{19}]$ + 2Cs]²⁺ (to assist ionization, cesium acetate (CsOAc) was added to the NC solution to form $[cluster + xCs]^{x+}$ adducts before ESI-MS analysis), indicating that the single I doping was achieved on the gold NC surface. NC neutrality was evidenced by the equal numbers of Cs⁺ and ion charge, as well as by the absence of a rational signal without the addition of Cs⁺. Likewise, ESI-MS analysis revealed the compositions of Au₃₈S and Au₃₈IS, with dominant peaks at m/z 5564.66 and m/z5543.88 readily assigned to $[Au_{38}S(S-Adm)_{20} + 2Cs]^{2+}$ and $[Au_{38}IS(S-Adm)_{19} + 2Cs]^{2+}$, respectively, see Figure S1b,c, indicating successful single S replacement and addition on the Au₃₈I surface. The elemental composition of the three Au₃₈ NCs was further confirmed by X-ray photoelectron spectroscopy (XPS) and energy dispersive spectrometry (EDS) elemental mapping (Figures S2-S4).

Detailed structural information on the three Au₃₈ NCs was revealed by SCXC analysis, confirming the successful achieve-

ment of successive single nonmetal atom doping, replacement, and addition on the gold NC surface. Compared with the reported $Au_{38}S_2(S-Adm)_{20}^{53}$ (Figure S5), the three as-obtained NCs possessed a more complete $3 \times 3 \times 2$ bcc array of kernel atoms. For comparison, the three NCs were disassembled into "kernels" and "staples" (Figures 2 and S5). As shown in Figure 2e-k, Au₃₈I contained an Au₃₀ bcc kernel, while the other two NCs contained Au₂₉ kernels with incomplete bcc arrays. The Au₃₀ kernel of Au₃₈I consisted of two hourglass-like Au₆ units (marked in pink) and one regular $3 \times 2 \times 1$ bcc Au₁₈ unit (consisting of four quasi-octahedral Au₆ units sharing six Au atoms) (Figure 2f). The Au-Au bond lengths of the hourglasslike Au₆ unit and the Au₁₈ unit were 2.84 and 2.75 Å, respectively, and the average Au-Au distance between the Au₁₈ unit and the hourglass-like Au₆ unit was 2.85 Å. Both Au₃₈S and Au₃₈IS possessed similar Au₂₉ kernels, which consisted of two hourglass-like Au₆ units and one $3 \times 2 \times 1$ bcc Au₁₇ unit (composed of three quasi-octahedral Au₆ units and one pyramidal Au₅ unit by sharing six Au atoms) (Figure 2k). The average Au–Au bond lengths of the Au_{17} units in Au₃₈S and Au₃₈IS were both 2.86 Å, and the average Au–Au distances between the Au₁₇ unit and the hourglass-like Au₆ unit in Au₃₈S and Au₃₈IS were 2.86 and 2.87 Å, respectively. The integrality of the bcc array endowed Au₃₈ NCs with structural

stability, which was consistent with the observation that the thermostability of $Au_{38}I$ was higher than that of $Au_{38}S$ and $Au_{38}IS$ (Figure S6).

The pyramidal Au₅ unit served as the skeleton of the quasioctahedral Au₆ unit, which could be formed by unfolding two Au–Au bonds of the quasi-octahedral Au₆ unit through S atom doping. As shown in Figure 2k, the average distances between Au(a)-Au(b) and Au(a)-Au(c) in all pyramidal Au_5 units for Au₃₈S and Au₃₈IS were 3.71 and 3.70 Å, respectively, exceeding the normal Au–Au σ -bond distance,^{4,55,56} and were also far longer than the corresponding Au-Au bond distances of the undoped Au₆ units (Au₃₈I: 2.70 Å; Au₃₈S: 2.72 Å; Au₃₈IS: 2.70 Å). These bond lengths indicated that cationized Au(a), Au(b), and Au(c) in the quasi-octahedral Au₆ unit were neutralized by the S^{2-} anion, which was supported by XPS analysis. As shown in Figure S7, the neutral Au⁰ to cationic Au1+ ratios were 18:20 for Au₃₈I and 16:22 for Au₃₈IS and Au₃₈S, demonstrating that S atom doping degraded the integrality of the bcc kernel and counteracted the charge state of the metal atoms in the metal NCs.

The kernels of all Au₃₈ NCs were selectively protected by Au₂(S-Adm)₃, AuS(S-Adm), S-Adm, and I. Specifically, four Au₂(S-Adm)₃ units, seven bridging S-Adm molecules, and one I atom shielded the Au_{30} kernel of $Au_{38}I$ (Figure S5a-d). Two hourglass-like Au₆ units of the Au₃₀ kernel were separately immobilized by two Au₂(S-Adm)₃ "staples", with an average Au-Au bond length of 2.80 Å and an average Au-S-Au bond angle of 91.60°. All quasi-octahedral Au₆ units were bridged and stabilized by an independent S-Adm molecule and I atom, with an average Au-S bond length of 2.38 Å and a Au-I bond length of 2.74 Å. Au₃₈S and Au₃₈IS possessed the same Au₂₉ kernel. For Au₃₈S, the Au₂₉ kernel was capped by an outer shell consisting of one AuS(S-Adm) unit, four Au₂(S-Adm)₃ units, and six S-Adm molecules; For Au₃₈IS, the components of the outer shell were similar to those of Au₃₈S, except that one S-Adm molecule was replaced by one I atom (Figure S5f-i). Especially, as illustrated in Figure 2k, one AuS(S-Adm) unit was located on the quasi-octahedral Au₆ unit and the pyramidal Au5 unit reinforcing the connection between them and resulting in the short Au-(S-Adm) bond lengths of 2.34 Å for Au₃₈S and 2.32 Å for Au₃₈IS. Notably, such a connector was absent in the outer shell of Au₃₈I. The Au–Au distances of the hourglass-like Au₆, Au₁₈, and Au₁₇ units, and their distributions in Au₃₈I, Au₃₈S, and Au₃₈IS are shown in Figure S8, demonstrating that the average Au-Au distances in the corresponding locations for the three NCs were nearly equal. Figure S5 displays the total structures of the three Au₃₈ NCs, which clearly shows that single atom replacement of I with S, and single atom addition of S, led to the local structure change of Au₃₈I. Au₃₈S and Au₃₈IS possessed identical structural frameworks, suggesting that the single I atom, unlike the single S atom, did not significantly impact the kernel atomic structure. Note that our previous study also demonstrated that single S addition resulted in kernel structure evolution.⁵ Although single atom replacement of I with S did lead to a change in the local atomic structure, it did not obviously influence the crystallographic arrangement, since both Au₃₈I and Au₃₈S adopted the stacking sequence of "AB" in their single crystals. Interestingly, single S addition on Au₃₈I induced a crystallographic arrangement change from 2H to 4H, as seen in Figure 1b, indicating that the atomic and crystallographic structures of the metal NCs were not synchronously changed with surface single nonmetal atom replacement or addition.

Optical Properties. The electronic structures of the three Au₃₈ NCs were experimentally probed by ultraviolet–visiblenear-infrared (UV–Vis/NIR) spectroscopy after dissolving the crystals in CH₂Cl₂. The results indicated that the breaking of the bcc structure led to a notable blue shift in the absorption peaks. Specifically, Au₃₈I with a complete bcc Au₃₀ kernel exhibited two strong peaks at 558 (2.22) and 712 nm (1.74 eV) (Figure 3a), while Au₃₈S and Au₃₈IS with similar



Figure 3. Absorption and PL comparisons of the three Au_{38} NCs. (a–c) UV–Vis/NIR absorption spectrum of $Au_{38}I$, $Au_{38}S$, and $Au_{38}IS$, respectively; (d) PL spectra of three Au_{38} NCs. The insets show the corresponding spectra on the energy scale.

incomplete Au₂₉ kernels exhibited two strong peaks at 530 (2.34) and 659 nm (1.89 eV). Au₃₈S and Au₃₈IS also exhibited weak peaks at 730 (1.70) and 740 nm (1.68 eV), respectively (Figure 3b,c). By extrapolating the lowest-energy absorption peak to zero absorbance, the optical energy gaps of Au₃₈I, Au₃₈S, and Au₃₈IS were determined to be \sim 1.57, 1.44, and 1.47 eV, respectively. All experimental UV-Vis/NIR absorption peaks of the three Au₃₈ NCs were well reproduced by timedependent density functional theory (TD-DFT), as shown in Figures S9-S11. Kohn-Sham molecular orbital analyses revealed that the simulated peak at 532 nm for Au₃₈I primarily arose from the HOMO-4 to LUMO+1 (I(p) accounting for approximately 50% of the electron transition), HOMO-1 to LUMO+3, HOMO-4 to LUMO, and HOMO-1 to LUMO +2 electronic transitions and that the peak at 650 nm arose from the HOMO-1 to LUMO+2, HOMO to LUMO+3, and HOMO to LUMO+2 electronic transitions (Figure S9). The three simulated absorption peaks of Au₃₈S primarily arose from the HOMO-4 to LUMO+1, HOMO-1 to LUMO+3, HOMO-2 to LUMO+1, and HOMO to LUMO+5 electronic transitions at 460 nm, from the HOMO-2 to LUMO, HOMO-1 to LUMO, and HOMO to LUMO+3 electronic transitions at 545 nm, and from the HOMO to LUMO electronic transition at 673 nm, respectively (Figure S10). The simulated absorption of Au₃₈IS exhibited three peaks, with the 450 nm peak primarily arising from the HOMO-5 to LUMO +1, HOMO to LUMO+6, and HOMO-1 to LUMO+3 electronic transitions, the 552 nm peak primarily arising from the HOMO-2 to LUMO, HOMO-1 to LUMO, and HOMO to LUMO+2 electronic transitions, and the 685 nm peak primarily arising from the HOMO to LUMO electronic



Figure 4. Synthesis and structural characterization of $Au_{38}@UiO-66-X$ (X = F₄, H, COOH, and NH₂) composites. (a) Illustration of the synthetic route to partial-ligand-removed $Au_{38}@UiO-66-X$ composites based on the self-assembly of Au_{38} NCs and UiO-66-X MOF precursors; (b) TEM image of UiO-66-H; (c) HAADF-STEM image of $Au_{38}S$ NCs; (d) TEM image of $Au_{38}S@UiO-66-H$ composites; (e) XPS spectrum of $Au_{38}S@UiO-66-H$ composites; (f–j) HADDF-STEM image and corresponding EDS elemental (Zr, Au, C, and S) mapping of $Au_{38}S@UiO-66-H$ composites.

transition (Figure S11). The change in bcc kernel structure significantly affected the absorption of gold NCs, even if two NCs shared almost the same size and composition, which was consistent with cases of nonbcc gold NCs.^{58–61} However, different from previous reports,^{62–64} single ligand replacement of bcc NCs had almost no influence on their absorption, which indicated that the absorption of bcc gold NCs was mainly determined by the kernel rather than the protecting ligands.

All three NCs exhibited NIR photoluminescence (PL) upon excitation at 514 nm. Although their PL spectra exhibited similar profiles, the intensities differed, indicating that surface single atom replacement or addition did not notably change the radiative excitation electron transfer gap but it dramatically influenced competition between radiative and nonradiative excitation electron transfer. The quantum yield (QY) values were calculated as 2.09×10^{-4} , 6.379×10^{-4} , and 1.032×10^{-3} for Au₃₈I, Au₃₈S, and Au₃₈IS, respectively (Figure 3d) on the

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Figure 5. Catalytic performance of $Au_{38}@UiO-66-X$ (X = F₄, H, COOH, and NH₂) composites in 4-NP reduction. (a) Catalytic performance of UiO-66-H, $Au_{38}I$, $Au_{38}S$, $Au_{38}IS$, and corresponding $Au_{38}@UiO-66-H$ composites; (b) catalytic performance of $Au_{38}S@UiO-66-X$ composites; (c) catalytic cycle of $Au_{38}S@UiO-66-NH_2$ composites; (d) HAADF-STEM (left) and SE-STEM (right) images of $Au_{38}S@UiO-66-H$ before and after catalysis; (e) DFT calculation of vacancy formation energy of each site on $Au_{38}I$, $Au_{38}S$, and $Au_{38}IS$ after the removal of the S or SCH₃ ligand groups.

basis of equation⁶⁵ $Q = Q_r \times (I/I_r) \times (A_r/A) \times (\eta^2/\eta_r^2)$, where Q is the QY, A is the absorbance at the excitation wavelength, η is the average refractive index of the relevant solution, and I is the integrated area under the corrected emission spectrum for the sample (the QY of 1×10^{-4} for Au₂₅(PET)₁₈ was selected as the reference sample (r), Figure S12). These findings indicated that surface S atoms were more conducive to PL than I atoms and I atoms were more conducive to PL than S-Adm molecules.

Bottom-Up Construction of MOF Loricae on Au_{38} NCs. To test the bottom-up construction of MOF loricae on the NC surface, we mixed Au_{38} NCs with terephthalic acid (BDC) and zirconium (Zr) ion building blocks and successfully synthesized the composites denoted as $Au_{38}l@$ UiO-66-H, $Au_{38}S@UiO$ -66-H, and $Au_{38}IS@UiO$ -66-H (Figures 4a and S13, see Methods for the synthesis details). The powder X-ray diffraction (XRD) patterns revealed that UiO-66-H in the composites retained its original crystallinity (Figure S14a), and UV–Vis/NIR spectroscopy indicated that the NC structure was not essentially changed in the composites (Figure S14b). Scanning electron microscopy

(SEM) images demonstrated that the three Au₃₈@UiO-66-H composites possessed similar shapes and sizes (Figure S15). Transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) images revealed that the morphology of UiO-66-H did not change significantly, but the average size reduced from 180.1 ± 15.3 to 101.4 ± 9.5 nm in diameter (Figure S16) before and after complexing with Au₃₈ NCs, which were evenly distributed inside UiO-66-H (Figures 4b-d,f, 5d, and S17). These results were further confirmed by elemental analysis via XPS and EDS for Zr, Au, C, and S as well as Au content analysis via inductively coupled plasma atomic emission spectroscopy (1.51–1.60 wt %) (Figure 4e–j and Table S1). The nitrogen sorption results indicated that the Brunauer-Emmett-Teller (BET) surface areas of Au₃₈S@UiO-66-H, Au₃₈IS@UiO-66-H, and Au₃₈I@UiO-66-H were 1131, 1133, and 1151 m²/g, respectively, reflecting the close cavity occupation ratios in the three composites (Figure S18a,c).

After the successful construction of MOFs on the metal NC surface, the catalytic performance of the composites in the reduction of p-nitrophenol (4-NP) was investigated. Although

the three Au₃₈ NCs were unable to catalyze the reduction reaction alone, as monitored by UV-Vis/NIR spectroscopy (Figures S19a-c and S20a,b), their composites exhibited considerable activity, following the order of Au₃₈S@UiO-66-H > Au₃₈IS@UiO-66-H > Au₃₈I@UiO-66-H (Figures 5a and S21). XRD and UV-Vis/NIR spectroscopy of the three composites did not show any obvious change before and after catalysis (Figure S14c,d), indicating that the composites (including metal NCs and UiO-66-H) retained structural integrity. From HAADF-STEM and SE-STEM images, no particles can be observed, which revealed that Au₃₈ NCs might be encapsulated in UiO-66-H without notable leakage or aggregation (Figure 5d). To exclude the influence of UiO-66-H, we tested the catalytic performance of UiO-66-H alone, observing no catalytic activity. Contact angle measurements indicated that the three composites were hydrophilic to a certain extent (Figure S22a-c), which inspired us to tune the catalytic activity by modifying the water solubility of the MOF sheath. To achieve this, we modified the functional group of UiO-66 and constructed the MOF in situ on the Au₃₈S surface. Three functionalized composites were successfully obtained, namely, Au₃₈S@UiO-66-NH₂, Au₃₈S@UiO-66-COOH, and $Au_{38}S@UiO-66-F_4$ (see Methods for synthesis details). XRD and UV-Vis/NIR spectroscopy revealed that the three functionalized UiO-66 MOFs and Au₃₈S NCs were essentially unaltered after complexing (Figure S23a,b). SEM images indicated that Au₃₈S NCs were encapsulated inside UiO-66-X with similar shapes and sizes (Figure S24). HAADF-STEM and SE-STEM images clearly revealed that Au₃₈S remained uniformly inside the MOF in the investigated Au₃₈S@UiO-66-NH₂ (Figure S25a,b). The BET surface areas of Au₃₈S@UiO-66-X (X = NH₂, COOH, and F_4) were investigated by nitrogen adsorption at 77 K (Figure S18b,d), which indicated that the decrease in BET surface area after the introduction of different functional groups was attributed to the MOF functional group occupying part of the pore volume. Contact angle measurements indicated that Au₃₈S@UiO-66-F₄ was hydrophobic, while the other three composites were hydrophilic. The hydrophilicity, as displayed in Figure S22, was in the order of $Au_{38}S@UiO-66-NH_2 > Au_{38}S@UiO-66-COOH > Au_{38}S@$ UiO-66-H > Au₃₈S@UiO-66-F₄. Initially, the catalytic activity of the three functionalized UiO-66 MOFs toward 4-NP reduction was examined, as shown in Figure S19d-f. The influence of defective UiO-66-X (defective UiO-66-NH₂, for example) was also investigated, given the possible generation of defects during encapsulation of Au₃₈ NCs (Figure S20c,d). Subsequently, the catalytic performance of functionalized Au₃₈S@UiO-66-X was evaluated, revealing that hydrophilic Au₃₈S@UiO-66-NH₂ and Au₃₈S@UiO-66-COOH possessed remarkable catalytic activity and completely catalyzed the conversion of 4-NP within 30 and 40 min, respectively. In contrast, hydrophobic Au₃₈S@UiO-66-F₄ could catalyze only 40% 4-NP conversion within 1 h (Figures 5b and S26). The catalytic activity of the functionalized composites was in the order Au₃₈S@UiO-66-NH₂ > Au₃₈S@UiO-66-COOH > $Au_{38}S@UiO-66-H > Au_{38}S@UiO-66-F_4$, which was consistent with the hydrophilicity order, indicating that composite catalytic activity was positively related to the MOF lorica hydrophilicity and could be enhanced by improving the MOF water solubility. Note that, the introduction of functional groups can change the pore size of MOFs as shown in Figure S18, however, the pore sizes are not regularly correlated to the catalytic activity of the composites, indicating that such an

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influencing factor is not the major one in our case. The catalytic stability of three additional Au₃₈S@UiO-66-X composites was assessed by XRD, UV-Vis/NIR, HAADF-STEM, and SE-STEM analyses of recycled samples (Figures S23c,d and S25c,d), which demonstrated an almost unchanged conversion rate of 4-NP (\sim 77%) after five catalytic cycles. These findings demonstrated that constructing MOF loricae on the metal NC surface is an efficient way to improve the catalytic activity and stability of metal NCs, and both MOF and metal NC surface tailoring can sensitively influence the catalytic performance of the composite.

Catalytic Mechanism. We conjectured that the introduction of single nonmetal atom ligands might affect the catalytic performance of surface-tailored metal NCs. Although we did not detect free S and I species in the catalyzed reaction mixture, surprisingly we found the free thiolates via gas chromatography (GC) and mass spectrometry (MS) (Figure \$27) in the extracted reaction mixture when synthesizing Au₃₈@UiO-66 composites. This finding indicated thiolate loss during the MOF construction on the NC surface, which was not previously reported and might be responsible for the improved catalytic activity of metal NCs. Quantified calculations revealed that Au₃₈S, Au₃₈IS, and Au₃₈I lost \sim 5, 4, and 1 thiolates, respectively (Tables S2 and S3), and the order of thiolate removal was consistent with the order of catalytic activity ($Au_{38}S > Au_{38}IS > Au_{38}I$), providing evidence for the enhanced catalytic activity. DFT calculations of vacancy formation energy (VFE) revealed that the lowest three VFEs of thiolates were 3.19, 3.20, and 3.47 eV for Au₃₈S; 3.35, 3.40, and 3.49 eV for Au₃₈IS; and 3.41, 3.49, and 3.54 eV for Au₃₈I, respectively as shown in Figures 5e and S28, and Table S4. These results indicated that Au₃₈S could lose more thiolates than Au₃₈IS; however, the latter could lose more thiolates than Au₃₈I within the energy limits, providing an explanation for the experimental results. Notably, the single nonmetal S atom in Au₃₈S and Au₃₈IS was easier to lose than a thiolate, whereas the I atom in $Au_{38}I$ and $Au_{38}IS$ was more difficult to lose. The easy loss of the S atom might be related to the fact that the resulting structures were more bcc-complete with relatively low energies (Figure S29). Unfortunately, S was not detected by GC-MS due to its ultralow content or serious interference from thiolates. The NCs remained stable after partial ligand removal (including thiolates and S), as monitored by UV-Vis/NIR spectrometry, XRD, SEM, and TEM, as mentioned above, providing evidence that surface MOF construction is an efficient strategy for protecting NCs.

CONCLUSIONS

Herein, we developed a synthesis method that enabled the realization of challenging single nonmetal atom doping, replacement, and addition on the metal NC surface, and we successfully synthesized and precisely characterized three novel NCs: Au₃₈I, Au₃₈S, and Au₃₈IS. Au₃₈I and Au₃₈S possessed slightly different atomic structures but similar 2H crystallographic arrangements, while Au₃₈IS and Au₃₈S possessed similar atomic structures but different crystallographic arrangements, indicating that I and S atoms had different influences on the atomic and crystallographic structures of metal NCs, which were not synchronously changed. Au₃₈S and Au₃₈IS exhibited almost identical absorption profiles, but Au₃₈I showed slightly shifted absorption profiles, indicating that the UV-Vis/NIR spectra of metal NCs were correlated to their structures. Au₃₈I, Au₃₈S, and Au₃₈IS exhibited similar PL profiles; however, their

QY values followed the order $Au_{38}IS > Au_{38}S > Au_{38}I$, indicating that their PL profiles were not sensitive to their atomic structures. I or S introduction did not notably change the radiative excitation electron transfer gap but obviously influenced the competition between radiative and nonradiative excitation electron transfer, and the ligand contributions to PL followed the order of S > I > S-Adm. Furthermore, MOFs were constructed on the NC surface by a bottom-up method. Although surface MOF construction did not essentially alter the metal NC structure, it led to the partial release of ligands and stimulated the catalytic activity of metal NCs, which was not previously reported. NC surface tailoring and MOF functional group modification efficiently impacted the catalytic activity of metal NCs, indicating new ways to modify the properties of metal NCs after coating with MOFs. The surface MOF acted as a lorica to protect the NC and enhanced its water solubility, which is significant for catalysis in the aqueous phase. Thus, the findings in this work have important implications for structure (composition) and property tailoring, providing insights into the structure (composition)-property correlation of metal NCs that is expected to stimulate more research in related fields.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c13635.

Experiment details, DFT calculation details; XPS, ESI-MS, SEM, TEM, XRD, and ICP-AES; N_2 sorption; contact angle; GC-MS; more single crystal data; and catalytic data (PDF)

Accession Codes

CCDC 2311980 and 2311982–2311983 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/ cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; Fax: +44 1223 336033.

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The authors declare no competing financial interest.

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