Soft nanobrush-directed multifunctional MOF nanoarrays

Controlled growth of well-oriented metal-organic framework nanoarrays on requisite surfaces is of prominent significance for a broad range of applications such as catalysis, sensing, optics and electronics. Herein, we develop a highly flexible soft nanobrush-directed synthesis approach for precise in situ fabrication of MOF nanoarrays on diverse substrates. The soft nanobrushes are constructed via surface-initiated living crystallization-driven self-assembly and their active poly(2-vinylpyridine) corona captures abundant metal cations through coordination interactions. This allows the rapid heterogeneous growth of MOF nanoparticles and the subsequent formation of MIL-100 (Fe), HKUST-1 and CUT-8 (Cu) nanoarrays with tailored heights of 220~1100 nm on silicon wafer, Ni foam and ceramic tube. Auxiliary functional components including metal oxygen clusters and precious metal nanoparticles can be readily incorporated to finely fabricate hybrid structures with synergistic features. Remarkably, the MIL-100 (Fe) nanoarrays doped with Keggin H$_3$PMo$_{10}$V$_2$O$_{40}$ dramatically boost formaldehyde selectivity up to 92.8% in catalytic oxidation of methanol. Moreover, the HKUST-1 nanoarrays decorated with Pt nanoparticles show exceptional sensitivity to H$_2$S with a ppb-level detection limit.

Nanoarrays that combine the characteristics of nanosize and directional arrangement have aroused widespread attention in a variety of fields. In particular, metal-organic frameworks (MOFs) featuring tailorable pore dimension and chemical functionality present prominent advantages in the construction of multifunctional nanoarrays. The uniform alignment of intrinsically porous nanopillars creates a hierarchically open environment for full exposure of active sites and free transfer of reactive substrates, which is favorable for catalysis, sensor, lithium storage, and drug delivery. Generally, highly oriented MOF nanoarrays may grow directly on substrates through “one-pot” solvothermal reactions. This approach is simple yet powerful, but usually requires selected MOFs with inherent one- or two-dimensional crystalline structures. Alternatively, template-directed synthesis is applied to construct multidimensional MOF nanoarrays. Notably, metal oxides and hydroxides [e.g., ZnO, CuO, Cu(OH)$_2$ and CoO] arrays have been widely used as hard templates to direct the growth of MOF nanoarrays. While these templates facilitate the nucleation of MOFs and rationally direct the growth of MOFs along the templates, they normally decompose to release essential metal sources for the growth of desired MOFs. Consequently, the category of MOF nanoarrays is substantially limited by the composition of templates. Besides, it remains a major challenge to handily manipulate the height of the nanoarrays or to simultaneously introduce complementary functional species.
Here, we develop a highly flexible soft nanobrush-directed strategy for the precise fabrication of MOF nanoarrays. The soft nanobrushes are facilely introduced onto various substrates via living crystallization-driven self-assembly19, and their abundant pyridine groups provide the active sites for the capture of copious metal cations to direct the growth of diverse MOFs. By simply immersing in specific precursor solutions, various well-aligned MOF nanoarrays with high aspect ratios and controllable heights can be readily grown on silicon wafer, Ni foam and ceramic tube. Subsequently, polyoxometalates and noble metal nanoparticles are elaborately introduced into the nanoarrays for synergistic catalytic oxidation of methanol and ultra-sensitive sensing of hydrogen sulfide.

Results and discussion

Soft nanobrush was firstly prepared on a silicon wafer via surface-initiated living crystallization-driven self-assembly of $\text{PFS}_{24}-b-\text{P2VP}_{314}$ on pre-immobilized $\text{PFS}_{44}-b-\text{P2VP}_{526}$ seeds ($\text{PFS} = \text{polyferrocenyldimethylsilane}$, $\text{P2VP} = \text{poly(2-vinylpyridine)}$, the subscripts refer to the number-average degree of polymerization of each block) (Supplementary Fig. 1)19. The abundant pyridine groups in the P2VP corona were capable to bind with various metal ions through coordination interactions20. Initially, FeCl$_3$ and 1,3,5-benzenetricarboxylic acid (H$_3$BTC) were introduced simultaneously into the soft nanobrush system, but it unfortunately led to the formation of irregular composites (Supplementary Fig. 2).

Nevertheless, by alternately immersing the soft nanobrush-coated silicon wafer into ethanol solutions of FeCl$_3$ and H$_3$BTC at room temperature five times (Fig. 2a), a uniform array of nanorods with a high aspect ratio and an average diameter of ~35 nm was eventually obtained (Fig. 2b). The contour of each nanorod was obviously sharper compared to the soft nanobrush (Supplementary Fig. 3), indicating a fine coating of nanoparticles on the soft nanobrush.

Upon further increasing the immersing cycles, the diameter of the nanorods increased to ~43 nm for eight cycles and to ~55 nm for ten cycles (Supplementary Fig. 4). In contrast, no growth of nanoarray was observed on naked silicon wafers (Supplementary Fig. 5).
be assigned to the (220), (311), (333), (822) and (842) planes of MIL-100 (Fe), respectively. X-ray photoelectron spectroscopy (XPS) spectra of N 1s of the MIL-100 (Fe) nanoarray shifted to a higher binding energy value (399.68 eV) compared to the pristine soft nanobrush (398.96 eV) (Supplementary Fig. 6), indicating a strong coordination interaction between the pyridine groups on the soft nanobrush with the Fe centers in the MIL-100 (Fe) nanoparticles. 

N2 sorption isotherm of the MIL-100 (Fe) nanoarray grown on a piece of Ni foam (Supplementary Fig. 7) showed a prominent sorption in a low relative pressure region (Fig.2d), revealing a typical microporous feature for MIL-100 (Fe).

Soft nanobrushes with variable lengths were further used to direct the growth of MIL-100 (Fe) nanoarrays. Cross-sectional SEM images showed that the height of the dried soft nanobrushes gradually increased from ~21 to ~86 nm with the addition of 2, 4, 6, 8 and 16 µL of a THF solution (10 mg/mL) of PFS24-b-P2VP314 unimers (Fig.3a, and Supplementary Fig. 8). In contrast to these mostly collapsed soft nanobrushes, the resultant MIL-100 (Fe) nanoarrays revealed erect morphologies, and their height was considerably higher and constantly increased from ~220 to ~1100 nm (Fig. 3b and Supplementary Fig. 9). Notably, the MIL-100 (Fe) nanoarrays were comprised of very uniform cylindrical pillars with a constant diameter of ~35 nm from root to top, indicating a highly controllable growth of MIL-100 (Fe) along the soft nanobrush. Generally, the height variation of the MIL-100 (Fe) nanoarrays was almost linearly consistent with the addition of PFS24-b-P2VP314 unimers (i.e. the length of the soft nanobrushes)19 (Supplementary Fig. 10). Consequently, it is very convenient to modulate the height of the MOF nanoarrays through surface-initiated living crystallization-driven self-assembly.

To explore the synthesis generality, the soft nanobrushes were further employed to direct the growth of HKUST-1 nanoarrays by repeatedly immersing the soft nanobrush-coated silicon wafer into ethanol solutions of Cu(OAC)2 and H2BTC five times (Fig. 4a, see Supplementary Figs. S11–14 for more details). The resultant nanoarrays were also comprised of well-defined rod-like pillars with an average diameter of ~45 nm (Fig. 4b). XRD pattern of the nanoarray revealed...
characteristic peaks for HKUST-1 at 6.8° (200), 9.5° (220) and 11.7° (222), respectively (Fig. 4c). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) confirmed the formation of hard rods with a clear profile, and the corresponding element mapping images demonstrated the typical composition of HKUST-1 (Supplementary Fig. 11f). Furthermore, CUT-8 (Cu) nanoarrays with dual-ligands were also fabricated on silicon wafers by repeatedly immersing in ethanol solutions of Cu(OAC)$_2$, H$_2$ndc and dabco for five cycles. The XRD pattern of the obtained HKUST-1 nanoarray and simulated XRD pattern of HKUST-1. The right image shows the crystal structure of HKUST-1.

d SEM images of a CUT-8 (Cu) nanoarray obtained by alternately immersing a soft nanobrush-coated silicon wafer into ethanol solutions of Cu(CH$_3$COO)$_2$ and H$_3$BTC for five cycles. e XRD pattern of the obtained CUT-8 (Cu) nanoarray and simulated XRD pattern of CUT-8 (Cu). The right image shows the crystal structure of CUT-8 (Cu). The soft nanobrushes were formed by adding 6 µL of a solution of PFS$_{24}$-b-P2VP$_{314}$ unimers (10 mg/mL in THF). Source data are provided as a Source Data file.

Fig. 4 | Extension of soft nanobrush-directed MOF nanoarrays. a Scheme illustration of the fabrication process for HKUST-1 and CUT-8 (Cu) nanoarrays. b SEM images of an HKUST-1 nanoarray obtained by alternately immersing a soft nanobrush-coated silicon wafer into ethanol solutions of Cu(CH$_3$COO)$_2$ and H$_3$BTC for five cycles. c XRD pattern of the obtained HKUST-1 nanoarray and simulated XRD pattern of HKUST-1. The right image shows the crystal structure of HKUST-1. d SEM images of a CUT-8 (Cu) nanoarray obtained by alternately immersing a soft nanobrush-coated silicon wafer into ethanol solutions of Cu(CH$_3$COO)$_2$, H$_2$ndc and dabco for five cycles. e XRD pattern of the obtained CUT-8 (Cu) nanoarray and simulated XRD pattern of CUT-8 (Cu). The right image shows the crystal structure of CUT-8 (Cu). The soft nanobrushes were formed by adding 6 µL of a solution of PFS$_{24}$-b-P2VP$_{314}$ unimers (10 mg/mL in THF). Source data are provided as a Source Data file.

MOF nanoarrays provided a remarkable platform for catalysis in consideration of the open and free space as well as the abundant metallic active sites. It was previously found that Fe-based materials are promising redox catalysts for selective oxidation of CH$_3$OH into formaldehyde (FA), an important chemical intermediate for polyacetal resin and adhesive, via oxidative dehydrogenation. Consequently, the Fe-containing MIL-100 nanoarrays were used to catalyze the oxidation of methanol under industrially relevant conditions (Fig. 5a). Compared to the pristine or supported (immobilized on a silicon wafer) MIL-100 (Fe) powder, the MIL-100 (Fe) nanoarrays (2 µL, 6 µL, 16 µL) showed remarkably higher activity at higher temperatures (>160 °C) and enabled 100% conversion of methanol over 200 °C (Fig. 5b). As a reflection of the intrinsic activity of the iron center, the turnover frequency (TOF) of the MIL-100 (Fe) nanoarray (16 µL) (216.25 h$^{-1}$) was also obviously higher than that of the pristine (0.0355 h$^{-1}$) and supported MIL-100 (Fe) powder (0.773 h$^{-1}$) (Supplementary Table 1). Besides, the erect MIL-100 (Fe) nanoarray showed a significantly faster reaction rate than the collapsed sample (Supplementary Fig. 16), indicating a faster mass transfer within the highly open MIL-100 (Fe) nanoarray.

Previous studies have demonstrated that the addition of vanadium centers can considerably boost the selectivity of FA via promoting the dehydrogenation of CH$_3$OH molecules. However, these vanadium-containing active components were rarely incorporated into MOF arrays probably due to the unfavorable interactions. Fortunately, the P2VP corona of the soft nanobrush can simultaneously bind with the vanadium species in the growth process of MOFs and hence may function as a Trojan horse to incorporate the
vanadium-based components into the MOF nanoarrays. To this end, the soft nanobrush-coated silicon wafer was additionally immersed in an ethanol solution of vanadium-substituted Keggin polyoxometalate (H$_3$PMo$_{10}$V$_2$O$_{40}$, MPAV2) during the growth of the MIL-100 (Fe) nanoarray (Fig. 5d and Supplementary Fig. 19). Element mapping of the hybrid nanoarray revealed a uniform distribution of MPAV2 throughout the MIL-100 (Fe) nanorods (Supplementary Fig. 19c). The hybrid nanoarray doped with 21.5 wt% of MPAV2 exhibited an initial reaction rate of 0.0198 mmol·g$^{-1}$·min$^{-1}$, which was significantly higher than that of the MIL-100 (Fe) nanoarrays doped with 11.1 and 71.0 wt% of MPAV2, and the collapsed MIL-100 (Fe) nanoarray doped with 21.5 wt% of MPAV2 (Fig. 5e and Supplementary Fig. 20). Meanwhile, the nanoarray doped with 21.5 wt% of MPAV2 revealed a significantly enhanced FA selectivity of 92.8%, much higher than the MIL-100 (Fe) nanoarray (16 μL) (72.7%), the MPAV2 powder (42.7%), the pristine MPAV2 nanoarray (16 μL) and the previously reported Fe-based materials (Fig. 5f and Supplementary Table 2). These findings demonstrated the presence of a synergistic catalytic effect between the MPAV2 and MIL-100 (Fe), where the abundant Fe$^{3+}$ active sites on the highly aligned MIL-100 (Fe) nanoarray dominate the oxidative dehydrogenation of CH$_3$OH, while the doped MPAV2 moieties provide additional redox catalytic sites (V$^{V}$) and acid sites involved in the acetolization reactions. On the contrary, the phosphotungstic acid PW$_{12}$ only provided the acid sites$^{33}$ and hence the PW$_{12}$ (18.6 wt%)-doped MIL-100 (Fe) nanoarray only led to the formation of MF (methyl formate) as the major product (Supplementary Fig. 21). Notably, the morphology and catalytic activity of the nanoarray doped with 21.5 wt% of MPAV2 were well retained after 7 cycles of methanol oxidation (Supplementary Figs. 22, 23), indicative of a high recyclability.

The MOF nanoarrays also provided a promising platform for gas sensing because of the highly open structure and abundant metal active sites$^{38}$. To this end, the HKUST-1 nanoarrays were specifically grown on the ceramic tubes devices (Fig. 6a and Supplementary Figs. 24, 25) with an aim to study their gas sensing performance toward H$_2$S by taking advantage of the affinity of cupric ions for H$_2$S$^{39,40}$. Unfortunately, the pristine HKUST-1 nanoarrays only showed irreversible response to H$_2$S (1 ppm) even at 200 °C, probably as a consequence of its poor conductivity and strong binding with H$_2$S (Fig. 6d). To solve this problem, Pt nanoparticles were deliberately introduced to the HKUST-1 nanoarray through in situ reduction to improve the conductivity and increase the desorption rate of H$_2$S (Fig. 6b,c and Supplementary Figs. 26–31). Compared to the pristine HKUST-1 nanoarray (16 μL), the HKUST-1 nanoarray (16 μL) loaded with 0.36 wt% of Pt nanoparticles [HKUST-1 nanoarray (16 μL)/Pt-0.36] displayed a remarkably higher sensitivity and cycling reversibility to 1 ppm H$_2$S at 200 °C and the resistance quickly recovered to the baseline within 17.9 s (Fig. 6e and Supplementary Figs. 32, 33). Meanwhile, the resistance value of the HKUST-1 nanoarray (16 μL)/Pt-0.36 reached 2.1 × 10$^9$ Ω, which was a magnitude lower than the pristine HKUST-1 nanoarray (16 μL) (2.3 × 10$^9$ Ω). As a parameter to evaluate the desorption dynamics, the recovery time (24.8 s) of the HKUST-1 nanoarray (16 μL)/Pt-0.36 in 1 ppm H$_2$S was apparently shorter than that of the pristine HKUST-1 nanoarrays (over 125 s) and the collapsed HKUST-1 nanoarray (16 μL)/Pt-0.36 (37 s) (Fig. 6f, and Supplementary Figs. 34, 35), indicating a fast desorption of H$_2$S. Besides, the HKUST-1 nanoarray (16 μL)/Pt-0.36 showed a quick response to H$_2$S with various concentrations from 0.1 to 10 ppm (Fig. 6g) and the response value ($S = R_p/R_s$) continuously increased from 1.22 to 7.55 (Fig. 6h). XPS analysis and density functional theory (DFT) calculations both showed that the transformation of H$_2$S molecules is dynamically and thermodynamically more favorable on the HKUST-1/Pt nanoarray (Supplementary Figs. 36–38). Notably, the
HKUST-1 nanoarray (16 μL)/Pt-0.36 demonstrated exceptional sensitivity to H2S along with prominent cycling performance (Supplementary Table 3). Notably, additional doping of Keggin-type MPAV2 into the MIL-100 (Fe) nanoarray further improved the selectivity of FA to a remarkable value of 92.8% for the oxidation of methanol. Besides, the HKUST-1 nanoarrays loaded with 0.36 wt% of Pt nanoparticles presented exceptional sensitivity to H2S along with prominent cycling stability. It is expected that the soft nanobrush template approach demonstrated in this work would not only facilitate the growth of more types of MOFs but also offer a facile pathway to other inorganic functional nanoarrays.

**Methods**

**Preparation of MIL-100 (Fe) nanoarray on silicon wafer**

Typically, a silicon wafer coated with the PFS-b-P2VP soft nanobrush was immersed alternately in an ethanolic solution of FeCl3·6H2O (10 mM, 1 mL) for 10 min and then in an ethanolic solution of 1,3,5-benzene tricarboxylic acid (H3BTC) (10 mM, 1 mL) for 10 min at room temperature in a static reaction vessel. Between each step, the sample was rinsed with 1 mL of ethanol to remove the excess reagent. This process was repeated 5 times and the resulting sample was then lyophilized to obtain the MIL-100 (Fe) nanoarray.

**Preparation of MIL-100 (Fe) nanoarray on Ni foam**

Typically, a piece of Ni foam coated with the PFS-b-P2VP soft nanobrush was immersed alternately in an ethanolic solution of FeCl3·6H2O (10 mM, 1 mL) for 10 min and then in an ethanolic solution of 1,3,5-benzene tricarboxylic acid (H3BTC) (10 mM, 1 mL) for 10 min at room temperature in a static reaction vessel. Between each step, the sample...
was rinsed with 1 mL of ethanol to remove the excess reagent. This process was repeated 5 times and the resulting sample was then lyophilized to obtain the MIL-100 (Fe) nanoarray.

**Preparation of HKUST-1 nanoarray on silicon wafer**

Typically, a silicon wafer coated with the PFS-b-P2VP soft nanobrush was dipped alternately in an ethanolic solution of (Cu(CH$_3$COO)$_2$·H$_2$O (2 mM, 1 mL) for 10 min an ethanolic solution of NaBH$_4$ (0.2 mM, 1 mL) for 10 min and an ethanolic solution of dabco (0.2 mM, 1 mL) for 10 min at room temperature in a static reaction vessel. Between each step, the sample was rinsed with 1 mL of ethanol to remove excess reagent. This process was repeated 5 times and the resulting sample was then lyophilized to obtain the CNT-8 (Cu) nanoarray.

**Preparation of MPAV2-doped MIL-100 nanoarray on silicon wafer**

Typically, a silicon wafer coated with the PFS-b-P2VP soft nanobrush was dipped alternately in a mixed solution of water and ethanol (1:1 v:v) for 10 min an ethanolic solution of NaBH$_4$ (0.2 mM, 1 mL) for 10 min and an ethanolic solution of dabco (0.2 mM, 1 mL) for 10 min at room temperature in a static reaction vessel. Between each step, the sample was rinsed with 1 mL of ethanol to remove excess reagent. This process was repeated 5 times and the resulting sample was then lyophilized to obtain the MIL-100 (Fe) nanoarray.

**Preparation of Pt-loaded HKUST-1 nanocrystals on ceramic tube**

In a typical process, the ceramic tube coated with the HKUST-1 nanoarray was firstly placed in 0.5 mL of isopropanol and then 1 μL of an aqueous solution of Na$_3$PtCl$_6$·6H$_2$O (1 mM) was added, and the mixture was shaken for 2 h. Subsequently, a chilled aqueous solution of NaBH$_4$ (37.5 μL) was quickly added and the mixture was shaken on an oscillator for 20 min to allow the in situ formation of Pt nanoparticles. The resulting sample was rinsed with isopropanol and further lyophilized to obtain the Pt-loaded HKUST-1 nanoarray.

**Catalytic oxidation of methanol**

The oxidation of methanol was performed in a fixed-bed tubular reactor with an inner diameter of 12 mm and a length of 550 mm. The catalyst sample was mixed with quartz sand (1.0 g) and then loaded into the reactor. Methanol was introduced into the reactor with a liquid hourly space velocity (LHSV) of 0.19 h$^{-1}$ by a constant flow pump along with a flow of O$_2$ (22.5 mL/min) and the gas hourly space velocity (GHSV) of reactant gases (methanol and oxygen) was 2832 mL/h/g. The products were analyzed by an on-line GC equipped with a thermal conductivity detector (TCD) and a Porapak-T column. The reaction was performed at atmospheric pressure and the gas lines between the reactor and GC were kept at 120 °C. The product selectivity was calculated as $S_i = n_i / n_0 \times 100\%$, where $i$ represents the specific product (CH$_3$OCH$_2$OCH$_3$, HCOOH, HCHO, CH$_2$OCH$_3$, CO, or CO$_2$), and $n_0$ is the carbon atom molar of the specific product.
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Author contributions

S.W. and H.Q. conceived the project. S.W. prepared the soft nano-brushes with assistance from G.L.; S.W. prepared the MOF nanorays; S.W., P.W. and G.Z. performed the catalytic experiments; Y.C. and J.T. performed the HR-TEM; S.W., W.X. and Y.D. performed the gas sensing experiments; S.W. and H.Q. analyzed the data and prepared the manuscript with input from all the other authors. The project was supervised by H.Q.

Competing interests

The authors declare no competing interests.

Additional information

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