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Capillary-bound dense micelle brush supports for continuous flow catalysis

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Abstract: Flow reactors are appealing alternatives to conventional batch reactors for heterogeneous catalysis. However, it remains a key challenge to firmly immobilize the catalysts in a facile and flexible manner and to simultaneously maintain a high catalytic efficiency and throughput. Herein, we introduce a dense cylindrical micelle brush support in glass capillary flow reactors through a living crystallization-driven self-assembly process initiated by preimmobilized short micelle seeds. The active hairy corona of these micellar brushes allows the flexible decoration of a diverse array of nanocatalysts, either through a direct capture process or an in situ growth method. The resulting flow reactors reveal excellent catalytic efficiency for a broad range of frequently utilized transformations, including organic reductions, Suzuki couplings, photolytic degradations, and multistep cascade reactions and the system was both recyclable and durable. Significantly, this approach is readily applicable to long capillaries, which enables the construction of flow reactors with remarkably higher throughput.

Nanosized particles exhibit impressive catalytic reactivity because of their exceptionally large surface area and high surface energy,^[1] which makes them promising candidates for continuous flow heterogeneous catalysis where chemical reactions occur in a relatively confined space.^[2] To prevent aggregation or leaching it is essential to immobilize catalytic

nanoparticles on a static substrate.[3-5] Over the past few decades a series of supports with distinct length scales, morphology and compositions have been developed to anchor nano-catalysts in flow reactors (Fig. 1a). These include silica, [6,7] zeolites,^[8,9] and polymeric materials such as dendrimers,^[10] polymer brushes,^[11] porous organic polymers,^[12,13] and metal-/covalent organic frameworks.[14] Nevertheless, it remains a major challenge to obtain a solid and flexible nanocatalyst loading while simultaneously balance the flow throughput and long-term catalytic performance. We have recently demonstrated^[15] a facile strategy to fabricate micellar brushes on various material surfaces by using the seeded growth strategy termed living crystallization-drive assembly (CDSA)^[16-19] from pre-immobilized micelle seeds derived from crystallizable block copolymers. Micelle elongation via the addition of additional dissolved polymer (unimer) led to brush layer heights of > 165 nm,^[15] far exceeding the values accessible using surface-grafted polymers (typically < 10 nm).^[20] Herein, we have used this platform to facilely grow micellar brushes on the internal wall of capillaries under ambient conditions. Upon the incorporation of a rich array of nanocatalysts, the micellar brush functions as a highly efficient catalytic platform for a broad range of transformations under conditions of continuous flow (Fig. 1b).

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Figure 1. Advantageous features of micellar brush support in flow reactors. a) Traditional supports for nanocatalysts in flow reactors. b) Micellar brush support used in this work.

Short glass capillaries with diameter of 0.5 mm and length of 10 cm were selected to construct the flow reactors. Short cylindrical micelle seeds ($L_n = 66 \text{ nm}$, $L_w = 68 \text{ nm}$, $L_w/L_n = 1.03$, where L_n and L_w are the number- and weight-average lengths, respectively) comprising a diblock copolymer PFS₃₀-b-P2VP₂₂₆ (the subscripts refer to the number-average degree of polymerization) with a crystallizable polyferrocenyldimethylsilane (PFS) core-forming block and a surface- and nano-particlebinding poly(2-vinylpyridine) (P2VP) segment. A colloidal solution of the PFS₃₀-b-P2VP₂₂₆ seeds in isopropanol (a selective solvent for P2VP) was syphoned into glass capillaries by immersing one end of the tube into the solution. The pyridine groups on the P2VP corona strongly associated with the silanol groups on the glass wall via hydrogen bonding (H-bonding) and (after proton transfer) electrostatic interactions^[15,21] leading to immobilization on the internal walls of the capillaries (Figs. 2a,b,

S1). Subsequently, the seed-coated glass capillary was soaked in isopropanol, a selective solvent for P2VP, followed by the addition of PFS₃₀-b-P2VP₂₂₆ unimers in tetrahydrofuran (THF, 10 mg/mL), a good solvent for both blocks. Unimer addition led to growth at the termini of the immobilized micelle seeds and eventually formed dense, forest-like micellar brushes on the inner glass wall as revealed by SEM (Figs. 2c,d, S2). The micelle brush layer was clearly denser and more erect than those prepared by homogeneous nucleation or direct deposition of relatively long (ca. 500 nm) pre-prepared cylindrical micelles which gave rise to sparse surface coverage (Figs. S3, S4). The length of the micellar brushes increased with the amount of added unimer and can be increased to several micrometers (Figs. 2c,d, S2). It should be noted that although the micellar brushes are in the collapsed state after drying, they become more upright when solvent is present.^[15]



Figure 2. Growth of micellar brushes in short glass capillaries. a, Schematic illustration of the fabrication process where the solutions of PFS_{30} -*b*- $P2VP_{226}$ micelle seeds and unimers were sequentially added through syphoning and soaking. **b**, SEM images (after solvent evaporation) of the internal wall of a glass capillary coated with PFS_{30} -*b*- $P2VP_{226}$ micelle seeds ($L_n = 66 \text{ nm}, L_w = 68 \text{ nm}, L_w/L_n = 1.03, 0.5 \text{ mg/mL}$ in isopropanol, fed with 200μ L). The micelle seeds were immobilized on the glass wall via H-bonding and electrostatic interactions. **c**, **d**, SEM images of the internal walls of two glass capillaries after the growth of forest-like PFS_{30} -*b*- $P2VP_{226}$ micellar brushes in the collapsed state after drying. The brushes were prepared by adding (c) 9 μ L and (d) 12 μ L of solutions of PFS_{30} -*b*- $P2VP_{226}$ unimers (10 mg/mL in THF), respectively. The resulted micellar brushes possessed $L_n > 300 \text{ nm}$ (c) and $L_n > 400 \text{ nm}$ (d), respectively. For SEM analysis, the capillaries were broken into small pieces and then fixed on conductive tape with the internal surfaces facing up.

The pyridine groups on the P2VP corona of the PFS₃₀-b-P2VP₂₂₆ micellar brushes enable the introduction of a rich variety of nanocatalysts through various bonding interactions.^[22] For example, when a solution of gold nanoparticles (Au NPs, Fig. S5a, number-average diameter, $D_n = 13.3$ nm) in water was syphoned into the glass capillary, the Au NPs spontaneously adsorbed onto the micellar brushes through coordination interactions. SEM images revealed a relatively even distribution of Au NPs on the micellar brushes with a very small spacing of < 3 nm (Fig. 3b, Fig. S6a) while no obvious aggregation was observed. Titanium dioxide (TiO₂) NPs (D_n = 32.8 nm) were also attached to the micellar brushes via H-bonding and electrostatic interactions (Fig. S6b), although the intrinsic clustering of TiO₂ NPs resulted in a less uniform distribution. We also introduced glucose oxidase (GOx) to the micellar brushes utilizing a similar combination of interactions (the isoelectric point of GOx is pH = 4.26, indicating that the enzyme is acidic). Although the GOx enzyme was not detected by SEM due to its small size (Fig. 3c), EDX mapping definitively demonstrated the presence of sulfur

assigned to the GOx thiol and disulfide groups (Fig. 3c, Fig. S6c). ^[23] The P2VP coronas also provide an efficient environment for the adsorption of metal ions and the subsequent in situ generation of nanoparticles (Figs. S7-S9).^[24] To this end, aqueous solutions of NaPdCl₄, Na₂PtCl₆ and NaAuCl₄ precursors were syphoned into the glass capillaries before the addition of NaBH₄, a typical reductant. This immediately led to the in situ formation of palladium (Pd) NPs ($D_n = 7.3$ nm), platinum (Pt) NPs ($D_n = 8.4$ nm), and Au NPs ($D_n = 6.9$ nm) on the micellar brushes (Figs. 3d,e, Fig. S10, size analysis was based on SEM images). Compared to the direct immobilization method, the in situ reduction approach generated smaller nanocatalyst particles with denser packing on the micellar brushes (Fig. 3). Notably, the loading capability of nancatalysts by the micellar brushes was apparently higher than the sparsely coated cylindrical micelles or a layer of block copolymer (denoted as BCP film, which consisted of much more polymer, see Figs. S3b, S4d, Table S1 for more details) (Figs. 3f-i).

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Figure 3. Decoration of nanocatalysts on micellar brushes in short glass capillaries. a. Schematic illustrations of direct immobilization (a solution of a desired nanocatalyst was syphoned into a glass capillary coated with PFS₃₀-*b*-P2VP₂₂₆ micellar brushes and the nanocatalyst spontaneously adsorbed via coordination, H-bonding, or electrostatic interactions) and in situ generation methods (the solutions of metallic salts and NaBH₄ were sequentially added through syphoning and soaking). **b,c**, SEM images of collapsed PFS₃₀-*b*-P2VP₂₂₆ micellar brushes in the dry state after direct immobilization of (b) Au NPs (inset is the size distribution of the immobilized Au NPs) and (c) GOX (inset is the EDX mapping of S). **d,e**, SEM images of collapsed PFS₃₀-*b*-P2VP₂₂₆ micellar brushes in the dry state after direct immobilized to not the generated Pt NPs). For SEM analysis, the capillaries were broken into small pieces and then fixed on conductive tape with the internal surfaces facing up. **f-i**, Rough loading amounts of (f) Au NPs, (g) GOX, (h) Pd NPs on the micellar brushes, sparsely coated cylindrical micelles and BCP film (see Supporting Information for experimental details).

After the decoration of nanocatalysts, the PFS₃₀-b-P2VP₂₂₆ micellar brush-coated glass capillaries (length = 10 cm, diameter = 0.5 mm) were assembled as a reactor with other simple accessories to form a continuous flow device (Fig. S11) to carry out a rich array of flow reactions (Table S2). The capillary coated with Au NP-decorated micellar brushes exhibited excellent flow catalytic performance over the reduction of 4-nitrophenol (Nip),^[25] a well-known model reaction, where the reaction was complete within a residence time (t_R) of 120 seconds (s) (Figs. 4a,b). In contrast, the sparsely coverage achieved on the internal surface with deposited pre-prepared cylindrical micelles $(L_n = 527 \text{ nm}, L_w = 532 \text{ nm}, L_w/L_n = 1.01)$ and BCP film treated with an equivalent amount of Au NPs only gave a conversion of < 60% under the same conditions (Fig. 4b). The micellar brush clearly significantly boosts the loading and performance of catalysts, presumably on account of the erect structure in the presence of solvent.^[15] Besides, the micellar brushes effectively raised the catalytic activity of the supported Au NPs as revealed by the turnover frequency (TOF) values (61.88 h⁻¹ for the micellar brushes, 41.80 h⁻¹ for the sparsely coated cylindrical micelles and 45.69 h⁻¹ for the BCP film). Moreover, as shown in

Fig. 4c, the Au NP-decorated micellar brushes demonstrated a superior long-term stability compared to the controls with the morphology of the micellar brushes and NPs well retained (Fig. S12). No obvious leaching of Au NPs was detected after the reaction was carried out for 24 h. However, ca. 11.8% and ca. 12% of leaching were detected in cylindrical micelle and BCP film systems. Apparently, the Au NPs were much more firmly immobilized by the micellar brushes. On the other hand, the capillaries coated with Pd NP-decorated micellar brushes demonstrated efficient catalytic performance for the Suzuki coupling reactions (Figs. 4d-f, S13, S14),^[26] a classic Pdcatalyzed reaction, where a conversion of ca. 99% was achieved within a residence time of 4800 s (Fig. 4e, Fig. S14). By contrast, the capillaries that sparsely deposited with cylindrical micelles or a BCP film which treated with the same amount of NaPdCl₄ and NaBH₄ only gave conversions of < 75% within a residence time of 9600 s (Fig. 4e). The Pd NP loaded micelle brush system also showed a consistent and durable catalytic performance with conversion of ca. 99% over 72 h (Fig. 4f) and no obvious leaching of Pd NP was detected. On the contrary, ca. 0.9% and ca. 1.3% of leaching were detected in cylindrical micelle and

BCP film systems. The above results illustrated that the micellar brushes not only effectively raised the catalytic activity of the immobilized nanocatalysts, but also provided a superior loading stability during long-term flow reactions. Other reactions like chemical and photodegradation of methyl orange $(MO)^{[27,28]}$ were also successfully explored with the in situ generation of Au NPs and direct decoration of TiO₂ NPs on the micellar brushes (Figs. S15, S16).



Figure 4. Continuous flow reactions catalyzed by metal NPs supported on the micellar brushes, sparsely-coated cylindrical micelles and BCP film. a, Schematic illustration for the reduction of Nip in water catalyzed by Au NPs that directly mounted on PFS₃₀-*b*-P2VP₂₂₆ micellar brushes ($L_n > 400$ nm, see Fig. 2d) (see the Supporting Information for experimental details). **b**, Conversion-residence time plot of the reactions conducted through glass capillaries that coated with Au NP-decorated micellar brushes ($L_n > 400$ nm, see Fig. 2d), Au NP-decorated sparsely coated cylindrical micelles, Au NP-decorated BCP film and pristine micellar brushes ($L_n > 400$ nm) on the internal surface. All reactions were conducted at room temperature, t_R was adjusted by varying the flow rate and the conversions were calculated based on the UV-vis absorbance at 400 nm. **c**, Stability test of Au NP-decorated PFS₃₀-*b*-P2VP₂₂₆ micellar brushes, Au NP-decorated sparsely coated cylindrical micelles and Au NP-decorated BCP film. For all reactions, flow rate = 10 µL/min, $t_R = 120$ s (the volume of the glass capillary is ca. 20 µL). 0.080 mg of Nip were transformed after 24 h continuous flow reaction carried out through the glass capillary coated with Au NP-decorated micellar brushes ($L_n > 400$ nm, see Fig. 2d) (see the Supporting Information for experimental details). **e**, Conversion-residence time plot of the reactions conducted through glass capillaries that coated with Pd NP-decorated micellar brushes ($L_n > 400$ nm, see Fig. 2d) (see the Supporting Information for experimental details). **e**, Conversion-residence time plot of the reactions conducted through glass capillaries that coated with Pd NP-decorated micellar brushes ($L_n > 400$ nm, see Fig. 2d), Pd NP-decorated sparsely coated cylindrical micelles and Pd NP-decorated micellar brushes ($L_n > 400$ nm) on the internal surface. All reactions were conducted at 35 °C, t_R was adjusted by varying the flow rate and the conversions were calculated based on HP

Multistep cascade reactions in continuous flow were also explored by assembling different flow reactors in series. As a proof of concept, the oxidation of glucose catalyzed by GOx and the subsequent reaction of the resulting H_2O_2 for the oxidation of 3,3',5,5'-tetramethylbenzidine (TMB) catalyzed by Au NPs exhibiting peroxidase-like activity^[29] were organized as a cascade reaction in the presence of micellar brushes. First, the ability of the micellar brushes loaded with GOx through direct immobilization to efficiently catalyze the oxidation of glucose was demonstrated. After addition of TMB and horseradish peroxidase (HRP) to the collected solution (Fig. 5a), intense UV–vis peaks appeared at 370 nm and 652 nm (Fig. 5a, Fig. S17a), indicating the formation of oxidized TMB (oxTMB) as a charge transfer complex (Fig. 5b).^[29] In addition, due to the acidic environment (PBS, pH = 5.05), some conversion to a diimine derivative, which possesses an absorption at 450 nm,^[30] was also detected. This experiment therefore demonstrated the potential to oxidize TMB (to form ox-TMB) using the H_2O_2 generated from the glucose oxidation.^[23,30] Next, a micelle brush decorated with in situ generated Au NPs was shown to exhibit excellent catalytic activity for the oxidation of TMB by H_2O_2 (Fig. 5b, Fig. S17b). Finally, the two modules were connected to form a cascade reaction system (Fig. 5c) with the first flow reactor coated with a GOx-decorated micellar brush and the second coated with a brush decorated with Au NPs. The solution obtained after flowing through the two modules showed an obvious absorbance at 652 nm (Fig. 5c) attributed to oxTMB, which is fully consistent with the targeted cascade reaction. Again, the micellar brush-based flow system showed excellent durability as the micellar brushes in the two capillaries retained

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the original morphology with neglectable leaching of the nanocatalysts and micellar brushes after a 500 min-continuous

> b а Glucose oxidation and stepwise detection TMB oxidation by H₂O₂ $C_{a}H_{a}O_{a} + O_{3} \xrightarrow{GOx} C_{a}H_{12}O_{7} + H_{2}O_{2} H_{3}N_{2}$ H₂O₂ + TMB Au NPs H₂O + oxTMB HRP TMB тмв Glucose H₂O oxTMB H,0. 0.5 2.0 Reactants+TMB+HRP Reactants Products+TMB+HRP Products 1.6 0.4 Gluco H_oC Absorbance 8.0 Absorbance TMB 0.4 0.1 0.0 0.0 400 500 700 400 500 700 300 600 800 300 600 800 Wavelength (nm) Wavelength (nm) С Continuous flow cascade reaction 1.4 Reactants Products 1.2 $C_{e}H_{e}O_{e} + O_{2} + TMB \xrightarrow{GOx} H_{2}O_{2} + TMB \xrightarrow{Au NPs} oxTMB$ 1.0 Glucos Absorbance 9.0 тмв oxTMF 0.4 тмв H,O, oxTMB 0.2 Glucose тмв 0.0 300 400 500 600 700 800 Wavelength (nm)

flow reaction (Fig. S18).

Figure 5. Cascade reaction sequentially catalyzed by GOx- and Au NP-decorated micellar brushes. a, Schematic illustration and UV-vis spectrum for the oxidation of glucose in PBS (pH = 5.05) catalyzed by GOx that directly mounted on PFS₃₀-*b*-P2VP₂₂₆ micellar brushes (*L*_n > 1000 nm, see Fig. S2b) in a glass capillary (flow rate = 5 µL/min, t_R = 240 s). b, Schematic illustration and UV-vis spectrum for the oxidation of TMB in PBS (pH = 5.05) catalyzed by Au NPs that in situ generated on PFS₃₀-*b*-P2VP₂₂₆ micellar brushes (L_n > 400 nm, see Fig. 2d) in a glass capillary (flow rate = 5 µL/min, t_R = 240 s). c, Schematic illustration and UV-vis spectrum for the cascade reaction in PBS (pH = 5.05) sequentially catalyzed by GOx-decorated micellar brushes (Ln > 1000 nm) and Au NP-decorated micellar brushes ($L_n > 400$ nm) (flow rate = 5 µL/min, t_R = 480 s).

Substantially longer fused-silica capillaries (inner diameter = 0.5 mm, length 57 cm vs 10 cm) were selected to enhance the productivity of the flow reactors (Fig. S19). The solutions of PFS_{44} -b-P2VP₅₂₆ micelle seeds ($L_n = 96 \text{ nm}$, $L_w = 99 \text{ nm}$, $L_w/L_n =$ 1.03) and PFS₂₄-b-P2VP₃₁₄ unimers were sequentially injected to a long capillary, which led to the formation of dense and uniform micellar brushes on the internal surface (Fig. S20a). The micellar brushes were subsequently decorated with Au NPs (Fig. S5a, D_n = 13.3 nm) by injecting an aqueous solution of Au NPs into the long capillary (Fig. S20b). The reduction of Nip was carried out to evaluate the catalytic performance of the long capillary that coated with Au NP-decorated micellar brushes. With a longer reaction track (57 cm vs. 10 cm), the long capillary reactor permitted a remarkably higher flow throughput after 24 h continuous flow (780% increase of the mass of converted Nip and 56% increase of TON, Figs. S20c,d vs. Figs. 4a,c, Table

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S2) than the short capillary reactor. The micelle brushes in the

long fused-silica capillaries also exhibited excellent durability and were not eluted even under a relatively high flow rate (88 μ L/min, Fig. S21).

In summary, we have established a versatile continuous flow catalysis platform through the facile growth of the cylindrical micellar brushes on the internal wall of glass capillaries. A rich array of reactions, either in single-step or cascade manner, can be customized and conducted in flow simply by decorating specific nanocatalysts onto the micellar brushes through direct immobilization or in situ generation. Significantly, this strategy can be readily applied to relatively long capillaries to substantially increase the throughput, which is relevant for largescale industrial manufacture. In principle, the system developed in this work should be viable in a wide range of applications in the field of flow chemistry. This is attributed to the facile and versatile decoration of functional units on micellar brushes, leading to applicability that includes, but is not limited to, multistep synthesis, separations, photocatalysis, electrocatalysis, biocatalysis, and sensing.

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Forest-like micellar brushes fabricated under ambient environment in glass capillaries enable flexible decoration of various nanocatalysts and subsequently permit a broad range of continuous flow transformations. Notably, this strategy is feasible for not only short but also long capillaries, allowing the preparation of flow reactors with significantly higher throughput.