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Editorial

Unlocking stability: Preserving activity of biomimetic catalysts with covalent organic framework cladding

Enzymes are extremely complicated biocatalysts in several industrial processes due to their numerous advantages over conventional catalysts, including lower physiological and environmental toxicity, exceptional selectivity, and milder reaction conditions [1]. However, their widespread applications are constrained by the high production costs, low operational stability, and complexity involved in the recovery and reusability of enzymes [2]. During the previous decade, peptide-based biomimetic catalysts have been proven to be more operational and robust than certain advanced enzymes [3]. However, challenges in achieving operational stability, recyclability, and a limited operating range have hindered the widespread implementation of peptides in practical applications [4]. To tackle such stability barriers without compromising the activity of peptide assemblies, one of the favorable approaches is to immobilize them into an inert and robust matrix [5]. Various porous materials, like supramolecules [6], zeolites [7] and metal-organic frameworks [8], have been utilized. Beyond them, covalent organic frameworks (COFs) with atomic level of control render them an optimal selection for armoring the biomimetic catalysts [9,10].

Recently, Banerjee's group reported a new strategy to stabilize biomimetic catalysts within COF backbones through cladding technique [11]. As shown in Fig. 1, firstly, two different decanoic acid-functionalized peptide-amphiphiles (C_{10}FFVK and C_{10}FFVR) were prepared using the microwave-assisted Fmoc-based solid phase method in 40% acetonitrile/water (0.1% TFA) for 30 days. These two peptide-amphiphiles showed nanotubular morphologies (Fig. 1a). Secondly, COF-armored peptide nanotubes were produced using interfacial crystallization (Fig. 1b). The nanotubular morphology of COF-armored peptide assembly was confirmed by SEM (Figs. 1d and e), TEM (Fig. 1f), and AFM (Fig. 1g) characterizations.

To generalize this cladding technique, Banerjee and his co-workers prepared several biomimetic catalysts with hollow tubular morphology by different peptide-amphiphile-based tubular assemblies (C_{10}FFVK and C_{10}FFVR) and different COFs (TpAzo COF and TpDPP COF). Then, they investigated the growth mechanism of COF on peptide-amphiphile-based nanotubes and proposed that the noncovalent interaction between the surface-exposed imine groups on peptide-amphiphile-based nanotubes and carbonyl groups on COFs facilitate the generation of COF crystallites on the surface of peptide-amphiphiles. The electron microscopy images and TGA data confirmed the presence of peptide-amphiphile-based nanotubes inside the COF matrix.

Moreover, in order to exam the stability and activity of biomimetic catalysts prepared by the COF cladding technique, Banerjee and his co-workers probed the catalytic potential of these catalysts in carbon–carbon bond cleavage of methodol to produce 6–methoxy-2-naohthaldehyde (Fig. 1c). Owning to the porous nature and high stability of the coated TpAzo COF, the TpAzo–C_{10}FFVK biomimetic catalyst (yield 7%) displayed competitive performance to C_{10}FFVK (yield 6%) in buffer system (Figs. 2a

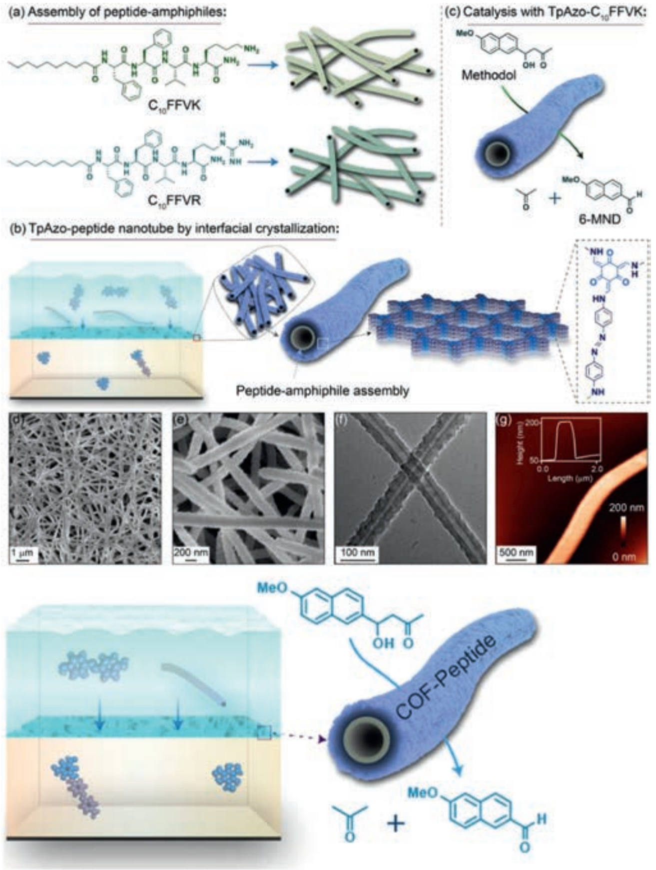

Fig. 1. Schematic representation of (a) self-assembly of C_{10}FFVK and C_{10}FFVR peptides into nanotubes, (b) synthesis of TpAzo-peptide nanotubes by interfacial crystallization with peptide nanotubes and zoomed-in structural representation of TpAzo COF backbone, and (c) catalysis with TpAzo–C_{10}FFVK nanotubes. (d, e) SEM images, (f) TEM image, and (g) AFM image of TpAzo–C_{10}FFVK nanotubes. Reproduced with permission [11]. Copyright 2023, American Chemical Society.

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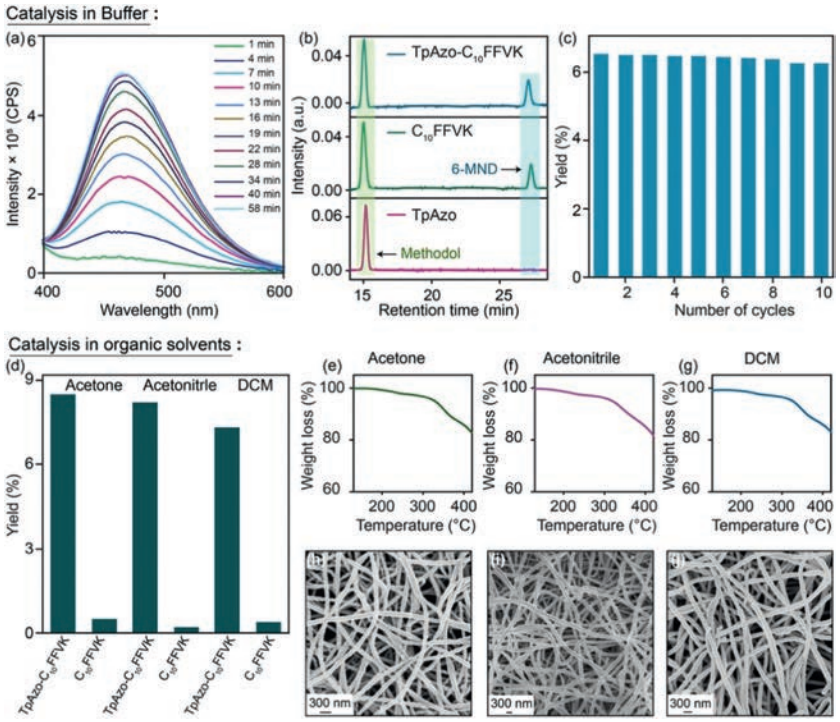

Fig. 2. (a) TpAzo−C_{10}FFVK nanotube catalysis fluorescence data of the product formation with reaction time. (b) HPLC data of the catalysis using TpAzo−C_{10}FFVK nanotubes, C_{10}FFVK nanotubes, and pristine TpAzo COF. (c) Bar diagrams represent the yields of catalysis recyclability data with TpAzo−C_{10}FFVK nanotubes. (d) Comparable yields of the catalysis in different solvents. (e − g) TGA data and (h − j) SEM images after treatment with acetonitrile, acetone, and DCM solvent, respectively. Reproduced with permission [11]. Copyright 2023, American Chemical Society.

and b). In addition, the yield of product barely declined after ten continuously reuses of TpAzo−C_{10}FFVK biomimetic catalyst, confirming its excellent recyclability (Fig. 2c). Impressively, TpAzo−C_{10}FFVK biomimetic catalyst promoted catalytic conversion of methodol to 6–methoxy-2-naohthaldehyde in different organic solvents (acetone, acetonitrile, dichloromethane, and ethyl acetate), where pristine C_{10}FFVK nanotubes were not that efficient in this process (Fig. 2d). After subjecting the TpAzo−C_{10}FFVK biomimetic catalyst to a stability test in organic solvents, specifically acetone, acetonitrile, and dichloromethane, for a duration of three days, it was observed that the C_{10}FFVK nanotubes remained intact within the TpAzo COF backbones even after exposure to the solvents (Figs. 2e-j). These results implied that the peptide-based biomimetic catalyst is highly efficient and stable in buffer and various general organic solvents after COF cladding.

In conclusion, this work from Banerjee's group has provided a systematic investigation on the contribution of COF cladding to COF-armored biomimetic catalysts. The strong noncovalent interactions between the peptide nanotubes and the COF backbones, as well as the porous nature and high stability of COF endow the biomimetic catalysts with enhanced stability and preserved activity. This universally applicable stabilization strategy shows immense promise in the advancement of versatile biomimetic catalysts across a range of practical applications, such as antimicrobial coating, tissue engineering, drug delivery, and bioinspired nanotechnology.

Acknowledgements

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Ting Wang
Xin Yu
Yaqiang Xie*
College of the Environment & Ecology, Xiamen University, Xiamen 361102, China

*Corresponding author.
E-mail address: yaqiang.xie@xmu.edu.cn (Y. Xie)

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