

Supporting Information for Chem Soc Rev

Bioinspired Construction of Multi-Enzyme Catalytic Systems

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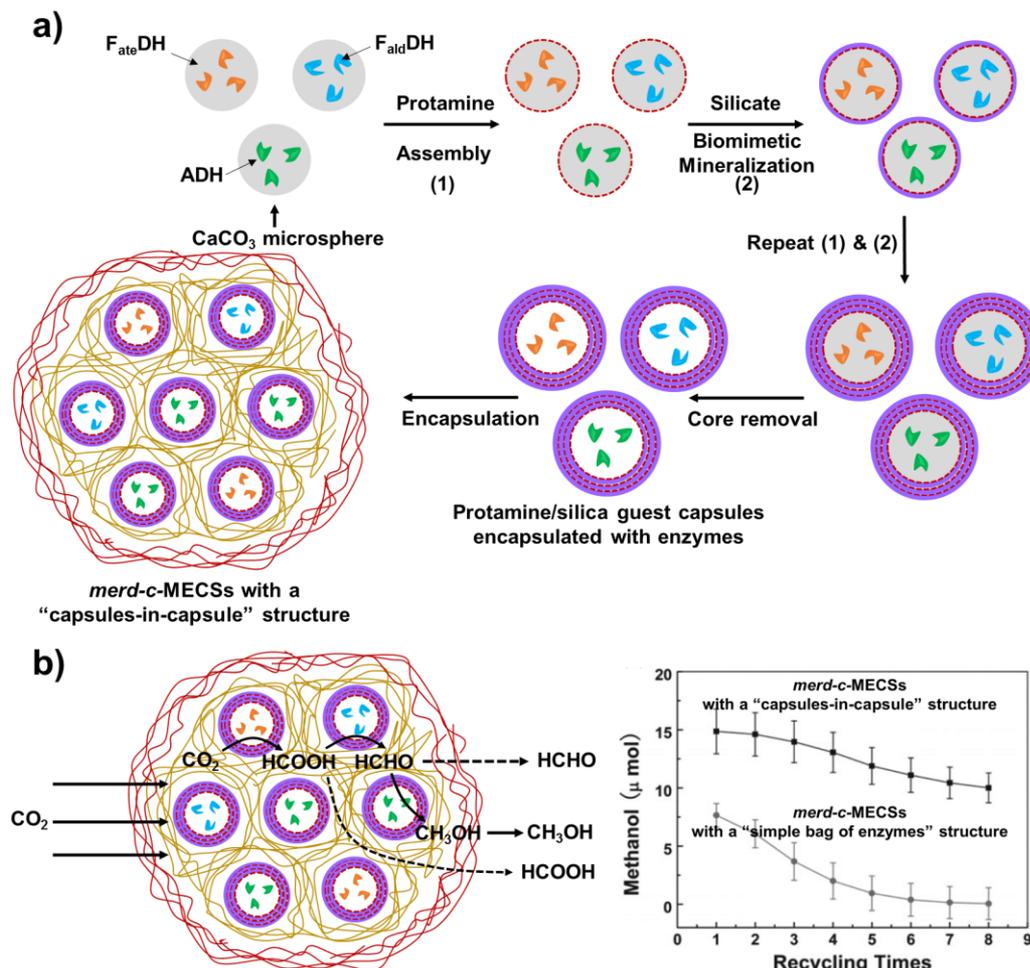


Figure S1. a) Construction of *merd-c*-MECSs through encapsulating protamine/silica guest capsules in the host capsule. Protamine/silica guest capsules were prepared through combining layer-by-layer assembly and biomimetic mineralization upon CaCO_3 sacrificial templates. $F_{\text{ate}}\text{DH}$, $F_{\text{ald}}\text{DH}$ and ADH were individually encapsulated in the guest capsules. b) CO_2 conversion enabled by *merd-c*-MECSs with a "capsules-in-capsule" structure. HCOOH and HCHO were the intermediates that may diffuse out of the *merd-c*-MECSs. c) Yield of methanol catalyzed by *merd-c*-MECSs with a "capsules-in-capsule" structure and a "simple bag of enzymes" structure. Reproduced with the permission from ref. 17. Copyright 2009 Royal Society of Chemistry.

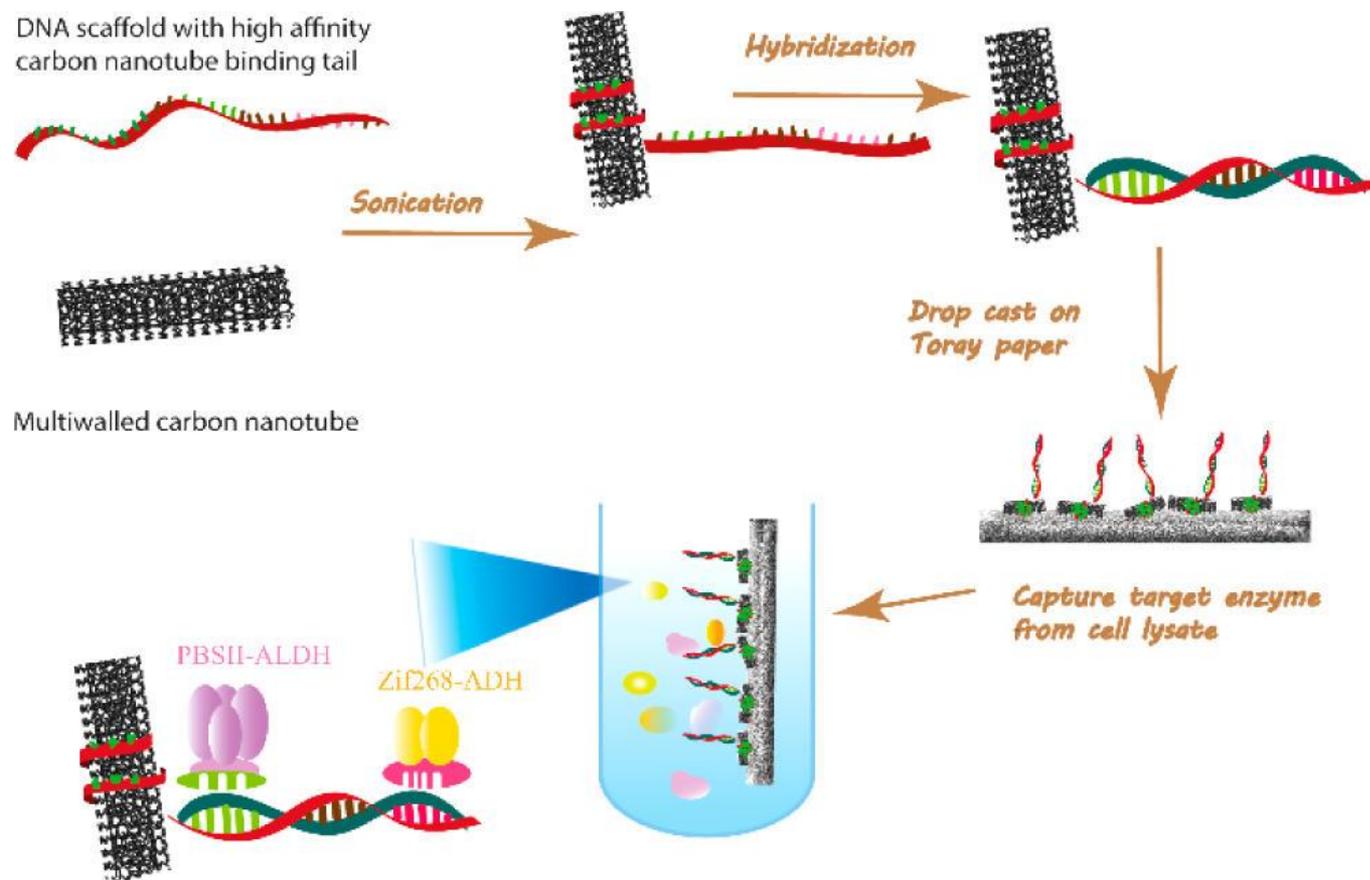


Figure S2. Construction of *mesp-s*-MECSs based on the adaptor-fused enzymes and DNA origami scaffolds for enzymatic methanol fuel cell. Reproduced with the permission from ref. 42. Copyright 2017 American Chemical Society.

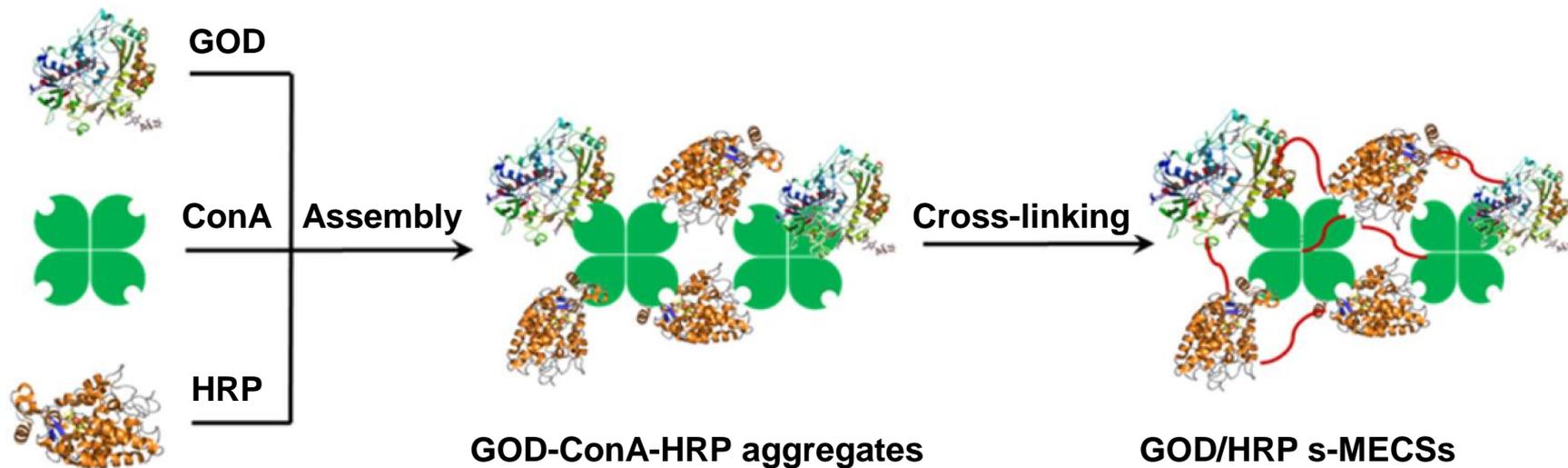


Figure S3. Construction of *mesp-s*-MECSs using ConA as agglutinant and glutaraldehyde as cross-linker. Reproduced with the permission from ref. 40. Copyright 2016 American Chemical Society.

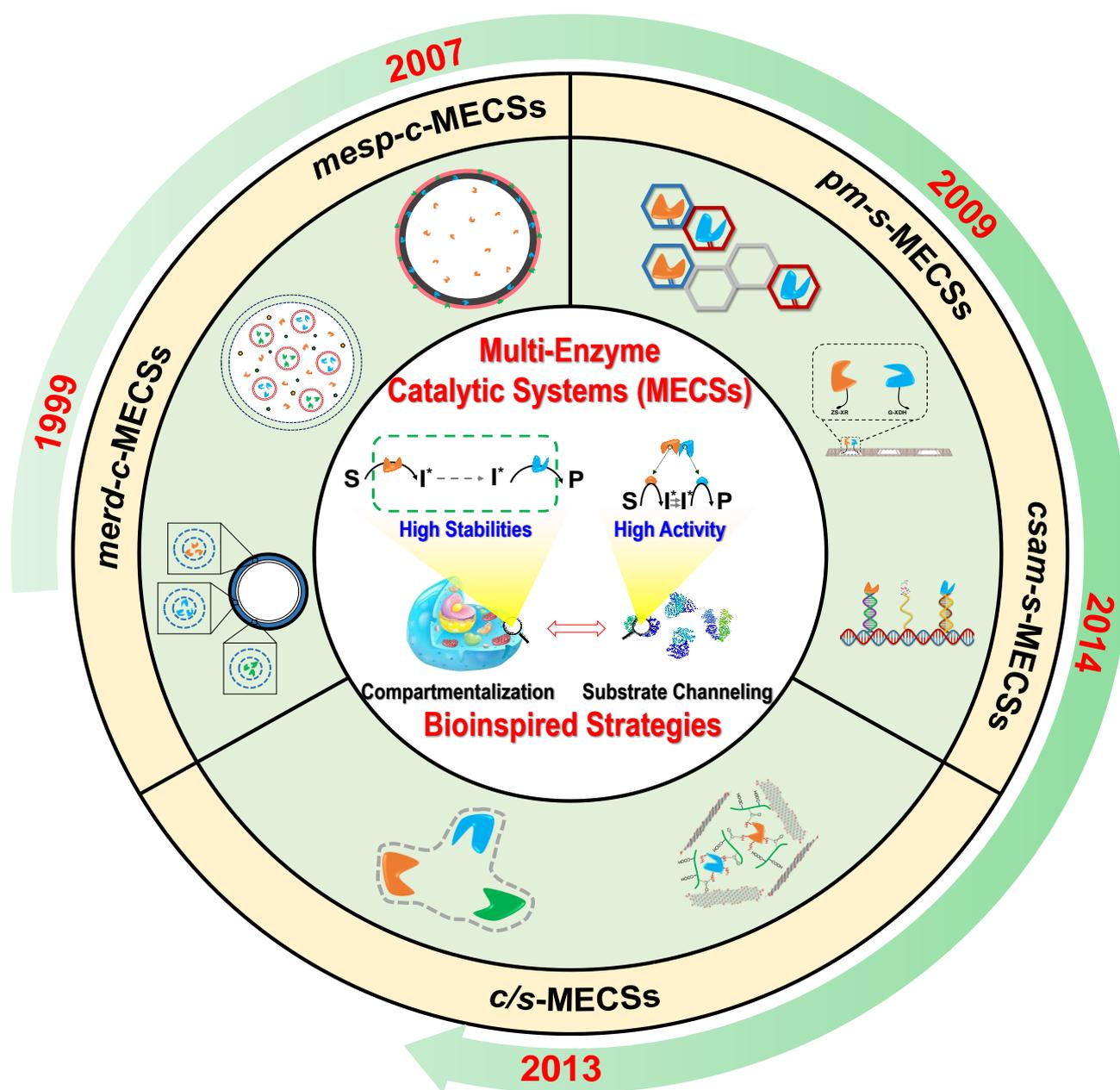


Figure S4. The content of this *tutorial review* with a timeline of the appearance of the various strategies: *merd-c-MECSs*, *mesp-c-MECSs*, *pm-c-MECSs*, *csam-s-MECSs*, *pm-c-MECSs* and *c/s-c-MECSs*. The appearance time of specific techniques related to the above strategies could be found in main text of the manuscript.

Table S1. Some examples of substrate channeling along with references.

Multi-enzymes	Channeling models	References
Malate dehydrogenase-citrate synthase	Electrostatic guidance	R1
Thymidylate synthase–dihydrofolate reductase	Electrostatic guidance	R2
Tryptophan synthase	Intramolecular tunnel	R3
Carbamoyl-phosphate synthase	Intramolecular tunnel	R4
Aldolase-dehydrogenases	Intramolecular tunnel	R5
Glutamine phosphoribosylpyrophosphate	Intramolecular tunnel	R6
Fatty acid synthase	Chemical swing arms	R7
Polyketide synthases	Chemical swing arms	R8
Fatty acid β -oxidation complexes	Chemical swing arms	R9
Pyruvate dehydrogenase complex	Chemical swing arms	R10

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