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Poly(ionic liquid) nanovesicles *via* polymerization induced self-assembly and their stabilization of Cu nanoparticles for tailored CO₂ electroreduction



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G R A P H I C A L A B S T R A C T

This study casts new aspects on using nanostructured PILs as new electrocatalyst supports in CO₂ conversion to C₁ products.



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ABSTRACT

Herein, we report a straightforward, scalable synthetic route towards poly(ionic liquid) (PIL) homopolymer nanovesicles (NVs) with a tunable particle size of 50 to 120 nm and a shell thickness of 15 to 60 nm *via* one-step free radical polymerization induced self-assembly. By increasing monomer concentration for polymerization, their nanoscopic morphology can evolve from hollow NVs to dense spheres, and finally to directional worms, in which a multilamellar packing of PIL chains occurred in all samples. The transformation mechanism of NVs' internal morphology is studied in detail by coarse-grained simulations, revealing a correlation between the PIL chain length and the shell thickness of NVs. To explore their potential applications, PIL NVs with varied shell thickness are *in situ* functionalized with ultra-small (1 ~ 3 nm in size) copper nanoparticles (CuNPs) and employed as electrocatalysts for CO₂ electroreduction. The composite electrocatalysts exhibit a 2.5-fold enhancement in selectivity towards C₁ products (*e.g.*, CH₄), compared to the pristine CuNPs. This enhancement is attributed to the strong electronic

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