Manipulating the Monolayer: Dynamic Covalent Nanoparticle Building Blocks

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Abstract: Monolayer-stabilized nanoparticles are a canonical category of nanomaterial that exhibit a range of potentially useful properties depending on the material composition. Colloidal stability allows nanomaterials of this sort to be manipulated in solution in much the same way as (macro)molecular systems. This raises the prospect of extending synthetic chemistry capabilities to include chemically active nanoscale components, which would be particularly attractive given that virtually every application of monolayer-stabilized nanoparticles requires optimization and interrogation of surface-bound chemical functionality. Yet, robust approaches for nanomaterial surface engineering are critically under-developed.[1]

'Dynamic covalent nanoparticle (DCNP) building blocks' introduce a conceptually distinct strategy for post-synthetic modification of nanoparticle-bound molecules, essentially independent of the underlying nanomaterial. Combining the error-correcting and stimuli-responsive features of equilibrium processes with the stability and vast structural diversity of covalent chemistry enables efficient, divergent routes to myriad functionalized nanomaterial products.

Here I will introduce the DCNP concept using the example of hydrazone exchange within gold nanoparticle-bound monolayers; I will discuss the role that monolayer-stabilized nanoparticles can play as 'pseudomolecular' models for surface-confined chemical processes; and I will demonstrate how understanding the molecular-level details of surface-bound reactions helps us to predictably modify nanoparticle surface chemistry, to tune nanoparticle properties, or to direct selective covalent assembly of specific nanoparticle building blocks.[2–5]

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