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Copper nanoparticles loaded polymer vesicles as environmentally amicable nanoreactors: A sustainable approach for cascading synthesis of benzimidazole

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ABSTRACT

This paper reports the synthesis and characterization of Cu nanoparticle loaded, surfactant free metallovesicles (CuNPs@vesicles) as nanoreactors to produce benzimidazoles via cascade reaction. The vesicles exhibited uniform size distribution, spherical morphology, excellent stability and efficient Cu loading. This strategy is unique for the fact that, environmental contaminants like nitroaniline have been utilized as precursor and converted into fine chemicals of commercial significance via non-toxic intermediates. CuNPs@vesicles reduces 2-nitroaniline to o-phenylenediamine which further acts as precursor for benzimidazole synthesis. Thus the reaction occurs via two step cascade pathway comprising reduction and C—N cross coupling reactions in water. The preliminary studies suggest encouraging results for performing dehydrogenative coupling under relatively mild conditions using CuNPs@vesicles as a catalyst. All the products are obtained in good to excellent yield with facile catalyst regeneration and recyclability upto 5 cascading cycles.

1. Introduction

Polymersomes are assemblies of amphiphilic copolymers in aqueous medium which bear resemblance to liposomes. These polymersomes exhibits unique morphology, with a hydrophobic membrane and a hydrophilic corona mediating a non-covalent self assembly. Due to distinct hydrophilic and hydrophobic pockets, polymersomes are excellent auxiliaries for potential applications in drug delivery [1–3], and waste water remediation [4]. The success of employing polymersomes for aforementioned applications is due to their stability, robustness and potential of advaced chemical functionalization. This has motivated researchers to design polymersome derived nanoreactors for applications in catalysis.

Polymersomes with various morphologies like micelles [5,6], vesicles [4,7,8,9], micro emulsions [10,11] etc. have been known to serve as nanoreactors for organic transformations. However, reports of literature suggest that vesicles are more efficient nanoreactors as compared to other nanoassemblies. This is because polymeric vesicles not only protect the catalyst within its compartments, but also facilitates a facile on-site isolation of reactive compounds enabling cascade reactions. They possess the ability to convert hydrophobic substrates in water and allow catalyst recovery. Such polymer vesicles can also encapsulate hydrophobic molecules and offer surfactant free metallovesicle assemblies [12].

With suitable functionalities polymer vesicles can also support metal nanoparticles encapsulation resulting in metallovesicles formation. Such metallovesicles can aid to adopt an approach where reactions can be performed under relatively mild conditions. For instance Sun et al., have demonstrated the potential of silver decorated homopolymeric vesicles to reduce water insoluble *p*-nitrophenol in aqueous media [13]. In yet another report, Jianzhong Du and co-workers have reduced 4-nitrophenol (4-NP) using Au encapsulated vesicles [14]. This is a crucial development, as nitroaromatics have been listed as “priority pollutants” by US EPA and its straightforward hydrogenation into its amino analogue can be a green strategy [15–19].

Metallovesicles capable of performing cascade reactions can further be deployed to convert these amino derivatives into organic compounds of commercial importance. Thus fabrication of metallovesicle with appropriate rationale can turn out to bring a new advent in sustainable chemistry due to their ubiquitous assistance in synthesis of commercially important compounds.

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