



Functionalized hollow double-shelled polymeric nano-bowls as effective heterogeneous organocatalysts for enhanced catalytic activity in asymmetric Michael addition



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ABSTRACT

A facile and robust strategy to fabricate organocatalyst-functionalized hollow double-shelled nano-bowl was developed for the first time by hard-templating synthesis. After the core was etched by DMF, the outer shell thicknesses below 50 nm and above 50 nm deformed into hollow nano-bowl and hollow nanosphere, respectively. Furthermore, the outer shell with the average thickness of 20–50 nm deformed into hollow double-shelled nano-bowl with a void between two semi-shells. However, the shell with the thicknesses below 20 nm severely deformed into hollow nano-bowl with no void owing to the overlapping of two semi-shells. Compared with hollow nanosphere and nano-bowl with no void, hollow double-shelled nano-bowl displayed superior catalytic performances owing to the thin shell thickness and a void between two semi-shells. In heterogeneous asymmetric Michael addition, the double-shelled nano-bowl exhibited good to excellent yields (86–98%), stereoselectivities (*syn/anti* = 81–93/19–7 and 93–99% *ee syn*) and good reusability.

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1. Introduction

Hollow spheres have attracted broad interests in recent years owing to their interior void structure, the most attractive characteristics of which are well-defined morphology, high specific surface area, low density and unique optical, electric and magnetic property [1–7]. All of these fascinating properties endow them with superior potential applications including energy storage and conversion [8–12], biomedical applications [13], catalysis [14–17], environmental science [18–20], and so forth. Recently, the bowl-like particles with a broken centrosymmetry as a class

of asymmetric structure have drawn attentions due to the anisotropic effects, thus allowing the new or enhanced properties in drug delivery [21,22], battery [23–25] and catalysis [26–30]. Furthermore, many efforts have been devoted to the development of hollow double-shelled nano-bowls, including nitrogen-doped carbon particles *via* pyrolysis using kippah vesicle as template [31], NiO nanosheets@carbon particles *via* thermal treatment using hollow polystyrene as template [32], polysilsesquioxane particle *via* toluene as liquid soft template [33], carboxyl-containing polymer particles *via* alkali post-treatment [34] and carbon nanobowls *via* hydrothermal method [35].

In the field of heterogeneous catalysis, the fabrication of the catalysts with controlled shapes and well-defined facets or surface structures is one of the most crucial issues for the design and development of highly efficient heterogeneous catalysts [36–39]. Tuning the surface morphology of heterogeneous catalysts allows the preferential exposure of catalytic sites, which can maximize the number of active sites available to reactants [40], improve the activity and also mediate the reaction route to achieve a higher selectivity for a particular chemical reaction [7,41]. As interest in asymmetric organocatalysis is on the increase as a new and powerful methodology in organic chemistry, the immobilization of organocatalysts has attracted increasing attentions [42–45].

Abbreviations: AA, acrylamide; St, styrene; PS, poly(styrene/acrylic acid); PVA, poly(vinylalcohol); ProTMS, (S)- α , α -bis(4-vinylphenyl) prolinol trimethylsilyl ether; EGDMA, ethanol ethyleneglycol dimethacrylate; KPS, potassium peroxydisulfate; Poly(St-co-ProTMS-co-AA) HBs, hollow nano-bowls; Poly(St-co-ProTMS-co-AA)HNs, hollow nanospheres; Poly(St-co-ProTMS) HBs(a), standard condition; Poly(St-co-ProTMS) HBs(b), without AA; Poly(St-co-ProTMS-co-AA) HBs(c), increased ProTMS; Poly(St-co-ProTMS-co-AA) HBs(d), doubled KPS; Poly(St-co-ProTMS-co-AA) HBs(e), doubled PS; Poly(St-co-ProTMS-co-AA) HBs(f), doubled EGDMA; Poly(St-co-ProTMS-co-AA) HN (a), DMSO/H₂O = 2/1; Poly(St-co-ProTMS-co-AA) HN (b), DMSO/H₂O = 1/1; Poly(St-co-ProTMS-co-AA) HN (c), DMSO/H₂O = 1/2.

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Recently, more attentions are paid to the enhanced catalytic performances in heterogeneous organocatalysis by means of the attractive and outstanding characteristics of hollow sphere to ensure low environmental impact and achieve more sustainable catalytic processes [46–49]. In terms of thinner shell thickness, hollow double-shelled nano-bowl is more favorable to seepage velocity of reactants than hollow nanosphere. However, the organo-functionalized fabrication of hollow double-shelled nano-bowl remains a great challenge due to the low control over precise bowl shape, poorly understood mechanisms and general synthetic strategy. Additionally, most of organocatalysts have a negative influence on the controlled fabrication of nano-bowl in hard templating process owing to its polarity, and cannot tolerate high temperature in commonly used hydrothermal synthesis.

In this study, novel hollow double-shelled nano-bowls [Poly(St-co-ProTMS-co-AA) HBs], functionalized by versatile Jorgensen-Hayashi organocatalyst [(*S*)- α , α -bis(4-vinylphenyl) prolinol trimethylsilyl ether, ProTMS] into the thin outer shell, was developed by hard-templating method for the first time. As shown in Scheme 1a, the hollow double-shelled nano-bowls were prepared by controlling the outer shell thickness *via* the first coating of ProTMS with acrylamide (AA) and styrene (St) on the surface of poly(styrene/acrylic acid) (PS) nanosphere in 0.5 wt% poly(vinyl-alcohol) (PVA) emulsifier to form core-shelled nanosphere through dispersion copolymerization, followed by selective removal of PS core in DMF. Moreover, to elucidate the superior catalytic performance of hollow double-shelled nano-bowl, ProTMS-functionalized hollow nanosphere [Poly(St-co-ProTMS-co-AA) HN] was also prepared as a control sample by altering the addition sequence of DMSO and H₂O (Scheme 1b). In heterogeneous asymmetric Michael addition, hollow double-shelled nano-bowls displayed excellent catalytic activity superior to hollow nano-bowl with no void and hollow nanosphere due to

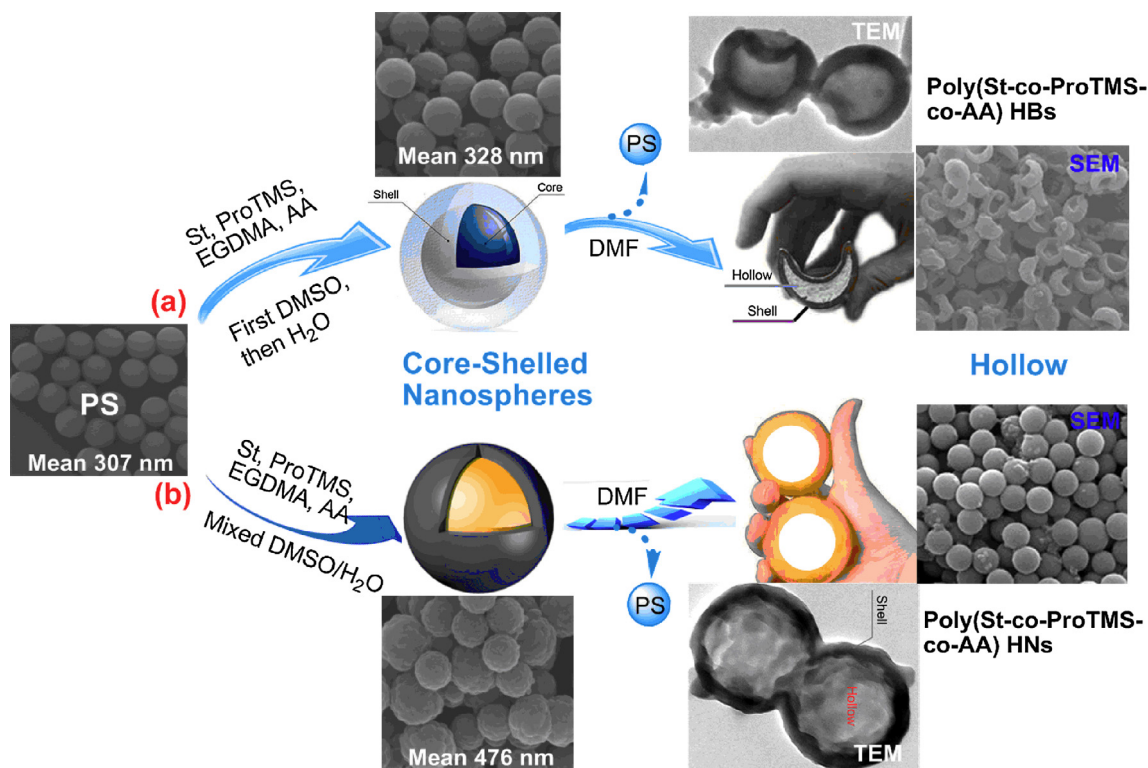
the thinner shell thickness and slightly higher specific surface area and pore volume.

2. Experimental

2.1. Materials and sample characterization

Styrene was purified by distillation under reduced pressure before use. (*S*)- α , α -bis(4-vinylphenyl)prolinol trimethylsilyl ether (ProTMS) was synthesized according to the reference (ESI[†]) [46]. The other chemicals were used as received without any further purification.

¹H and ¹³C NMR spectra were conducted using a Bruker av-600 NMR instrument, in which all chemical shifts were reported downfield in ppm relative to the hydrogen and carbon resonances of TMS. Elemental analysis was obtained using a vario Micro cube elemental analyzer. The morphology was observed by JSM-6510LV scanning electron microscopy and Tecnai G2 F20 transmission electron microscope, operated at 20 kV/15 mA and 200 kV respectively. N₂ adsorption–desorption isotherm was carried out at 77.4 K using an Autosorb-1 apparatus (Quantachrome), in which the sample was degassed at 105 °C for 12 h before measurement, and the specific surface area and pore volume were calculated by BET method and BJH model, respectively. FT-IR spectroscopy was performed on a Perkin-Elmer model GX spectrometer using KBr pellet. Thermogravimetry-differential thermal analysis was carried out on a thermal analyzer (SBTQ600) at a heating rate of 10 °C min⁻¹ from 40 to 600 °C using N₂ as protective gas (100 mL min⁻¹). The *anti*/*syn* ratios of Michael adducts were determined by ¹H NMR according to peak area ratios of proton in –CHO group, and the enantiomeric excesses (%*ee*) were monitored by Agilent LC-1200 HPLC with a 220 nm UV-vis detector using Daicel Chiralpak chiral



Scheme 1. Schematic illustration showing the synthetic process of hollow double-shelled polymeric nano-bowls (a) and hollow polymeric nanospheres (b).

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