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Facile one-pot approach to the synthesis of spherical mesoporous silica nanoflowers with hierarchical pore structure

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ABSTRACT

Hierarchically structured spherical mesoporous nanoflowers (HSMNF) with well-defined morphology and uniform size were synthesized by a hydrothermal method, in which a mixture of cyclohexane and water was used as the solvent, with cetylpyridinium bromide (CPB) as the template, tetraethyl orthosilicate as the source of inorganic silica, and urea as the hydrolysis additive. The flower size ranged from 200 nm to 500 nm, and the thickness of a "petal" was about 10 nm. We investigated the effects of solvent composition ($V_{cyclohexane}/V_{water}$), hydrothermal temperature, and molar ratio of Si to CPB on morphology and structure. The presence of cyclohexane was found to be crucial for the nanoflowers to form, and a solvent with high cyclohexane content was beneficial for the formation of smaller and more uniform nanoflowers, whereas low cyclohexane content resulted in the collapse of the nanoflower structure. The optimal ratio of cyclohexane to water was 1:1 by volume. The hydrothermal temperature and molar ratio of Si to CPB strongly affected nanoflower size and structure, as well as petal thickness. The optimal hydrothermal temperature was 120 °C, and the optimal molar ratio of Si to CPB was 4.37. The sample synthesized under optimal conditions exhibited well-defined morphology and uniform flower size. Its BET surface area reached 502 m^2/g. The nanoflowers were under 200 nm in diameter, and their average mesopore size was ca. 4 nm, as measured by N_2 adsorption–desorption. Using synthesized nanoflowers as the support, we prepared a supported PdAu bimetallic catalyst for the hydrogenation of phenol. This catalyst exhibited high activity (with a conversion rate of up to 90%) and high selectivity for cyclohexanone (up to 92%). This nanoflower's morphology, high surface area, and large pore size may make it a valuable and promising material for applications in the catalysis, adsorption and controlled release of drugs fields.

1. Introduction

Mesoporous nanoparticles with special morphologies are of great significance for their potential applications in many fields, such as catalysis, controlled-release of drug delivery, and adsorption etc, since the special morphology and structure can endow the materials with specific properties [1–6]. For example, hollow mesoporous structure makes it ideal support of nanoreactor for its well-defined pore structure and guest container [7–11]. Nanowires may be equipped with unique optical performance for its one-dimensional structure [12–17]. Chiral structured mesoporous materials may be used as catalyst or catalyst support for chiral synthesis [18–20]. Especially, the controlled-release of drug delivery can be often realized perfectly on the mesoporous materials with well defined morphology and structures [21–24], Actually, the synthesis and investigation of the mesoporous materials with special morphology and structure have become one of the most important topics in the material field.

Recently, mesoporous nanoflower has become attractive for its special flower-like morphology with higher surface area, hierarchical pores and channel, which may greatly benefit to the for the controlled release of drug delivery, catalysis and adsorption. Zhang [25] prepared novel chrysanthemum-like mesoporous silica nanoparticles by using cetyltrimethyl ammonium chloride as structure-directing agent, and the mixture of ethyl ether and water as solvent. This nanoflower particles exhibited excellent controlled release performance for pyrene; Zhang and coworkers [26] realized large-scale synthesis of monodisperse mesoporous nanoflower with a facile approach, by using cetyltrimethylammonium tosylate as template, water as solvent, and with addition of small organic

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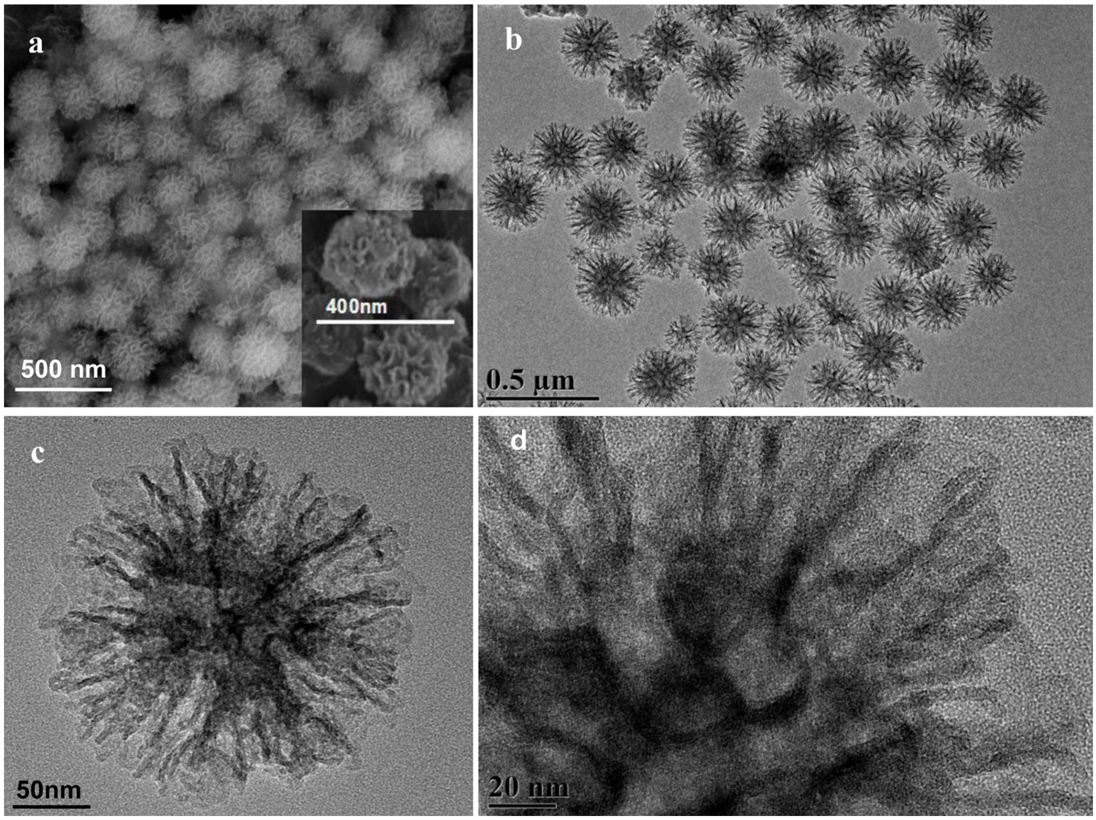

Fig. 1. SEM (a) and TEM (b–d) images of HSMNF sample.

amines (SOAs), particle size of nanoflowers is less than 130 nm. It was demonstrated that the SOAs played key roles in the formation of pore structure and nanoflower morphology. Recently, Basset [27] synthesized high surface area silica nanoflowers with fibrous morphology, which have received particular attention for their well-oriented, multi-level channel structure and controllable particle sizes. Up to now, only a few literatures about the synthesis of mesoporous nanoflowers can be searched, and the synthesis of mesoporous nanoflower with well-defined morphology, multi-level channel structure and a controllable particle size as small as 200 nm still remains a great challenge.

In this paper, we successfully synthesized silica nanoflower particles with hierarchical micro–meso–macro porous structures and a spherical morphology by a one-pot solvothermal method using cetylpyridinium bromide (CPB) as the template. The flower particles exhibit beautiful spherical flower morphology, uniform particle size distribution with size below 200 nm, and ultra high surface area. The effects of synthesis conditions on the morphology and structure of the synthesized materials have been investigated, and the nanoflower particles have been well characterized. Further, we prepared a PdAu bimetallic catalyst with the nanoflower particles as support, and it was found that the catalyst exhibited

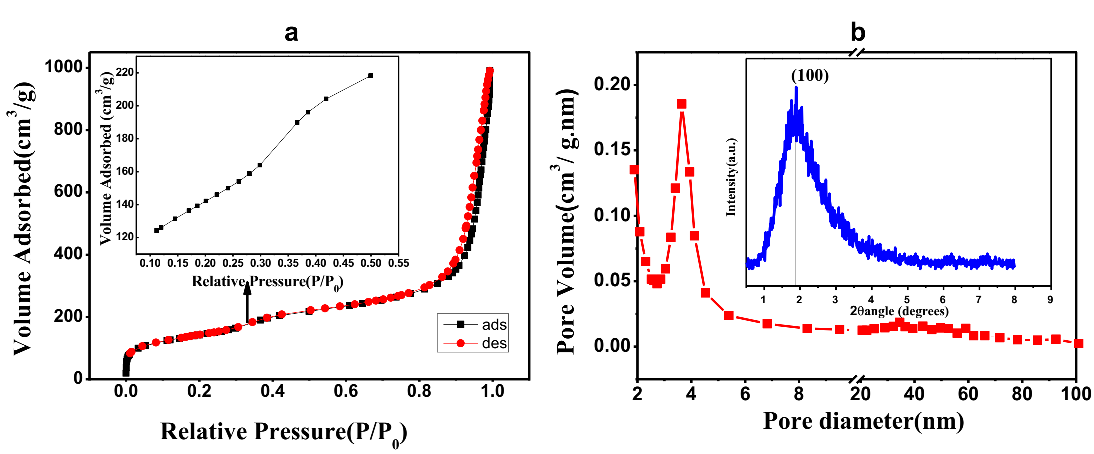

Fig. 2. (a) N_2 adsorption–desorption isotherms, (b) pore size distribution spectrum of HSMNF sample. The inset in (a) is a local amplification figure ($0.1 < P/P_0 < 0.6$); the inset in (b) is the small-angle XRD pattern result.