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A facile one-pot synthesis of monodisperse hollow hexanitrostilbene-piperazine compound microspheres

Peng Deng [a,b], Jinjiang Xu [a], Shichun Li [a], Shiliang Huang [a], Haobin Zhang [a], Junxia Wang [b], Yu Liu [a,*]

[a] Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang 621900, PR China
[b] School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, PR China

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ABSTRACT

Monodisperse hollow hexanitrostilbene-piperazine compound microspheres were fabricated successfully through a facile one-pot procedure based on the reaction of hexanitrostilbene (HNS) and piperazine without any template or surfactant. Synthesis conditions (ratio of reactants, stirring rate, reaction temperature and time) have been optimized to obtain compound microspheres with good monodispersion and narrow size distribution. And the results indicated that as-obtained microspheres possessed central hollow structures. Moreover, a possible formation mechanism for assembling hollow compound microspheres was proposed. This work may introduce a novel idea towards designing and fabricating the new hollow spheres materials.

1. Introduction

Hollow spheres materials have recently attracted considerable attention due to their promising applications in many fields, such as adsorption, energy storage, catalysis, and so on [1–5]. In the past ten years, there are a lot of useful methods towards fabricating hollow spheres materials [6,7]. For instance, Tan [8] has reported the uniform hollow polystyrene-Divinylbenzene organic crosslinked polymers spheres were prepared by using SiO_2 nanospheres as templates. Du [9] demonstrated an amphiphilic self-assembly procedure that was used to fabricate the poly (amic acid) homopolymer hollow nanospheres based on reversible addition and fragmentation chain transfer polymerization. And Wang [10] recently designed high N-doped carbon hollow spheres by pyrolysis of core-shell precursors, which used melamine-formaldehyle nanosphere as both template and nitrogen source and resorcinol-formaldehyde resin as carbon precursor. Despite their showing impressive performance in particular applications, these fabrication methods nevertheless involve drastic synthetic conditions, such as tedious steps, high temperature, hazardous solvents, and complicated post-treatment, significantly impeding their potential applications and even industrial implementation [1,8–10]. Therefore, to develop a simple, facile and scalable fabrication method towards exploring novel hollow spheres materials for satisfying their wider needs is of great significance.

Herein, a facile one-pot route is reported to fabricate monodisperse hollow HNS-piperazine compound (HHPC) microspheres materials by the reaction of HNS and piperazine without any template or surfactant. Various synthesis parameters have been investigated and optimized to obtain compound microspheres with favorable monodispersion and narrow size distribution. And central hollow structures were verified. Furthermore, a possible self-assembly formation mechanism for forming hollow compound microspheres was proposed. This facile one-pot method towards preparing hollow spheres materials maybe offer a novel idea to design and fabricate new hollow structured materials.

2. Experimental section

In a typical experiment, 0.450 g (0.01 mol) HNS, 0.387 g (0.045 mol) piperazine (molar ratio: 1:4.5) and 180 ml acetonitrile were added to 250 ml flask together. The mixture was moved into water bath. It was kept at 80 °C of constant temperature, 150 rpm of mechanical agitation and react completely for 5 h. After cooling to room temperature naturally, the products HHPC were obtained through filtration. Selected materials and synthesis conditions, such as molar ratios of reactants (1:1, 1:2, 1:3, 1:4, 1:4.5, 1:5, 1:6 and 1:8), stirring rates (0, 50, 100 and 150 rpm), reaction temperatures (20, 40, 60 and 80 °C) and reaction times(1, 3, 5 and 7 h), are introduced in the Supplementary Materials in detail.

Scanning electron microscopy (SEM) and transmission electron microscope (TEM) images were collected by the Sigma microscope and Libra 200 microscope (ZEISS, Germany) respectively. Syn-

* Corresponding author.
E-mail address: liuyu307@caep.cn (Y. Liu).

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chrotron radiation X-ray imaging technology images were further detected by the X-ray scattering apparatus (National Synchrotron Radiation Light, China). The particle size distribution was measured with Malvern Mastersizer 2000. Powder X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance X-ray diffractometer (Bruker, Germany). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Scientific). Nuclear Magnetic Resonance (NMR) data were obtained by Bruker Avance 600 (Bruker, Switzerland).

3. Results and discussions

A serendipitous phenomenon of fabricating a novel hollow compound material by the reaction of HNS and piperazine (chemical structures are shown in Fig. 1a) was discovered, and synthesis parameters were further optimized. Firstly, as shown in Fig. 1c-h, the influence of the reactant ratio was investigated by adding 0.01 mol HNS and different piperazine contents. A small amount of about 450 nm nanospheres appeared at the ratio of 1:1 in Fig. 1c. Massive bulks, which are similar to raw HNS in Fig. 1b, existed obviously and broken surfaces showed the reaction sites. XRD patterns demonstrated reactant HNS still retained but a new phase appeared at this ratio in Fig. 3a. The intensity of this intermediate phase rose and raw material disappeared with increased piperazine contents. When piperazine contents added to the ratio of 1:3 in Fig. 1d, the relative number of compound spheres, of which the diameter increased to ~800 nm, had risen, but non-spherical particles still existed. With the piperazine contents expanding sequentially, non-spherical particles and the intermediate phase disappeared gradually. From the Fig. 1e, it is seem that the reactants could be almost completely converted into compound microspheres at ratio of 1:4.5, where the diameter is close to 1 μm. With the expansion of piperazine contents further in Fig. 1f-h (the ratio of 1:5, 1:6 and 1:8 respectively), special multi-layer petal-like nanostructure samples were found. For distinctive morphological particles, it is not our mission here to delve into this phenomenon. Thus, an optimum ratio determined by compared experiment is 1:4.5.

Furthermore, stirring rate, reaction temperature, and reaction time for HHPC were optimized based on the above optimum ratio. As-obtained samples by changing the stirring rate were shown in Fig. 1i-l. Tremendous microspheres were prepared at higher stirring rates of 100 and 150 rpm in Fig. 1k and l respectively, although many irregular micro-bulks or nanofibers existed at lower stirring rates of 0 and 50 rpm in Fig. 1i and j. Then, HHPC by different tem-

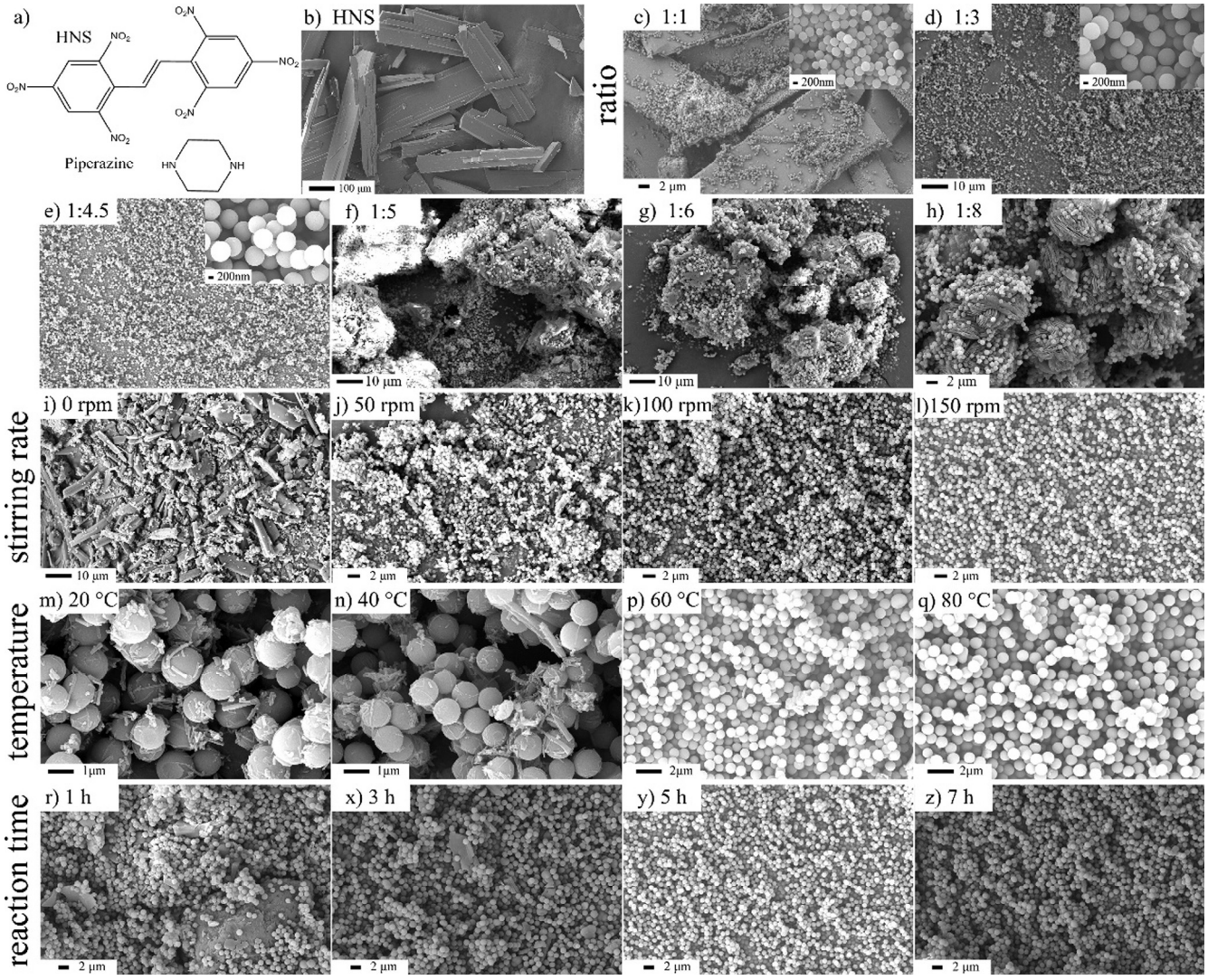

Fig. 1. (a) chemical structures of reactants, and (b-z) SEM images of HHPC under different conditions.