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Theoretical and experimental studies on the silica hollow spheres

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Abstract

The structures and properties of the silica hollow spheres have been studied by experimental and quantum chemical calculations. The structure of the silica hollow spheres was characterized by TEM, BET and XPS. According to the experimental results, a model of porous silica clusters has been proposed to represent the structure of the silica hollow spheres. The geometry of model was optimized by the semi-empirical PM3 method and the density of states for the model was calculated by ab initio methods at the level of 3-21G and 6-31G. Both the influences of model size and the effect of basis set are discussed. It is found that the calculated binding energies of O1s, Si2s and Si2p are in fairly good agreement with the experimental results. The studies indicate that the small cluster model can be used to reasonably analyzed the structure and properties of silica hollow spheres.

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1. Introduction

In recent years, hollow spheres have an interesting field of study because of their potential applications in functional materials and smart systems. For example, they can serve as extremely small containers for drug delivery, catalyst carriers as well as micro-reactors [1–3]. Hollow spheres may also provide some immediate advantages over their solid counterparts because of their relatively low densities [4]. Many papers have described the formation of hollow spherical materials, and several of them are on silica hollow spheres [5–7]. However, studies of detailed structures and properties of silica hollow spheres (SHSs) have not been found in the literature until now.

Understanding the relationship between the molecular structure and the chemical and physical properties of real materials is one of the most significant topics in material science. The structures and properties of silica have received considerable experimental as well as theoretical attention in past decades; most of the reported structures are small and simple cluster [8,9]. For example, photoelectron spectra of a number of silica cluster including Si_3O_y ($y = 1$–6), Si_nO_n ($n = 3$–5), $(SiO_2)_n$ ($n = 1$–4) and Si $(SiO_2)_n$ ($n = 2,3$) have been studied extensively [10–12]. These experiments have provided useful information regarding the electronic structures of the clusters, but the information about the geometric structures is indirect. Meanwhile, the geometric structures and electronic properties of small silica clusters have been studied by many researchers using ab initio calculations, density functional theory and semi-empirical methods [13–17]. However, the efforts to correlate the structure of complex molecules with physical properties at a quantum chemistry level have been restricted

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due to limitations in the quantum chemistry models used to represent the electronic structure and in the computational power available. So far, to our knowledge, the XPS experimental and theoretical studies on silica materials with special morphologies (such as hollow spheres) have never been reported.

XPS is a very useful technique for obtaining the binding energy (BE) of the core and valence band for occupied electron levels. Ground state related information about the occupied states can be more directly obtained in this way [18]. Relative BE values are useful parameters to check the validity of electronic structure calculations [19].

In this paper, a joint experimental and theoretical investigation on silica hollow spheres (SHS) is presented. The SHSs were modeled as porous silica clusters according to their experimental characterizations. The model geometries are optimized using the semi-empirical PM3 method and the density of states (DOS) of the system is calculated using the ab initio self-consistent field (SCF) method. The calculated results are compared to the experimental XPS data.

2. Experimental section

Silica hollow spheres was prepared using a double-templated method [20,21], in which calcium carbonate nanoparticles ($CaCO_3$) served as core templates and the cetyltrimethyl-ammonium bromide (CTAB) as wall structure-directing agents. Scheme 1 displayed the synthesis procedure.

TEM was viewed on a Philips TECNAI-20 electron microscope operated at 200 kV. The sample was prepared by dipping a Cu grid coated with carbon films in sample suspension with ethanol as solvent.

BJH pore size distribution was determined from desorption branch of the isotherm of nitrogen at 77 K using a volumetric adsorption analyzer ASAP2010 manufactured by Micromeritics.

XPS were obtained on a PHI 5300× Physical Electronics Spectrometer using 250 W (12.5 KV × 20 mA) MgK_α X-rays (1253.6 eV) and analyzer pass energies of 81.95 eV (broad scan) with step of 0.10 eV as well as 35.75 eV (high resolution) with step of 0.05 eV at vacuum 10^{-9} Torr. Drift of the electron binding energy due to surface charging effects was calibrated with the reference to C1s peaks (284.6 eV). Data were processed on Apollo Series 3500 workstation. The measurement precision of binding energy was ±0.2 eV.

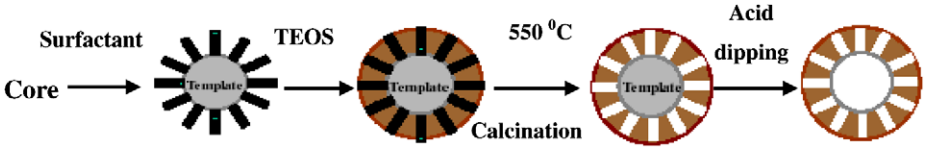
3. Computational details

A semi-empirical method was adopted to optimize the geometric structure of the models of the silica hollow spheres because the size of the system preculded computation at the ab initio level. Preoptimization was performed by applying the molecular-mechanics method [22] using an MM2 force field [23], this made it easier to perform a full optimization by extended methods. The PM3 semi-empirical method [24,25] was used to fully optimize the geometry of the SHSs's model with a conjugate gradient technology [26]. The molecular orbitals of the model were calculated by using an ab initio self-consistent field (SCF) method with 3-21G and 6-31G basis sets. All calculations were carried out using GAUSSIAN 03 packaged code.

4. Results

4.1. Modeling

The real structure of the silica hollow spheres is so complicated that it is necessary to construct an effective model



Scheme 1. Procedure for preparation of silica hollow spheres.

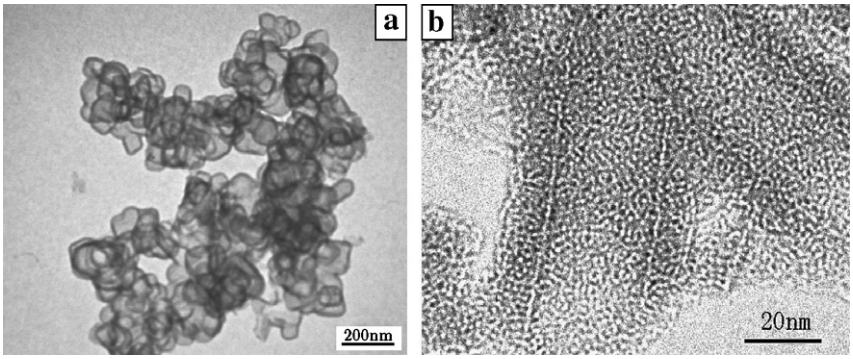


Fig. 1. TEM (a) and HRTEM (b) images of the silica hollow spheres.