Synthesis of core–shell AlOOH hollow nanospheres by reacting Al nanoparticles with water

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Abstract
A novel route for the synthesis of boehmite nanospheres with a hollow core and the shell composed of highly crumpled AlOOH nanosheets by oxidizing Al nanopowder in pure water under mild processing conditions is described. The stepwise events of Al transformation into boehmite are followed by monitoring the pH in the reaction medium. A mechanism of formation of hollow AlOOH nanospheres with a well-defined shape and crystallinity is proposed which includes the hydration of the Al oxide passivation layer, local corrosion of metallic Al accompanied by hydrogen evolution, the rupture of the protective layer, the dissolution of Al from the particle interior and the deposition of AlOOH nanosheets on the outer surface. In contrast to previously reported methods of boehmite nanoparticle synthesis, the proposed method is simple, and environmentally friendly and allows the generation of hydrogen gas as a by-product. Due to their high surface area and high, slit-shaped nanoporosity, the synthesized AlOOH nanostructures hold promise for the development of more effective catalysts, adsorbents, vaccines and drug carriers.

Keywords: hollow nanospheres, aluminum nanoparticles, core–shell nanostructures, oxidation, boehmite, nanosheets

(Some figures may appear in colour only in the online journal)

1. Introduction

The synthesis of hollow nanospheres with various compositions and complex shell structures is a topic that has attracted considerable research attention [1–4]. These nanostructured materials are characterized by low density, high specific area and large void fraction and are increasingly used in catalysis [5], drug delivery [6, 7], chemical reactors [8], controlled delivery of biologically active agents [9], and in the design of organic/inorganic hybrid materials [10]. Over the past decade, the synthesis of diverse hollow nanoparticles, including Fe₃O₄ nanoparticles [11], Co oxide nanoparticles [12], ZnO microspheres [13], Ag₂ZnGeO₄ microspheres [14], SnO₂ spheres [15], alumina based nanospheres [16–17], and so on, have been reported. Among other metal oxides/hydroxides, aluminum oxyhydroxide (AlOOH) nanostructures are of special interest due to their unique physicochemical properties and biocompatibility. In addition to its wide use as a catalyst, adsorbent and precursor for the synthesis of nanoscale γ-Al₂O₃, nanocrystalline aluminum oxyhydroxide exhibits immune stimulating properties and is one of few compounds approved as a human vaccine adjuvant [18–20]. In existing
and potential applications, the properties and performance of AlOOH can be strongly affected by its crystallinity and hydroxyl content, as well as by its particle size, shape and morphology. Hollow AlOOH nano- and microspheres are of particular interest, and several processing routes for such particles have been proposed. In [21–24], AlOOH (boehmite) microspheres were synthesized hydrothermally by reacting inorganic Al salts with organic compounds. At the same time, there are no reports on the synthesis of hollow boehmite nanospheres that employ environmentally friendly methods. In the present work, we report the synthesis of hollow nanospheres covered by boehmite nanosheets by the mild hydrothermal oxidation of aluminum nanopowder. The proposed route is simple and environmentally safe and allows one to not only produce high-purity boehmite with extremely large surface area but also to generate hydrogen gas as a by-product.

2. Experimental details

Core–shell hollow nanospheres of AlOOH were synthesized by water oxidation of aluminum (Al) metal nanoparticles. Al nanoparticles were produced by electrical explosion of Al wire in argon [25] (‘Advanced Powder Technologies LLC’, Russia) and passivated by atmospheric oxygen. Hollow nanospheres were synthesized by heating the suspension of aluminum nanoparticles in deionized water (1 wt% Al) from 24 to 60 °C at a heating rate of 1–1.2 °C min⁻¹. During processing, four parameters were monitored as a function of time: the pH, temperature, Al³⁺ ion concentration of the reactive medium and hydrogen release rate. The process reproducibility was confirmed in at least 15 independent experiments with five different batches of Al nanopowder. To determine the concentration of Al³⁺ in suspension, 2 ml aliquots were drawn from the solution at set time points (0, 16, 21, 33, 35, 36, 37, 38, 39 and 46 min). The concentration of Al³⁺ was measured in a UV spectrophotometer (PE-5400 V, PromEcoLab, Russia) at a wavelength of 535 nm using Eriochrome Cyanine R as the complexing agent. The amount of hydrogen gas formed in the reaction was measured volumetrically at set time intervals (14, 19, 24, 29, 34, 34.4, 35.4, 36.2, 36.7, 37.1, 37.2, 37.4, 38.2, 39, 44, 49 min). In order to determine the intermediate oxidation products, the reaction was quenched at predetermined times: the reacting suspension was poured into 0.5 l of alcohol at 5 °C after which the precipitate was filtered and dried at 120 °C for 2 h. Phase identification was performed by x-ray diffraction, XRD, in an automatic powder Shimadzu XRD 6000 diffractometer with a long-focus Cu Ka tube operating at 40 kV and 30 mA. Microstructure characterization was performed in a transmission electron microscope, TEM (JEM-2100, JEOL), and high resolution SEM Zeiss Ultra-Plus FEG-SEM (Carl Zeiss Group, Germany). The specific surface area of the synthesized powder was measured by the Brunauer–Emmett–Teller method (BET), and pore size distribution was determined by the analysis of nitrogen adsorption and desorption isotherms at 77 K employing the method of Barrett–Joyner–Halenda (BJH). Zeta potential measurements were performed using a Zetasizer Nano ZSP (Malvern Instruments, UK) at pH 7.4 and 37 °C.
3. Results and discussion

The obtained spherical Al nanoparticles had an average diameter of 92 nm and were uniformly coated by a 4–5 nm thick oxide layer (figure 1).

As it can be seen in the representative graph in figure 2, the reaction of aluminum nanopowder with water was accompanied by a non-monotonic change in the reactive medium parameters. The analysis of the curves in figure 2 allows one to define four stages of the reaction process. These four stages were reproducibly observed in all the conducted experiments, with the shift of the beginning/ending time points not exceeding 2 min. Stage I is the induction period during which all of the parameters remain constant. At stage II, the pH of the reactive medium increases monotonically from 6.1 to 8.1, presumably due to the hydrolysis of the Al$_2$O$_3$ layer on the surface of the Al nanoparticles [26, 27]. A similar increase in pH from approximately 7 to 8.2 was observed by other authors during the addition of 5 g of alumina powder to 100 ml of water [28]. During stages I and II, the Al$^{3+}$ ion concentration remains constant, and no hydrogen evolution and no temperature increase beyond that expected due to external heating are observed.

Stage III is characterized by the sharp increase in the Al$^{3+}$ ion concentration (curve 3), hydrogen gas evolution (curve 4) and self-heating of the reactive medium to approximately 70 °C (curve 2). These findings suggest that at stage III, an exothermic reaction of Al corrosion takes place. The Al$^{3+}$ ions released into aqueous solution tend to complex with six H$_2$O molecules to form aluminum hexahydronium, Al(H$_2$O)$_6^{3+}$. The continued hydrolysis of this compound involves the formation of several Al hydroxides and release of H$^+$ ions [29]. This explains the formation of H$_2$ gas and the small drop of pH observed at stage III, figure 2. The time corresponding to the lowest pH value (7.9) and the most vigorous H$_2$ release defines the end of stage III and the beginning of stage IV.

At stage IV, the pH of the suspension starts to rise again, while hydrogen evolution and self-heating still go on. All these processes come to a halt once the maximum pH value of 8.4 has been reached. This roughly corresponds to the point of zero charge of the boehmite–water interface [30] and thus suggests the formation of boehmite by the end of stage IV. Finally, the concentration of Al$^{3+}$ in the reactive media drops to practically zero, indicating the end of the dissolution of the Al core of the initial nanoparticle.

To gain a deeper insight into the reaction mechanism of boehmite formation, the oxidation products of Al nanoparticles were studied at different process stages. At stage I, no structural and compositional changes of the initial Al nanoparticles were observed. At the later reaction stages, the oxidation process resulted in a gradual change in the particles’ shape and composition, as shown in figure 3. Thus, at stage II, small nanoscale (5–10 nm) islands can be seen on the surface of Al nanoparticles, apparently the hydration products of the Al$_2$O$_3$ surface layer. These islands are amorphous as indicated by the absence of any diffraction peaks other than of metallic Al (JCPDS PDF No. 03-065-2869) in the corresponding XRD pattern. It has been previously reported that the hydration process of alumina that consists essentially of the formation of bayerite, proceeds via a transient step corresponding to an amorphous phase [31]. In [32], water-suspended alumina nanoparticles were found to be surrounded by a cloud-like disordered hydration overlayer containing Al(OH)$_3$ and AlOOH.
In the beginning of stage III (pH = 8.1), very thin (less than 5 nm) sheets not exceeding 50 nm in width and length start to form on the surface of the nanoparticles, figure 3(b). Small peaks of boehmite (AlOOH) can be discerned in the corresponding XRD pattern (JCPDS PDF No. 00-017-0940). Most likely, the hydration of alumina at stage II introduces defects in the barrier layer that may initialize a local electrochemical attack. It has been reported, for example, that the hydration of the Al oxide layers on Al films not only leads to the partial conversion of the oxide to hydroxide but also significantly increases the electronic defect concentration within the remaining oxide layer, manifested in a large increase of its electric conductivity [33]. Sites in the aluminum oxide layer that are particularly susceptible to hydration will exhibit a higher electronic defect density and thus be more susceptible to local electrochemical breakdown. This will lead to the formation of local pits in the oxide barrier, making it more permeable to water. The formation of defects may be further favored by the small size and corresponding large curvature of the Al nanoparticles.

Once the defects in the passive film have been formed, water penetrating through these defects will locally react with metallic Al generating hydrogen gas bubbles at the interface between the Al core and the protective surface layer. The growing H₂-gas pressure will eventually rupture the protective layer thus activating metallic Al for reaction with water. This reaction is accompanied by a rapid temperature increase and strong hydrogen gas evolution, as shown in figure 2. By the end of stage III, strong peaks of boehmite appear in the XRD pattern along with the peaks corresponding to metallic Al. The dimensions of boehmite nanosheets reach 100 nm. Boehmite nanosheets with a similar crumpled morphology have been recently synthesized in [24] by reacting aluminum sulfate with hexamethylenetetramine. The darker contrast in the particle center must be due to the presence of metallic Al and indicates that in some (presumably the largest) particles Al has not yet been fully consumed. At stage IV, the corrosion process of aluminum proceeds, eventually leading to the formation of single-phase boehmite nanoparticles, figure 3(d). At the end of stage IV, no residual Al metal is detected by.
XRD analysis. The absence of the metallic Al core upon the completion of the reaction is also confirmed by the brighter TEM contrast in the center of the newly formed spherical particle.

As one can see in figures 3(d) and 4(a), the final outer diameter of the boehmite shell in the fully reacted nanoparticle is ~300 nm, which corresponds to a 27-fold volume increase of the initial Al nanoparticle (~100 nm). Having in mind that the molecular volume of boehmite is twice that of Al, it can be easily shown that if all the Al is consumed by the formation of boehmite, the shell should be ~8% dense (~92% porous). If some Al was left inside the core, the density of the shell would be less than 8%; for example if 2% of Al was left, the density of the shell would be 4%. The EDS line scans across the fully converted particle, figure 4(a), show that both the Al and oxygen signals originating from the particle interior are noticeably weaker those from the particle shell. This is in contrast to the partially reacted particle, figure 4(b), whose interior contains much more Al. These observations indicate that the core of the boehmite particle is less dense than its shell, suggesting that the particle is either hollow or almost hollow (~2% dense or less, according to our estimation).

In figure 5, HRSEM images of the fully reacted Al nanoparticles are shown. The flower-like spherical morphology and the hole inside the particle with a broken shell (figure 5(b)) are clearly seen. The measured EDS spectrum of the hydrolyzed nanopowder is identical to the calculated spectrum of AlOOH, confirming the formation of the stoichiometric boehmite (figure 5(c)).

Figure 6 shows the N2 adsorption–desorption isotherm of the synthesized boehmite nanoparticles. The isotherm can be classified as type IV and exhibits an H3-type hysteresis loop at p/p0 > 0.4. Such isotherms are characteristic of plate-like nanostructures that have slit-shaped pores [34]. The large BET specific surface area determined from the isotherm (303.4 m² g⁻¹) is comparable with the numbers reported in [22–24] for hollow and core–shell spherical AlOOH particles. The pore size obtained using BJH analysis is less than 19 nm, which represents the slit width between the AlOOH nanosheets in the synthesized mesoporous structure. The positive zeta potential of 36.5 ± 0.7 mV (measured at pH 7.4) indicates that the synthesized AlOOH nanoparticles are positively charged.

The formation of boehmite nanoparticles with hollow interiors can be explained by the relatively low reaction rate achieved due to the strong dilution (powder-to-water
ratio $= 1:100$) of the initial Al nanopowder suspension. The moderate temperature increase observed under these conditions leads to only a modest acceleration of the Al corrosion and of the accompanying hydrogen evolution. As a result, the hydrated shell of the Al particles is not fully disrupted, and Al dissolves from the particle interior and deposits, as AlOOH nanosheets, on the shell exterior surface leaving a void inside. Most probably, powders with different morphology and different composition (e.g., bayerite) would be obtained under different hydrolysis process conditions. In [35], for example, no formation of hollow boehmite nanoparticles was reported for one gram of 80–100 nm diameter Al nanoparticles suspended in 200 ml of distilled water at different temperatures from 30 to 80 °C.

Due to their high nanoporosity (>90%), the synthesized nanostructured boehmite nanospheres can be considered as a possible controlled drug delivery matrix. Biomolecule loading into the nanospheres can be achieved by high pressure application or vacuum loading. The stored drugs and/or proteins confined in <19 nm thick slit-like nanospheres between the AlOOH nanosheets are expected to be slowly released through the water-filled nanochannels due to the slow dynamics of nanoconfined liquids [36]. To demonstrate drug-loading capacity, the AlOOH nanopowder was consolidated at 500 MPa into 10 mm diameter, 4 mm thick, disc-like compacts. This led to the porosity decrease from ~92% to ~40%. The immersion of the AlOOH compacts in water (modeling drug solution) under the vacuum of 13 Pa (0.1 Torr) for 30 min resulted in the filling of 36% of the available hollow space (~14.5% water loading efficiency). This result suggests that the described disc-shaped specimen can be loaded with 45 mm$^3$ of an aqueous drug solution. As AlOOH is biocompatible and is being used as a drug adjuvant for human use, the synthesized hollow boehmite nanostructures may provide new options for drug delivery and drug therapies.

4. Conclusion

A novel mildly hydrothermal route to synthesize nanospheres with the hollow core and the shell composed of highly crumpled AlOOH nanosheets has been proposed. The formation of regular-shaped AlOOH nanoparticles is accomplished by water oxidation of aluminum nanoparticles under conditions of slow heating at a high water-to-Al ratio. The proposed method is attractive due to its simplicity and environmental friendliness, as well as due to the generation of hydrogen gas as a by-product. The synthesized hollow nanoparticles of boehmite with a well-defined shape and crystallinity and a permeable shell can be potentially applied for the development of more effective catalysts, adsorbents, vaccines and drug carriers. The unique combination of an extremely large surface area and measured positive surface charge of AlOOH with hydrophilicity and positive surface charge of AlOOH reported also in [37] make these boehmite nanostructures especially attractive as cancer-targeted nanocarriers since hydrophilic surfaces are known to allow for longer circulation times, and positively charged surfaces can enhance internalization into cancer cells [38, 39].

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