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# Solvent-polarity-induced hematite ($\alpha$-$Fe_2O_3$) nanostructures for lithium-ion battery and photoelectrochemical applications

Rajendra C. Pawar[a,1], Ji Hyun Um[b,1], Suhee Kang[a], Won-Sub Yoon[c], Heeman Choe[d], Caroline S. Lee[a,*]

[a] Department of Materials Engineering, Hanyang University, Ansan, Gyeonggi-do 15588, South Korea
[b] Integrated Energy Center for Fostering Global Creative Researcher, Sungkyunkwan University, Suwon, Gyeonggi-do 16419, South Korea
[c] Department of Energy Science, Sungkyunkwan University, Suwon, Gyeonggi-do 16419, South Korea
[d] School of Materials Science & Engineering, Kookmin University, Seoul, 02707, South Korea

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ABSTRACT

A range of morphology-controlled hematite superstructures, including two-dimensional sheet assembly, microspheres with a vein-like network, hollow urchin with tapered nanorods, and flowers with porous branch-like structures, were obtained from different solvents via the solvothermal approach. The results showed that the variation of the solvent from protic to aprotic facilitated morphological modifications, with the solvent playing a key role in determining the overall architecture of the oxide particles under different polar conditions. A porous microsphere grown from water solvent delivered a reversible capacity of 880 mAh $g^{-1}$ over 60 cycles at 200 mA $g^{-1}$ with good rate stability. Here, the bicontinuous nanoporous structure, with well-developed mesoporosity in the microsphere, reduced the severity of volume changes during the cycling process and stabilized passivation layer growth. The hematite nanostructure grown from water/dimethylformamide solvent exhibited the highest photocurrent density of 190 $\mu A/cm^{-2}$ vs. Ag/AgCl, which was attributed to the rapid transport of charge carriers in the porous nanostructure. Thus, solvent-mediated synthesis can be used to prepare a range of hematite porous nanostructures for use as an anode in lithium-ion batteries and as a photoanode in photoelectrochemical cells, as well as for water splitting, gas sensors, and catalytic applications.

## 1. Introduction

Control of the growth of metal oxide structures at the nanometer scale remains an ongoing challenge in the field of nanomaterial-based devices for advanced technologies. Morphology-tuned nanostructures have contributed significantly to improved device performance in lithium-ion batteries (LIBs), photoelectrochemical cells, and gas sensors and in thermoelectric power generation and adsorbent applications in water treatment and biotechnology [1–5]. The functionality of synthesized nanostructures depends on their dimensionality, tailored shapes and sizes, and surface characteristics. In particular, the assembly of one-dimensional (1D, nanoparticles or dots) nanostructures into two-dimensional (2D, sheets) and three-dimensional (3D, hierarchical shapes) superstructures has resulted in material structures with excellent chemical and physical properties [6–9]. Simultaneously, highly porous 3D structures with hollow cores and a number of fine pores are of interest to researchers due to their superior permeability, low density, large specific surface area, and stability. Therefore, the fabrication of specifically controlled metal-oxide nano-architectures and morphologies is worthwhile.

Thus far, a number of strategies, including hard/soft templates, sol-gel, co-precipitation, molten salt corrosion, microemulsion, Ostwald ripening, and other chemistry-based synthetic methods, have been used to grow nanomaterials with enhanced properties [10–12]. Of these, the controlled chemical approach has been the most viable due to the relatively low processing temperature. The anisotropic growth of crystals leads to hierarchical shapes and slight variations in parameters (pH, concentration, and metal precursors) for novel nanostructure production; no template is required, leading to a cost-effective, single-step process. Thus, this method has been utilized for metal-oxide nanostructure synthesis (ZnO, $TiO_2$, $Fe_2O_3$, $WO_3$, etc.), resulting in structures with enhanced properties for applications across a range of fields [13–18].

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[*] Corresponding author.
*E-mail address:* sunyonglee@hanyang.ac.kr (C.S. Lee).
[1] Both authors contributed equally to this work.

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However, the ability to generate the desired nanoporous morphology using a simple approach is still a challenge for advanced energy technologies.

Among metal oxides, hematite ($\alpha$-$Fe_2O_3$) is the most thermodynamically stable and an important *n*-type semiconductor, with a band gap of 2.1 eV. It has been extensively studied in a wide variety of fields, including photoelectrochemical (PEC) cells and LIBs, due to its environmental friendliness, natural abundance, high resistance to corrosion, and low cost [19,20]. To date, a range of specific morphologies have been synthesized, such as wires, rods, belts, cubes, polyhedrons, dendrites, hexagonal prisms, spindles, flakes, flowers, and porous/hollow spheres, using both chemical and physical routes [21–24]. As predicted, these hematite structures have shown improved and shape-dependent properties. However, there are still a number of limitations to developing these structures with sufficient efficiency for commercial use. For example, in PEC applications, the recombination of photogenerated electron–hole pairs hinders catalytic performance significantly. In the case of LIBs, the electrode capacity and cycling ability are significantly limited by low conductivity and the extreme volume change during charging/discharging [25,26]. Substantial research efforts have been dedicated to addressing these limitations in an attempt to enhance performance (e.g., the solvothermal/hydrothermal growth of superstructures and metal nanoparticle and carbonaceous material incorporation) [27–30].

Among these approaches, controlled nanostructure growth is an effective and simple method for improving performance. In this process, anisotropic crystal growth can be facilitated by the addition of surfactants, chelants, and solvents of different polarities [31]. Precursor solubility plays a crucial role in dissolving metal precursors and modifying crystal facets [32]. The variation in solvent polarity determines the final shape of the nanostructures because it controls the kinetic rate and the interactions between primary nucleation centers [33]. Therefore, it is interesting to explore the growth of nanostructures in the presence of solvents of different polarities.

In this paper, we have grown different morphologies, including 2D nanosheets, 3D polydispersed microspheres with a vein-like network, agglomerates, hollow urchin, and porous branched flowers, starting from simple combinations of protic/aprotic solvents. Simultaneously, we used ascorbic acid during hydrothermal treatment, which acted as a reducing agent and source of carbon. In addition, one more sintering step induced the crystallinity and pores throughout the nanostructures. The formation of porous and crystalline structures created the channels for the intercalation/de-intercalation of lithium ions into the interior part of the nanostructures. Consequently, we propose a possible growth mechanism for the final structure and applied a range of analytical tools to characterize this structure. Outstanding performance in both LIB and PEC applications was demonstrated by the fabricated hematite $\alpha$-$Fe_2O_3$ micro/nanostructures.

## 2. Experimental procedures

### 2.1. Materials

Ferric chloride hexahydrate ($FeCl_3{\cdot}H_2O$), L(+)-ascorbic acid ($C_6H_8O_6$), and N-N-dimethylformamide (DMF) were purchased from Junsei Chemicals Co. Ltd. (Tokyo, Japan). Hexamethylenetetramine (HMTA, $C_6H_{12}N_4$) was obtained from Daejung Chemical Co., Ltd (Seoul, South Korea). Absolute ethanol (EtOH) was provided by Merck, Ltd. (Seoul, South Korea). All chemicals were used directly without additional purification or processing. Distilled water with a resistivity of $\sim$3.2 M$\Omega$ cm was collected from a water purification system (Hanascience, South Korea).

### 2.2. Preparation of hematite nanostructures

The hierarchical hematite nanostructures were grown using a single-step hydrothermal method at a relatively low temperature. In these experiments, 0.5 M of $FeCl_3{\cdot}H_2O$ (4.055 g) was dissolved in 60 mL of distilled water with magnetic stirring. Next, 0.5 M of HMTA (2.103 g) was added to the solution with continuous stirring at room temperature. Then, 30 mL of absolute EtOH was poured into the solution with constant stirring. After the addition of EtOH, the iron chloride and HMTA dissolved completely, forming a dark yellow solution. AA (1.5 g) was mixed with the growth solution. After 30 min of uniform stirring, the color of the solution changed to dark brown, indicating $Fe^{3+}$ ion reduction. The solution was then transferred to a 100-mL Teflon-lined stainless-steel autoclave and maintained at 180 °C for 5 h. The autoclave was allowed to cool to room temperature. The solution was filtered and then repeatedly washed with distilled water and ethanol. The obtained product was dried in an oven. Finally, the dried powder was thermally treated in air at 500 °C for 1 h at a heating rate of 10 °C $min^{-1}$ to form a hematite phase. To produce different hematite nanostructures, different solvents were used, including EtOH, $H_2O$, DMF, a mixture of $H_2O$ and EtOH (50/50 vol%), and $H_2O$/DMF, under the same experimental conditions.

### 2.3. Characterization

The surface morphology and detailed growth of microstructures were studied using field-emission scanning electron microscopy (FE-SEM; Hitachi S4800) and transmission electron microscopy (TEM; JEOL 2100), respectively. The phase formation of hematite nanostructures grown from different solvents was examined with X-ray diffraction (XRD) patterns obtained with Cu-K$\alpha$ radiation (D/MAX-2500/PC, Rigaku). Nitrogen adsorption–desorption isotherms were recorded at 77 K to determine the specific surface area of the nanostructures via the Brunauer–Emmett–Teller method (BET; Quantachrome). The diffused reflectance spectra were recorded using an ultraviolet–visible (UV–Vis) spectrophotometer (Jasco; V-600) with barium sulfate as the reference. The existence of different chemical groups inside the grown nanostructures was determined using Fourier transform infrared spectroscopy (FTIR; Bruker IFS 66/S).

### 2.4. Electrochemical measurements

A working electrode was fabricated using the morphology-controlled hematite nanostructure as the active material, Super P as the conductive agent, and polyvinylidene fluoride (PVDF) as the binder in an N-methyl-2-pyrrolidone (NMP) solvent at a weight ratio of 70:15:15. The mixed slurry was uniformly plastered onto copper foil as a current collector using doctor-blade processing. The electrode was dried under a vacuum at 120 °C for 8 h. A 2032-type coin cell comprising a working electrode, a counter electrode of lithium metal, and a reference electrode separated by a polypropylene separator was assembled in a glove box in a dry argon atmosphere. The organic electrolyte used was 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) at a 1:1 volume ratio. Galvanostatic testing (WBCS3000 Cycler, Wona Tech Co., Ltd., Korea) was performed on the coin cell over a voltage range of 0.01 to 3.0 V (vs. $Li^+$/Li).

The photoelectrochemical (PEC) characteristics of the prepared hematite nanostructures were examined using a standard three-electrode electrochemical workstation (Model VersaSTAT 4, Princeton Applied Research, USA). The working electrode, counter electrode, and reference electrode were fabricated from the as-prepared $\alpha$-$Fe_2O_3$ hematite photoanode, platinum foil, and Ag/AgCl, respectively. The photocurrent was measured by linear