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Luminescent tubular precipitation structures from reactant-loaded pellets

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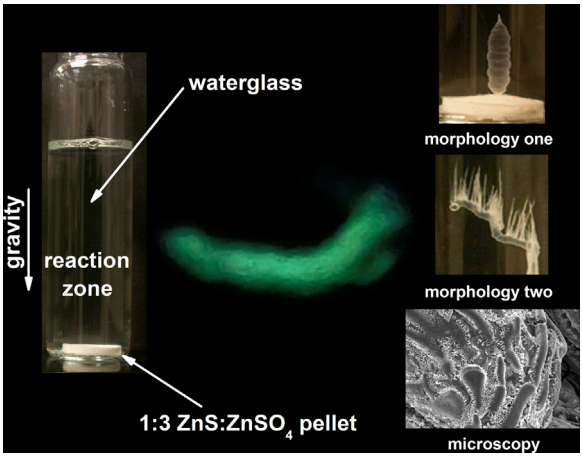
HIGHLIGHTS

- Pellets containing $ZnSO_4$ and ZnS form tubes when sodium silicate is poured on them.
- Tube growth is directed by a gas bubble attached to the surface of the colloidal membrane.
- The growth kinetics and morphology of tubular precipitates are monitored by a time-lapse camera.
- Scanning electron microscopy (SEM) is used to characterize the precipitation patterns.
- The tubes exhibit photoluminescence upon excitation.

GRAPHICAL ABSTRACT



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ABSTRACT

Using reaction conditions far from equilibrium, we are able to produce hollow tubes formed from reactant-loaded pellets. The latter pellets are composed of zinc sulfate and phosphorescent zinc sulfide by mass. During the experiment, a single pellet is fixed at the bottom of a container and then a small volume of concentrated sodium silicate is poured on the pellet's surface. Dilatory tube growth is directed by a single gas bubble which is monitored by a time-lapse camera. Using procedures of image acquisition and processing we are able to quantify the spatio-temporal dynamics. Systematic measurements include induction period and growth velocity. We describe two distinct morphologies of precipitation tubes which form at the interface of the two reactants. The resulting tubes can range from 1.1–1.8 mm to 450–900 μm in radii depending on the morphology. Scanning electron microscopy reveals that the precipitation tubes have intricate patterns on the outside surface. Lastly, the tubes exhibit photoluminescence upon exposure to ultraviolet light.

1. Introduction

Self-organization in aqueous reaction–precipitation systems often leads to the formation of permanent architectures. The two most prominent inorganic precipitation systems of laboratory

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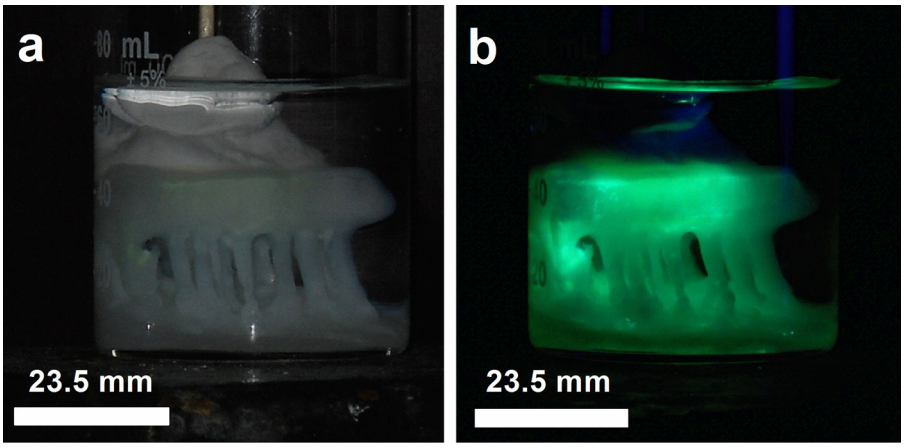

Fig. 1. (a) Reverse tube formation and (b) its photoluminescence under UV lamp at λ_{ex} = 325 nm. Experimental conditions: silica/ZnS particle placed in 0.075 M $ZnSO_4$ at 24 ± 1 °C.

study are silica biomorphs and chemical gardens or silica gardens [1]. Silica biomorphs are obtained from the precipitation of barium or strontium carbonates in silica-rich alkaline environments which yield crystalline aggregates that resemble the morphology of primitive organisms [2,3]. In the conventional chemical garden experiment, plant-like tubular structures are formed when water soluble metal salt crystals (e.g., $CaCl_2$, $CuSO_4$, $FeCl_3$) make contact with solutions of silicate or other anions [4]. In the context of chemical gardens, tube formation is based on a semipermeable membrane around the dissolving seed crystal [5]. The difference in the osmotic pressure on the two sides of the membrane allows for the inflow of water from the outside alkaline silicate causing the expansion and rupture of the inner acidic membrane. The continuous dissolution of the acidic seed crystal results in a far-from-equilibrium state via a continuous osmotic pumping action into the ambient basic silicate solution. The precipitation of amorphous silica with metal hydroxides (or oxides) give rise to tubular structures which grow upwards with speeds of mm/day or mm/s.

Chemical gardens have been explored since the 17th century [6]. Many of these early explorations were motivated by the colorful "life-like vegetation" observed during the reaction. In the early 20th century, researchers considered these structures to be pre-biotic and models for the origin of life because they exhibit similarity to biological structures [7,8]. Clearly, advances in biochemistry, in particular, the discovery of DNA during the middle of the 20th century dismissed these notions. Nevertheless, chemical gardens are familiar to scientists and non-scientists alike because they are widely used today as a demonstration experiment in chemical education.

In recent years, many different experimental techniques geared toward the synthesis and control of hollow tubular precipitation structures have been reported in the literature. Most of the literature discusses single day formation or rapid growth of tubes from reactants including seed crystals [9,10], pressed pellets of pure compounds [11–14] and reagent-loaded polymer beads [15]. All of the latter reactants are capable of being replaced by a seed solution of which is hydrodynamically delivered to the other reactant through a glass nozzle at predetermined flow rates [16–19]. In addition, the solution delivery or flow technique can be modified by templating a gas bubble to the forming tube thus creating highly linear structures [20,21]. The tubes generated by buoyant gas bubbles show many interesting materials features. For instance, the preparation of photocatalytically, photoluminescent silica/ZnO [22] and superparamagnetic silica/magnetite tubes [23]. Recently, Roszol et al. demonstrated the postsynthetic processing of bubble-guided silica/$Cu(OH)_2$ tubes by physical and chemical means [24]. Another key advancement is the work done by Steinbock and coworkers who reported the incorporation of CdSe-ZnS quantum dots into macroscopic silica/ZnO tubes [25].

The purpose of this article is to demonstrate a synthetic strategy under non-equilibrium conditions for quantifying and controlling the production of precipitation tubes. Our approach is based on loading an insoluble salt (i.e., phosphorescent ZnS) with a soluble salt (i.e., $ZnSO_4$) into a pressed pellet. In this respect, our study follows in part a technique developed by Boulay et al. that has only been employed in the area of polyoxometalate chemistry [26]. For our experiments, the reactant-loaded pellets are then exposed to moderate volumes of concentrated sodium silicate solution. This allowed for the slow morphogenesis of the ZnS/$ZnSO_4$ reactant-loaded pellets to yield macroscopic tubular precipitation structures. Furthermore, we studied their growth kinetics as well as their microstructure and photoluminescence.

2. Experimental

2.1. Materials

The reagents used in this work are phosphorescent laboratory grade zinc sulfide (ZnS, Flinn), zinc sulfate heptahydrate ($ZnSO_4{\cdot}7H_2O$, Fisher), and 37–40% sodium silicate solution (ρ = 1.40 g/mL, c = 6.25 M, Flinn).

2.2. Synthesis

Pellets of varying zinc sulfide and zinc sulfate composition were homogenized with an agate mortar and pressed into 400 mg pellets of 12.5–13.0 mm diameter using a cell at a pressure of 15,000 psi over a one minute time frame. This procedure permits uniform shape and precise control of the quantity and reactivity of the combined salts. The pellets are placed in a vacuum desiccator to remove any remaining moisture.

During the experiment, a single reactant-loaded pellet of predetermined composition is placed flatly against the bottom surface of a glass vial with an outer diameter × length = 25 × 95 mm. An approximate volume of 25.0 mL of 6.25 M sodium silicate solution is then poured on the surface of the pellet. The vials are supported on a flatbed platform mounted to a solid aluminum optical breadboard. Snapshots of the growing precipitation structures are acquired with a Wingscapes TimelapseCam 8.0 digital camera over a time period of three days. The images are collected at a typical rate of 1–2 frames/h and then analyzed using in-house software. For character-