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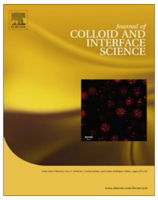

Up-scaling the synthesis of Cu_2O submicron particles with controlled morphologies for solar H_2 evolution from water

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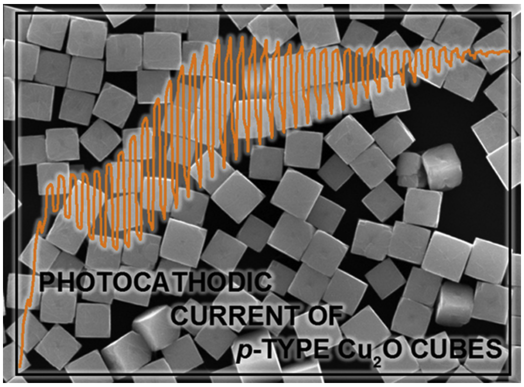
GRAPHICAL ABSTRACT



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ABSTRACT

The synthesis of Cu_2O was studied to examine the effects of up-scaling on the size and morphology of the resultant particles. As a result, a successful protocol employing an automated laboratory reactor was developed for large-scale synthesis of phase-pure Cu_2O colloids with specific sizes in the submicron to micrometer range (0.2–2.6 μm). The as-synthesized products have been studied by means of powder X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, UV–Vis–NIR spectroscopy, scanning electron microscopy, and photoelectrochemical measurements. A broad range of morphologies, both equilibrium (stellated octahedrons, cubes, cuboctahedrons, truncated octahedrons, truncated cuboctahedrons) and metastable (cage-like hierarchical structures, microspheres with flower-like texture), with uniform sizes have been selectively prepared either by careful tuning of synthesis conditions. Recrystallization of primary aggregates through Ostwald ripening is proposed as the formation mechanism for these Cu_2O structures. As a photocathode for photoelectrochemical H_2 evolution, Cu_2O submicron cubes with exposed {001} facets exhibit a high open-circuit potential of ca. 0.9 V vs. the RHE at pH 1.

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1. Introduction

Cu_2O belongs to a class of relatively rare *p*-type semiconducting oxide materials, and holds promise for applications in photovoltaics (PVs) [1], thin-film transistors (TFTs) [2], photocatalytic water splitting [3], and solar-assisted photoelectrochemical (PEC) H_2 evolution from water [4]. These intensive research activities in Cu_2O applications stem from several advantageous properties of this material. In particular, Cu_2O has direct electronic band gap of 1.9–2.1 eV [5–8], high absorption coefficient in the violet-to-green region above the gap [9], hole mobility of up to 100 $cm^2\ V^{-1}\ s^{-1}$ and minority-carrier diffusion lengths of 10 μm [8]. Moreover, copper is naturally abundant and a low-cost element.

Cu_2O is especially appealing to us given our continuing efforts to implement Cu_2O in solar H_2 fuel technology as a viable replacement for current Pt-containing photocathodes in PEC water splitting. Furthermore, interested in the possibility of fabricating large-area films using doctor blade technique, our attention was concentrated on large-scale synthesis of Cu_2O colloids that serve as precursors for ink formulation. Notably, doctor blade is particularly attractive for Cu_2O film manufacturing compared to the most common thermal oxidation, electrodeposition or physical evaporation techniques, because of the convenient large-area deposition using simple apparatus at ambient conditions. The need for large quantities of Cu_2O ink precursors with controlled morphologies and sizes is, however, a prerequisite for efficient film manufacturing by this process. Hence, a reproducible, robust, and controlled synthesis protocol is desirable for Cu_2O colloids to enable the ink preparation on a large scale, which is critical for the realization of emerging and future Cu_2O applications in clean-energy technology.

A major advantage of Cu_2O material is that it can be produced by cheap and environmentally friendly wet-chemistry methods. In particular, Cu_2O particles with various morphologies have been produced via different synthesis protocols, including thermal decomposition [10–12], solvothermal [13], and hydrothermal [14] methods, polyol synthesis [15,16], seed-mediated chemical deposition [17], and via the most common liquid-phase reduction of Cu^{2+} either by hydrazine monohydrate [18–20], sodium borohydride [21], ascorbic acid [22], or hydroxylamine hydrochloride [23]. These syntheses are often conducted under control of a surfactant, such as oleic acid, poly(vinylpyrrolidone), or sodium dodecyl sulfate, which is used to generate colloidal dispersions and to direct the microstructure of the resultant Cu_2O materials.

Despite the advances in Cu_2O synthesis, the reproducibility of synthesis protocols is a challenge. This is mainly due to the high sensitivity of the final Cu_2O products to quality of starting reagents, their concentrations, shelf-time, as well as to many reaction conditions, such as stirring speed, temperature, tempering time, etc. Moreover, scale-up production of nanomaterials is, in general, a non-trivial task [24], since mass and heat-transfer rates are significantly altered during up-scaling [25]. This alteration strongly affects the principal processes of nucleation and crystal growth of the targeted compound, leading to low reproducibility of the results from smaller scale protocol. Typically, this is reflected by e.g. different particle size, particle size distribution, morphology, and phase composition of the resultant up-scaled products.

There are only few reports focused on the preparation of gram quantities of uniform and shape-controlled Cu_2O particles in the nm–μm size regime [26]. Therefore, successfully adapting and further optimizing convenient and controllable synthesis protocols up-scaled from the original milligram-scale methods is not commonly achieved or reported for Cu_2O materials. Our recent success in developing large-scale synthesis of iron oxide nanocolloids using an automated laboratory reactor [27] motivated us to study the possibility of extending this approach to the synthesis of Cu_2O colloids. Accordingly, here we report (1) the effect of synthesis up-scaling on the properties of the resultant Cu_2O colloids, (2) preparation of large quantities of Cu_2O materials having different uniform shapes, (3) the mechanism of particle formation, and (4) a preliminary investigation of the PEC performance of the as-synthesized Cu_2O materials.

2. Materials and methods

2.1. Starting materials

$CuCl_2{\cdot}2H_2O$ (99%), sodium dodecyl sulfate (SDS) (98%), and $NH_2OH{\cdot}HCl$ (99%) were obtained from Sigma–Aldrich; NaOH (98.9%) and EtOH (analytical reagent grade) were purchased from Fisher Scientific. All reagents were used as received without further purification. Ultrapure water used in the study was produced using a Milli-Q Advantage A10 system (Millipore).

2.2. Synthesis

Cu_2O samples were prepared by modifying and up-scaling the procedure outlined by Huang and co-workers [23]. One batch of Cu_2O cubes was prepared following exactly the literature method. The 10-fold up-scaling of this synthesis was conducted following the same procedure in a single-neck round-bottom flask charged with 10 times larger amount of all reagents.

The 100-fold up-scaling was realized in an automated synthesis system (Atlas Potassium, Syrris), as illustrated by a typical time log of the synthesis in Fig. 1. First, a 2 L reaction glass vessel was charged with 1 L of water (pH 7.7) and mechanical stirrer was set to 300 rpm. The reaction system was heated up to 34 °C using a temperature-control system (LH85 PLUS, Julabo), while adding 55 mL of 0.1 M $CuCl_2$ solution at 20 mL/min via a syringe pump to obtain a clear faint-blue solution (pH 4.8). Next, 9.7 g of SDS was added, and the mixture was stirred for 10 min to achieve complete dissolution of SDS (pH 5.2). Then, 20 mL of 1.0 M NaOH solution was added at 10 mL/min using a second syringe pump to obtain a milky-blue slurry (pH $\approx$ 11.4). After the addition was complete, 45 mL of 0.1 M $NH_2OH{\cdot}HCl$ reducing solution was rapidly added into the system while stirring at 600 rpm for 20 s, turning

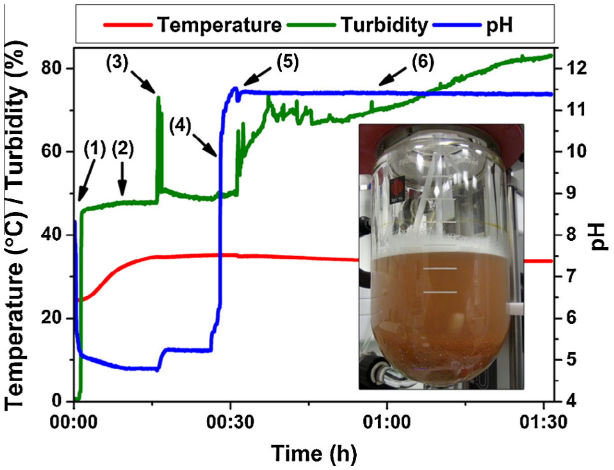

Fig. 1. Time log of an automated reactor synthesis of Cu_2O submicron cubes showing temperature, turbidity, and pH. (1) Addition of 0.1 M $CuCl_2$ solution; (2) adjusting temperature to 34 °C; (3) addition of SDS; (4) addition of 1.0 M NaOH solution; (5) addition of 0.1 M $NH_2OH{\cdot}HCl$ solution; (6) aging. The inset shows the automated reactor glass vessel at the final stage of the synthesis.