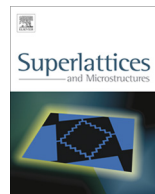




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Studies on formation mechanism of 3D Cu₂O nanospheres through self-assembly of 0D nanodots



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ABSTRACT

Cu₂O crystals with different morphologies (solid and porous) and sizes (from 25 to 282 nm) were synthesized controllably through a facile solvothermal route. The growth mechanism was investigated by SEM and TEM with varying the concentration of poly (vinylpyrrolidone) (PVP, K30), CH₃COO[−] (Ac[−]) and NO₃[−] acid ions in the precursor solution. The self-assembly of three types of Cu₂O nano-structures was observed through a general route of zero-dimensional (0D) → 2D → 3D. When Cu(Ac)₂·H₂O was used as the copper sources, 0D Cu₂O nanodots with size of 2–7 nm were firstly assembled to 2D quasi-spherical and bookmark-like structures via Oriented attachment (OA), and then converted into 3D hierarchical Cu₂O nanoclusters (a few tens of nm) and porous sub-microspheres with an average size of 282 nm, respectively. While Cu(NO₃)₂·3H₂O was used instead of Cu(Ac)₂·H₂O, the similar assembly process occurred leading to the formation of Cu₂O porous nanospheres of 40–140 nm which exhibit better adsorption ability toward methyl orange compared with activated carbon. In addition, we also investigated the dependence of Cu₂O crystals on the concentration of acid ions (Ac[−] and NO₃[−]). Compared with Ac[−], the size and morphology of the obtained products were less dependent on the concentration of NO₃[−] acid ions. This study might

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provide a new insight into the growth mechanism of Cu₂O based micro- or nanostructures.

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1. Introduction

Cuprous oxide (Cu₂O) is a p-type semiconductor with a direct band gap of 1.9–2.2 eV [1–3]. It has been demonstrated that Cu₂O was an attractive material for the potential applications in the fields of photocatalysts [1,3], solar energy conversion [2], gas sensing [4,5], adsorbents [6], lubricants [7], lithium ion batteries [8], magnetic memories [9] and so on. Different morphologies of Cu₂O crystals have their own advantages. For example, the smaller size of particles might facilitate increasing the specific surface area, resulting in better performance of the adsorption, photocatalysis or gas sensing. As a result, in the past years, the morphological control of Cu₂O crystals has attracted a worldwide interest from researchers. Various shaped Cu₂O micro- and nanocrystals have been synthesized by different chemical routes [10–14]. Generally, there were three main ways to control the morphologies of Cu₂O crystals: (1) Changing the pH values and concentration of solution, reaction temperature and time [15–19]. (2) Using different surfactants as soft templates and dispersants [20–23]. (3) Adopting different additives and reductants [2,24,25]. However, there were also a few disadvantages in the above synthesis methods, including the long reaction time, the high reaction temperature and the relatively large particles.

So far, much attention has been focused on the controllable synthesis and tailoring of the Cu₂O crystals with micron and submicron scales. Nevertheless, to the best of our knowledge, there were still limited reports on the small Cu₂O nanocrystals less than 100 nm because of a few considerable challenges [26–30]. Therefore, it is an urgent task to investigate the influences of surfactants, solute concentration or types of the acid ions (CH₃COO[−] (Ac[−]), NO₃[−]) on the final morphologies of Cu₂O nanocrystals, of which the formation mechanism should also be revealed. As well known, Ostwald ripening [24,31–33] and Oriented attachment (OA) [34–43] were two main growth mechanisms of hollow or porous nanostructures. Previous studies have inferred that OA was important in the early growth of TiO₂ [34], ZnO [35,36], SnO₂ [37], Cu(OH)₂ [38] crystals and so on. However, the pathway by which OA occurs was still reported limitedly [39]. Moreover, the self-assembly of Cu₂O crystals was also seldom reported [43]. Especially, the pathway by which the 2D units evolved into 3D Cu₂O structures remained unknown up to now. Can we provide some evidences for explaining the OA mechanism (0D → 2D) and ordered self-organization (2D → 3D) of Cu₂O crystals? This is the main motivation of the present work.

Herein, we developed a facile and effective way to synthesize various shaped Cu₂O crystals with average sizes of 25–282 nm in N,N-Dimethylformamide (DMF) medium by employing sodium borohydride (NaBH₄) as the reducing agent, vinyl pyrrolidone (PVP) as the surfactants and Cu(Ac)₂·H₂O and Cu(NO₃)₂·3H₂O as copper ion sources, respectively. Further, the adding contents of PVP, Ac[−] and NO₃[−] acid ions were optimized while the self-assembly process of three kinds of Cu₂O geometrical structures was investigated. The whole process could be summarized as several steps: (i) 0D Cu₂O nanodots with size of 1–7 nm were assembled to 2D quasi-spherical or bookmark-like structures via OA. (ii) 2D units were organized toward 3D Cu₂O nanoclusters or porous submicro- and nanospheres (a few tens or hundreds of nanometers). At last, we simply examined the application of porous nanospheres (NSs) as absorption materials for removing the pollutants such as methyl orange (MO) in water. It was found to exhibit much higher adsorption ability than activated carbon.

2. Experimental details

2.1. Synthesis of different shapes of Cu₂O crystals

All of the chemical reagents employed in the experiment were analytical grade and used as received without further purification. In a typical synthesis, 0.483 g Cu (NO₃)₂·3H₂O was dissolved

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