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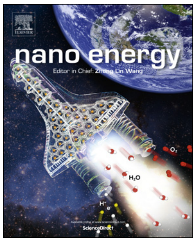

RAPID COMMUNICATION

Freestanding atomically-thin cuprous oxide sheets for improved visible-light photoelectrochemical water splitting

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Abstract

Atomically-thin sheet is a new class of two-dimensional materials that bring a wide range of extraordinary properties. However, the lack of intrinsic growth anisotropy makes the synthesis of atomically-thin non-layered materials a great challenge. Here, a versatile rapid-heating strategy is proposed and applied, in which the lamellar hybrid intermediate transforms into the clean and freestanding atomically-thin non-layered Cu_2O sheet with 4 atomic thicknesses at 300 °C in less than 8 min. Taking advantage of efficient visible-light harvesting, improved carrier density, and fast interfacial charge transfer as well as facile electrochemical reactions, the ultrathin Cu_2O sheets-based photoelectrode yields a photocurrent density up to 3.98 mA cm^{-2}, 36 times higher than that of bulk counterpart. Also, the photoelectrode reaches a visible-light-conversion-efficiency of 26.2% that is superior to most existing reports. The rapid-heating strategy guarantees the full exfoliation of lamellar hybrid intermediate into ultrathin Cu_2O sheets with the removal of organic component, opening a new way to produce atomically-thin non-layered materials and holding great promise in the applications of visible-light photoelectrochemical water splitting.

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Introduction

Photoelectrochemical (PEC) water splitting using semiconductor materials could provide a promising and environmentally benign pathway to produce clean and renewable hydrogen energy [1-3]. Among the abundant semiconductors, cuprous oxide (Cu_2O) has recently attracted extensive attention as a means of solar-to-hydrogen conversion [4-6]. In addition to possessing low cost and environmental friendliness, the fascination also comes from its peculiar conduction band lying 0.7 V negative of the hydrogen evolution potential [4,7], which theoretically points out its feasibility to drive the water splitting into hydrogen. In addition, the high theoretical photocurrent of -14.7 mA cm^{-2} and light-to-hydrogen conversion efficiency of 18.7% suggest its huge potential applications in solar hydrogen production [8]. Also, the relatively small direct band gap of 2.2 eV endows Cu_2O with efficient adsorption of visible light, which accounts for 43% of the incoming solar energy [9]. Moreover, the large absorption coefficient of $\sim 3.7 \times 10^6$ cm^{-1} facilitates efficient light absorption, while the high carrier mobility of $>10^5$ $cm^2\,V^{-1}\,s^{-1}$ favors for fast separation of photoexcited electron-hole pairs [10,11]. Furthermore, Cu_2O can effectively scavenge the photogenerated electrons through adsorbing molecular oxygen and hence constrain the recombination of electron-hole pairs, thus definitely improve the photoconversion efficiency [12]. Despite these excellent advantages of Cu_2O, the relatively low photoconversion efficiency, especially in the visible light range, unfortunately hinders the promising applicability. Therefore, further breakthroughs in the design and synthesis of novel Cu_2O structures with high visible light water splitting efficiency, hold the key to the development of PEC water splitting.

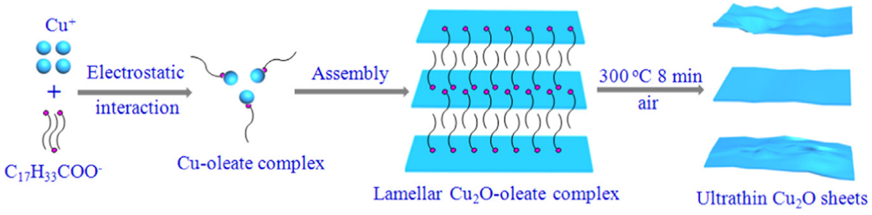
Recently, our studies have shown that the atomically-thick two-dimensional sheets provide the ideal architecture for promoting the solar hydrogen production [2,13]. The peculiar geometric structure can afford the atomic thickness for fast carrier transport from interior to surface, the two-dimensional (2D) conducting channels for quick separation of electron–hole pairs as well as the large surface area for efficient light harvesting and facile surface reactions. Also, the 2D configuration endows them with a much better grain boundary connectivity and allows for intimate contact with the substrate and high interfacial contact area with the electrolyte, thus facilitating fast interfacial charge transfer and electrochemical reactions as well as low corrosion rates. Enlightened by the above discussions, controllable synthesis of the atomically-thick Cu_2O sheets is of great importance. As is well-known, controllable exfoliation of anisotropic layered bulk materials have been regarded as the most effective pathway to obtain two-dimensional sheets with atomic thickness, owing to the strong in-plane bonds and weak van der Waals interaction between layers [14,15]. However, for the non-layered compounds such as cubic Cu_2O, controlling the synthesis of their atomically-thick two-dimensional sheets is extremely challenging on account of the difficulty in bond-cleavage and the lack of intrinsic driving force for anisotropic growth. Despite the recent progress in fabricating two-dimensional CdSe and PbS sheets with few atomic thickness [16,17], the hard removal of surface organic surfactant would inevitably obscure their properties.

Herein, we describe our efforts to develop a high-yield and scalable fast-heating strategy for fabricating clean and freestanding atomically-thick sheets with non-layered structures, taking the cubic Cu_2O as an example (Figure S1) [18]. As shown in Scheme 1, the successful fabrication of the atomically-thin Cu_2O sheets takes advantage of an intermediate precursor of lamellar Cu_2O-oleate complex microplates (Figures S2 and S3). Notably, the oleate ions play a fundamental role in the formation of this intermediate: the oleate ions initially interact with Cu^+ to form Cu-oleate complexes via an electrostatic interaction. After hydrothermal treatment at 100 °C for 24 h, the Cu-oleate complexes assemble into lamellar Cu_2O-oleate complex intermediate microplates, which are fully characterized in Figures S2 and S3. And then, upon heating at 300 °C for a short time of 8 min in air, the quick release of enormous H_2O and CO_2 gases contributes to weaken the interaction between the adjacent inorganic layers, and hence fully exfoliate the lamellar Cu_2O-oleate complex into clean and freestanding ultrathin Cu_2O sheets with 4 atomic thicknesses (Figure 1 and Figures S4 and S5). Of note, this developed fast-heating strategy is simple, high-yield and can be easily scaled up for large-scale synthesis of the atomically-thin non-layered materials.

Experimental section

Preparation of lamellar Cu_2O-oleate complex intermediate

The lamellar Cu_2O-oleate complex intermediate was synthesized by a hydrothermal method. In a typical procedure, 99 mg CuCl, 914 mg sodium oleate, 831 mg hexamethylenetetramine (HMT) and 100 μL $N_2H_4 \cdot H_2O$ were added into 40 mL distilled water orderly. After vigorous stirring for 10 min, the mixed solution was transferred into 50 mL Teflon cup and heated in a sealed autoclave at 100 °C for 24 h. Upon cooling to room temperature naturally, the final



Scheme 1 Schematic rapid-heating strategy for fabricating clean and freestanding atomically-thin Cu_2O sheets, taking advantage of the lamellar Cu_2O-oleate complex intermediate.