Journal of Alloys and Compounds 774 (2019) 668–676

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Ag ion kinetically tailored surface and interface engineering of Cu_2O nanocrystals to modulate the Li-ion battery performance

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ARTICLE INFO

Article history:
Received 12 March 2018
Received in revised form
23 September 2018
Accepted 28 September 2018
Available online 3 October 2018

Keywords:
Lithium-ion batteries
Cuprous oxide
Nanostructure
Metal particle
Surface and interface engineering

ABSTRACT

The surface and interface engineering of Cu_2O is successfully accomplished in one pot via an extremely simple solid-solute method with the assistance of Ag ions. In the synthesis process, the Ag ion plays dual roles. Specifically, Ag ions accelerate the nucleation rate of Cu_2O via engineering with kinetic control and act as precursors for the formation of metal Ag at the modified interface. This design avoids the use of presynthesized nano/microcrystals and a second deposition or epitaxial growth of a second material on the surfaces of prepared nano/microcrystals. The size of Cu_2O sharply decreases to 100 nm with the deposition of Ag nanoparticles. The electrode materials of sub-100 nm Ag-Cu_2O possess synergistic benefits of the reduced size and the interface engineering with metal nanoparticles. When evaluated as anode materials for lithium-ion batteries, the hybrid structure of Ag-Cu_2O showed an enhanced specific capacity and excellent rate performance.

1. Introduction

To meet the energy demand of the rapidly developing industry and to decrease the societal dependence on fossil fuels, it is necessary to expedite the development of renewable energy sources. Currently, lithium-ion batteries (LIBs), as excellent power sources, have received much attention for storage of intermittent renewable energy [1]. However, commercially used graphitic carbon-based anode materials for LIBs cannot satisfy the increasing demand for energy storage due to their limited specific capacity and poor rate performance [2]. The most utilized choices for the electrode of LIBs are insertion-type materials, which can accommodate lithium ions in the lattice [3]. Metal oxides, such as Co_3O_4, NiO, Cu_2O and CuO, are considered promising candidate electrode materials because of their low cost and high specific energies. Their reversible reaction with lithium proceeds according to the conversion-type reaction and endows them with outstanding reversible capacity and good cycling performance.

Cuprous oxide (Cu_2O) has been extensively investigated and applied in LIBs due to its advantages, including high natural abundance, low cost, environmental friendliness and facile synthesis [3–6]. As an example, Wong et al. prepared Cu_2O microspheres encapsulated by graphene oxide, which delivered a specific capacity of 458 mA h g^{-1} at a current density of 100 mA g^{-1} after 50 cycles [7]. Nevertheless, the unavoidable large volume (over 228%) expansion associated with lithiation/delithiation processes would easily result in the pulverization of the electrode materials and thus lead to rapid capacity decay during cycling. In addition, the practical application of Cu_2O in LIBs is also limited by its poor cycling stability, mainly caused by its low electronic conductivity. Xue et al. reported a reversible capacity of 648.3 mA h g^{-1} for the material whose structure contained truncated octahedra, and a capacity of 201.5 mA h g^{-1} remained after 50 cycles [8]. These issues, which have not yet been addressed, are common to metal oxide anode materials [7].

Surface and interface engineering is efficient in enhancing the electrochemical performance of electrode materials for LIBs. Surface and interface engineering includes many approaches, such as the decrease of the particle size and surface modification by metal nanoparticles, carbon materials, and other electronically conductive species [7,9,10].

Slow migration of Li^+ would cause the accumulation of Li^+ on the interface between the electrode and electrolyte, which would have a significant effect on the rate capability. The increased active surface for nanostructured particles would facilitate Li^+

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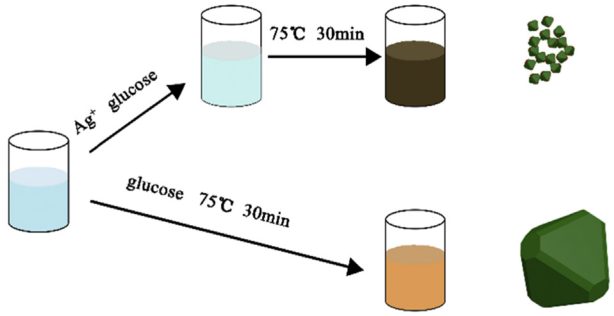
https://doi.org/10.1016/j.jallcom.2018.09.377

permeation from the electrolyte to the solid electrode through the increased number of pathways. In addition to the high specific surface areas available, the nanoparticles also increase the rate of lithium insertion/removal and electron transport owing to the shortening of the lengths of diffusion [11]. Nevertheless, nanostructured materials might be difficult to synthesize. In contrast, the synthesis of Cu_2O is not complicated, and the particle dimensions have mostly been in the range of over 100 nm to a few micrometers [12–15]. However, only few reports describing the growth of particles of Cu_2O with sizes below 100 nm without redundant processes and the use of surfactant or toxic reducing agents such as N_2H_4 are available [16,17]. In addition, it is difficult to overcome the low electronic conductivity of transition metal oxides (TMOs) as anode materials via the simple downsizing of particles. Surface modification with the anchoring of metal nanoparticles has been demonstrated to be effective in improving the cycling performance of TMO anodes. The overlap of the Fermi level for the metal material and the conductive band for TMO electrodes enhances the flow of electrons, which makes the metal particles good electron collectors and distributors [9]. Some of the literature on coating by metal particles has shown a recently achieved great progress [18–22].

Currently, most approaches suitable for surface and interface engineering require multistep procedures involving the consecutive deposition or epitaxial growth of a second material on the surfaces of presynthesized nano/microcrystals using harsh conditions [23–25]. A hybrid architecture of a Cu-Cu_2O concave cube resulted in a better performance than a pure Cu_2O truncated cube. However, the Cu particles only aggregated on one corner of the Cu_2O cube with an edge length of 980 nm, which may not improve the conductivity of Cu_2O [6]. Consequently, it is still challenging to synthesize Cu_2O nanoparticle composites with conductive materials using a universal and straightforward approach. Ag metal possesses the ability to provide superior electronic conductivity while maintaining a thermodynamically stable interface with TMOs to catalyze electrochemical reactions at the nanoscale [26]. In this work, we designed a very simple method to synthesize truncated octahedral Cu_2O with deposited Ag of different sizes. The addition of Ag^+ to the precursor can lead to a drastic downsizing of Cu_2O to a sub-100 nm range without variation of the original morphology. The size can be easily tuned by controlling the reaction time and the amount of Ag^+. In the synthesis process, Ag^+ accelerates the nucleation rate of Cu_2O and simultaneously acts as the precursor for Ag metal, avoiding the use of presynthesized nano/microcrystals and followed up by a deposition on the surfaces of prepared nano/microcrystals. No surfactants or toxic materials are involved in the entire preparation process. Some of the literature has reported on the metal ion-assisted modification of the morphology of Cu_2O without a drastic size variation in a simple way [27–30]. The as-prepared Cu_2O-Ag combines the synergistic benefits of nanosized structures and surface modification with metal materials. As an anode material in LIBs, the as-prepared Cu_2O-Ag shows excellent electrochemical properties. In addition, we also applied other metal ions in the manufacturing process, including Au, Pd and Pt ions, which have different reshaping effects on the final morphology of Cu_2O. More importantly, the metal-ion assisted synthesis approach might enjoy widespread structure-related applications.

A comparison of the preparation process of uniform Ag-Cu_2O polyhedra and bulk Cu_2O is presented in Scheme 1. The nanostructured Ag-Cu_2O polyhedra are obtained with an extra addition of Ag^+ as compared with the procedure for bulk Cu_2O.



Scheme 1. Schematic illustration of the fabrication process for bulk Cu_2O and Ag-Cu_2O.

2. Results and discussion

2.1. SEM/TEM/XRD characterizations of Ag-Cu_2O and Cu_2O

Fig. 1 illustrates the morphology of Ag-Cu_2O and its substantial size difference in comparison with large-size bulk Cu_2O. The difference lies in whether or not a minute quantity of Ag^+ is added to the precursor. Fig. 1a and b shows that the samples consist of truncated octahedral Cu_2O with an edge length of approximately 500 nm. The Cu_2O truncated octahedron is composed of six {100}, eight {111} and twelve {110} facets. With the addition of just a small amount of Ag^+ to the precursor solution, the same morphology of Cu_2O-hybridized Ag with an edge length of 40–50 nm was simultaneously obtained in a one pot way. As seen in Fig. 1 c and d under high magnification, Ag-Cu_2O is uniformly distributed with an obvious size difference as compared to bulk Cu_2O. In addition, particles of Ag are preferentially deposited on the {100} plane of Cu_2O.

The microstructure of Ag-Cu_2O was investigated by transmission electron microscopy (TEM) and high resolution TEM (HRTEM). Fig. 2a shows that the Ag-Cu_2O particles have good size and shape uniformity, which is consistent with the SEM images. In Fig. 2b, the metal particles of Ag, size of less than 10 nm, were anchored over the Cu_2O hosts without aggregation. In addition, HRTEM was conducted to further characterize the Ag-Cu_2O. The interplanar spacings of 0.205 and 0.213 nm are indexed to the (200) planes of Ag and Cu_2O. More importantly, the heterojunction between metal Ag and Cu_2O can facilitate the transfer of electrons between these two parts, which is beneficial for improving the electrochemical performance in LIBs. The hybrid junction between the Ag metal particles and Cu_2O is proved by the intimate contact of the clear lattice fringes presented in Fig. 2c [6]. The element mapping analysis confirmed the uniform distribution of the three elements of Cu, O and Ag (Fig. 2d).

Phase composition of Ag-Cu_2O and bulk Cu_2O was identified by XRD characterization. The strong peaks appearing in Fig. 3 can be indexed to cubic Cu_2O (PDF 75–1531), and the marked peak is assigned to Ag. However, no obvious characteristic diffraction peaks of Ag are observed in Ag-Cu_2O (2) because of its lower loading content, which also implies the good dispersion of the very small Ag nanoparticles on the Cu_2O surface. More characterizations are carried out to further demonstrate the existence of Ag and Cu_2O with results presented in Figs. S1 and S2.

2.2. Characterizations of Ag-Cu_2O formed in the reaction process and analysis of the interaction mechanism

The formation mechanism of the Ag-Cu_2O hybrid structure with a sharp decrease in particle size was investigated by exploring the