Alkyldimethylbetaine-Assisted Development of Hollow Urchinlike CuO Microspheres and Application for High-Performance Battery Anodes

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Supporting Information

ABSTRACT: A new approach to develop novel hollow urchinlike copper oxide (CuO) microspheres by the hydrothermal method was reported, and zwitterionic alkyldimethylbetaine (BS) surfactants were employed as templates in the classic copper—ammonia complex systems. Effects of numerous environmental factors on the morphology of CuO particles were studied systematically, in which the concentration and structure of BS predominantly affected the developed CuO materials. It was noticed that hollow urchinlike CuO microspheres were generally formed in the presence of BS regardless of the reaction temperature and time and the source of copper ions. Generally speaking, high concentrations of BS and BS with longer chain length strongly favored the formation of hollow urchinlike CuO microspheres. The microstructures of synthesized CuO particles were studied in detail, and the corresponding formation mechanism of hollow urchinlike CuO microspheres was also proposed based on the selective adsorption of BS on the particular crystal facets of CuO crystals. Moreover, hollow urchinlike CuO microspheres showed excellent performance in the lithium-ion batteries as anode materials with a reversible capability of 511 mA h g⁻¹ at 0.1 C after 40 charge–discharge cycles, which was one of the best values of CuO materials reported in this field.

INTRODUCTION

Functional nano-/micromaterials attracted much attention because of their significant advantages in various fields including electron, biotechnology, medicine, catalysis, and so forth.¹⁻¹⁸ Transition metal oxides such as those of Fe, Co, Ni, Cu, and Mn are one category of the most attracting anode materials in lithium-ion batteries and thereby were studied widely.¹⁻¹⁸ Beyond the inherent nature or limitation of materials themselves on the performance, their morphological characteristics were of great importance. It was well-known that the theoretical capability of CuO anode materials is as high as 670 mA h g⁻¹; however, the reversible capability of commercial CuO powders was often far lower than the theoretical one,¹⁹ that is, below 200 mA h g⁻¹. Wang and co-workers²⁰⁺²¹ studied the effect of morphological characteristics of CuO particles on the performance in the lithium-ion batteries and found out that those with particular microstructures, that is, three-dimensionally (3D) hierarchical CuO microspheres, could enhance both the capability and stability dramatically. In addition, the employment of composite materials was an alternative route to overcome the disadvantage, which showed a promising potential in this area. For example, the capability and stability of Co₃O₄/CuO composites with a suitable molar ratio as anode materials were much superior to that of either Co₃O₄ or CuO materials.²² However, the importance of materials with particular microstructures still remained. In other words, the corresponding performance could be enhanced through adjusting the morphological structures of materials further. Generally speaking, materials with 3D hierarchical and hollow microstructures benefited the performance, as mentioned in several recent works.²³⁻²⁶ Wang et al. developed a multilayer CuO@NiO hollow spheres based on the Cu–Ni bimetallic organic frameworks, which showed excellent electrochemical properties because the special hollow structure could overcome the critical volume expansion well.²⁷ Nowadays, numerous methods have been developed to synthesize functional materials with novel microstructures,⁹,¹⁶,¹²,²⁰,²⁷ whereas it is still challenging to develop them in a controlled manner.

Surfactants often show inherent adsorption and self-assembly behaviors at the interface and in the bulk phase, respectively, which endow them with the essential characteristics in wetting and spreading, solubilization, emulsification, foaming, and so forth, and thereby widely used in daily life, agriculture, and industry. Moreover, surfactants also showed a promising potential in controlling the formation of nano-/micromaterials with particular microstructures.²⁸ For example, the classic cationic surfactant cetyltrimethylammonium bro-

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mide (CTAB) was widely employed as a template to develop functional inorganic and metal materials such as mesoporous silicon dioxide and gold particles with various morphologies, respectively.\textsuperscript{29–31} Moreover, a slight chemical structure variation of surfactants might affect the appearance of developed materials significantly.\textsuperscript{32} Likewise, the hydrophobic chains and headgroups of surfactants also affected the formed materials dramatically.\textsuperscript{33–38} Undoubtedly, these works showed the importance of surfactants as templates in this field. The zwitterionic alkyl(dimethyl) betaine (BS) surfactants were widely used in the daily chemical products because of low skin irritation, excellent soil release and biodegradation, and so forth.\textsuperscript{39} However, they were rarely applied in the development of functional materials. Recently, our group reported a high-efficient and conveniently recyclable photodegradation membrane, in which cetyldimethylbetaine (BS-16)-assisted urchinlike CuO microparticles were the key.\textsuperscript{40} This work evidently confirmed the feasibility of BS surfactants in the controlled growth of CuO materials well.

In this work, novel hollow urchinlike CuO microspheres were developed from the classic copper–ammonia complex system by the hydrothermal method in the presence of BS surfactants including BS-10, BS-12, and BS-14. Effects of numerous factors, in terms of the reaction temperature and time, the source of copper ions, the molar ratio between surfactant and copper salt, and the hydrophobic chain length of BS, on the formation of hollow urchinlike CuO microspheres were studied in detail. Accordingly, the general formation mechanism was also proposed. The microstructures of developed CuO crystals were studied by scanning and transmission electron microscopy (SEM and TEM), high-resolution TEM (HRTEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) techniques systematically. To the best of our knowledge, this is the first example of the zwitterionic BS surfactant-assisted formation of hollow urchinlike CuO microspheres currently.\textsuperscript{35–38,41,42} According to the particular microstructural characteristics of the developed hollow urchinlike CuO microspheres, they were applied in the lithium-ion batteries as anode materials.

\section*{RESULTS AND DISCUSSION}

\textbf{BS-12-Assisted Formation of Hollow Urchinlike CuO Microspheres.} A study was carried out about the formation mechanism of CuO nano- /micromaterials by the hydrothermal method in different systems, and numerous factors, such as temperature, time, the source of copper ions, ligands, pH, additives, and so forth, could strongly affect the physicochemical properties of developed CuO materials including their morphology and reaction activity.\textsuperscript{43} In this work, all CuO materials were developed in the classic copper–ammonia complex system in the presence of BS surfactants, and the formation was mainly depended on the following three interrelated reactions.\textsuperscript{44–46}

\begin{align}
\text{Cu}^{2+} + 4\text{NH}_3 &\rightarrow \text{Cu(NH}_3)_4^{2+} \quad (1) \\
\text{Cu(NH}_3)_4^{2+} + 2\text{OH}^{-} &\rightarrow \text{Cu(OH)}_2 + 4\text{NH}_3 \quad (2) \\
\text{Cu(OH)}_2 &\rightarrow \text{CuO} + \text{H}_2\text{O} \quad (3)
\end{align}

The SEM image (Figure 1a) showed that the CuO microspheres developed in the presence of BS-12 were generally uniform both in size and morphology, which were urchinlike with the major size about 2–4 \(\mu\)m. These urchinlike CuO microspheres were the agglomerates of densely packed rodlike CuO particles with a hollow core, as shown in the inset image of Figure 1a. Moreover, these rodlike CuO particles are composed of smaller subunits, CuO nanoparticles, and similar observation was also reported previously.\textsuperscript{46} Figure 1b showed the TEM image of a single CuO microsphere about 3 \(\mu\)m, in which the cross-linked rodlike CuO subunits with width about tens of nanometers were observed clearly at the edge of particle. The HRTEM image (Figure 1c) showed its characteristic facet with the lattice fringe spacing \(d\) of 0.25 \(\text{nm}\), corresponding to the \{002\} facet of CuO crystals, which was also visible in the selected area electron diffraction (SAED) pattern of the sample (the inset image in Figure 1c). Figure 1d showed the corresponding XRD patterns of the developed hollow urchinlike CuO microspheres, in which all characteristic diffraction peaks were consistent with the standard monoclinic structure of CuO crystals well (PDF # 05-0661). Thus, the HRTEM, XRD, and SAED results confirmed that the developed CuO materials were well-crystallized.

Figure 2a showed the typical XPS spectrum of hollow urchinlike CuO microspheres, in which the concerned elements including Cu, O, C, and N were all observed. Figure 2b–d showed the corresponding Gaussian curve-fitting spectra of Cu 2P\textsubscript{3/2}, O 1s, and C 1s, respectively. Obviously, there presented three typical peaks including the dominant peak at 933.7 \(\text{eV}\) and two shake-up peaks at 941.1 and 943.3 \(\text{eV}\), respectively, in the Cu 2P\textsubscript{3/2} spectrum (Figure 2b), which were the primary characteristics of copper in the crystal CuO.\textsuperscript{40,47,48} The peaks with the binding energy of 529.6, 531.2, and 532.6 \(\text{eV}\) in the O 1s spectrum (Figure 2c) were often attributed to the Cu–O, O–O, and O–H bonds,\textsuperscript{40,49} respectively, suggesting the formation of CuO as well. Unlike the weak

\begin{figure}[ht]
\centering
\includegraphics[width=\textwidth]{Figure1.png}
\caption{SEM (a), TEM (b), HRTEM image (c), and XRD pattern (d) of hollow urchinlike CuO microspheres. The enlarged image in (a) is the hollow characteristic and the inset image in (c) is the corresponding SAED pattern.}
\end{figure}
signal of N 1s (Figure 2a), the characteristic peaks of C 1s was distinguished apparently, as shown in Figure 2c, because of its relatively abundant content in the adsorbed BS-12 molecules in comparison with that of N.50 Undoubtedly, the XPS results confirmed the formation of crystal CuO and the presence of BS-12 on the surface of CuO microspheres through adsorbing, and a similar observation was also reported previously.40 The energy-dispersive X-ray spectroscopy (EDXS) mapping images shown in Figure 2e–i also supported the presence of BS-12 on them. It was also noticed that the typical stretching vibration peaks of BS-12 were still remained in the Fourier transform infrared (FTIR) spectrum of the synthesized CuO powders (Supporting Information Figure S1a), and the corresponding TG result (Supporting Information Figure S1b) showed that a clear weight loss about 3.5% happened between 200 and 320 °C mainly owing to the thermal-induced degradation of BS-12.51,52 All results suggested the presence of BS-12 on the formed CuO particles, indicating the importance of BS-12 on the formation of hollow urchinlike CuO microspheres.

**Effect Factors on the Formation of CuO Microspheres.** To make a better understanding on the formation mechanism of the interesting hollow urchinlike CuO microspheres, numerous factors including the reaction temperature and time, the source of copper ions, the molar ratio between BS-12 and copper salt, and the hydrophobic chain length of BS-12 homologies were studied in detail. It was noticed that the employed reaction temperatures such as 100, 130, and 160 °C showed limited effect on the morphologies of BS-12 homologies were studied in detail. It was noticed that the employed reaction temperatures such as 100, 130, and 160 °C showed limited effect on the morphology of formed CuO particles (Figure 1a and Supporting Information Figure S2), and their urchinlike nature remained regardless of temperature. Similarly, the formation of hollow urchinlike CuO microspheres seemed to be independent on the reaction time (Supporting Information Figure S3), whereas the reaction time affected the yield of products strongly and the time of 8 h was enough. Accordingly, the reaction temperature of 130 °C and the time of 12 h were typically employed in this work. Moreover, the formation of hollow urchinlike CuO microspheres was commonly observed in the presence of BS-12 regardless of the source of copper ions including CuCl2, CuSO4, Cu(NO3)2, and Cu(CH3COO)2 (Figure 1a and Supporting Information Figure S4). Measurements of UV−vis spectra (Supporting Information Figure S5) showed that the electrostatic interactions between BS-12 and copper ions were essential in the CuCl2/BS-12 binary system. In other words, the introduction of BS-12 affected the copper−ammonia complex ions slightly, as mentioned in eq 1, and thereby generally resulting in the formation of CuO microspheres. However, the presence of the surfactant predominantly affected the microstructure of CuO microspheres.

**Molar Ratio of CuCl2/BS-12.** Figure 3 showed the effect of surfactant concentration on the morphology of the developed CuO microspheres, in which the concentration of CuCl2, reaction temperature, and time were all kept constant, whereas the molar ratio of [CuCl2]/BS-12 decreased gradually. Obviously, mainly irregular and defective CuO microspheres, the agglomerates of platelike CuO subunits, were formed in the absence of BS-12 (Figure 3a). Moreover, those platelike particles were composed of smaller CuO particles, as reported previously.50 However, the morphologies of CuO microspheres were improved significantly once BS-12 was introduced into the system even with a small amount. It was noticed that relatively regular CuO microspheres with a more rough surface were formed when the value of r = 3/1 was employed (Figure 3b). In particular, the wide and thick

![Figure 2. XPS spectrum of the urchinlike CuO (a) and the corresponding curve-fitting spectra of Cu 2p3/2 (b), O 1s (c), and C 1s (d), respectively. SEM image of a single urchinlike CuO particle (e) and the corresponding EDX mapping images of Cu (f), O (g), C (h), and N (i), respectively.](doi:10.1021/acsomega.8b01299)
platelike CuO subunits became narrower and thinner simultaneously. The tendency was further strengthened upon continuously decreasing the value of $r$ through increasing the concentration of BS-12. It should be mentioned that typical hollow urchinlike CuO microspheres composed of rodlike CuO subunits were generally formed once $r$ was below 1/2 (Figures 1a and 3d−f). Clearly, to facilitate the composed subunits of CuO, the microspheres becoming narrower and thinner was one of the most important characteristics of BS-12.

Hydrophobic Chain Length of BS Surfactants. The effect of hydrophobic chain length of BS-12 homologies including BS-10 and BS-14 on the morphologies of CuO microspheres was also studied, as shown in Supporting Information Figures S6 and S7, respectively. Similar morphological transitions of the developed CuO microspheres as that shown in Figure 3 were also observed in the presence of either BS-10 or BS-14. Figure 4 showed three typical CuO microspheres synthesized in the presence of BS-10 (Figure 4a), BS-12 (Figure 4b), and BS-14 (Figure 4c) with $r = 1/2$, respectively. Obviously, no significant difference was observed from their macroappearance. However, a distinguishing difference still presented that the subunits of hierarchical CuO microspheres formed in the presence of BS-12 and BS-14 were relatively uniform and rodlike, whereas large amounts of platelike ones still remained in the BS-10-assisted CuO microsphere. Indeed, CuO microspheres fabricated in the BS-10-containing systems were often irregular and defective (Supporting Information Figure S6), and the platelike CuO subunits were commonly presented even in the presence of high concentration of BS-10, that is, $r = 1/8$. In contrast, mainly regular CuO microspheres composed of rodlike CuO subunits were observed in the BS-12- and BS-14-containing systems when $r$ was arrived at 1/2 and 1/1, respectively. In other words, BS-12 and BS-14 were more efficient in assisting the formation of hollow urchinlike CuO microspheres.

The SEM results evidently confirmed that BS surfactants played a similar function during the formation of 3D hierarchical urchinlike CuO microspheres, owing to their similar physicochemical characteristics from both adsorption and aggregation aspects. However, the capability of them in controlling the morphology of CuO microspheres was depended on the hydrophobic chain length strongly. Concentration-dependent surface tension measurements (Supporting Information Figure S8) showed that the critical micelle concentration significantly decreased about 100 times from BS-10 to BS-14, and the equilibrium surface tensions also decreased about 6 mN/m simultaneously. The results strongly suggested that the BS surfactant with the longer hydrophobic chain length highly benefited the enhancement of adsorption and aggregation capability because the van der Waals interactions between BS molecules were strengthened upon increasing the hydrophobic chain length of the BS surfactant. Thus, the BS-assisted formation of CuO microspheres from the copper−ammonia complex systems can be generally illustrated by Scheme 1 based on the selective adsorption of BS surfactant on the particular facet of CuO crystal.53 In the absence of BS surfactants, the initially produced CuO nanocrystals preferred to grow along with {100} and {010} facets to form relatively larger and thick platelike CuO subunits because the ammonia molecules can selectively passivate the {001} facet of primary CuO nanocrystals because of its highest surface energy.53 As a result, these platelike CuO assembled

Figure 3. SEM images of CuO microspheres developed in the absence (a) and presence (b−f) of BS-12; images (b−f) represent the molar ratio of [CuCl₂]/[BS-12] of 3/1, 1/1, 1/3, 1/5, and 1/7, respectively. Bars represent 1 μm.

Figure 4. SEM images of CuO microspheres synthesized in the presence of BS-10 (a), BS-12 (b), and BS-14 (c), respectively. Bars represent 500 nm.
into hierarchical CuO microspheres through agglomerating directly for the purpose of energetic minimum.

Comparing BS surfactants with ammonia molecules, the adsorption capability of the former ones was much stronger attributing to the electrostatic interaction between copper ions and the carboxylate moiety of BS surfactants. As a result, BS surfactants, instead of ammonia molecules, were to be adsorbed in prior on the facets of primary CuO nanocrystals along with the order from \{001\}, \{100\} to \{010\} facet.53 Correspondingly, the growth of primary CuO nanocrystals was preferred to adapt a conforming manner along some particular directions, that is, the \{100\} and \{010\} facet, resulting in CuO subunits with the smaller size. Once the adsorption of BS surfactants on the \{001\} and \{100\} facets was arrived, the saturation upon sostenuto increasing the concentration of surfactant, the primary CuO nanocrystals would mainly grow along with the \{010\} facet, a facet with the lowest energy, and thereby result in the formation of rodlike CuO particles. Then, those rodlike ones further assembled into hollow urchinlike CuO microspheres. Since van der Waals interactions between BS-10 molecules were the smallest because of the short hydrophobic chain length, the intensity of the adsorbed surfactant layer on the CuO nanocrystals should be relatively weaker. In other words, the passivation degree of CuO nanocrystal facets was limited, resulting in partially confining the growth of CuO nanocrystals. However, the intensity of adsorbed BS-12 or BS-14 layer was strong enough, and the \{001\} and \{100\} facets of CuO nanocrystals were completely passivated, which ensured the confining growth along the \{010\} facet. Therefore, hollow urchinlike CuO microspheres with structurally well-defined microstructures were formed in these conditions.

**Application of Hollow Urchinlike CuO Microspheres in Electrochemistry.** As a typical transition metal oxide, CuO materials were widely employed in lithium-ion batteries as anode materials with excellent performance.20,21,43 Recent work by Lu and co-workers showed that 3D hierarchical nano-/micromaterials with hollow characteristics were essential in endowing them with new functionalities for a better lithium storage and effectively accommodate the volume expansion for anode materials in lithium-ion batteries.54 Certainly, these hollow urchinlike CuO microspheres might also shed some promising potential in this area owing to their particular size and microstructure. To avoid the influence of adsorbed surfactants, samples were treated at 350 °C according to the TG result (Supporting Information Figure S1b) for 2 h to ensure the complete decomposition of BS-12. The corresponding electrochemical performance of hollow urchinlike CuO microspheres developed in the presence of BS-12 is shown in Figure S.

**Figure 5a** showed the initial three cyclic voltammograms of hollow urchinlike CuO microspheres. Clearly, three typical cathodic peaks at 1.81 V (weak), 0.97 V (strong), and 0.75 V (medium) were visible in the first cathodic scan process corresponding to the following three reactions55−57

\[
\text{CuO} + x\text{Li}^+ \rightarrow \text{Cu}_{1-x}\text{Cu}^\text{II}_x\text{O}_1-x/2 + x/2\text{Li}_2\text{O} - xe^- \quad (4)
\]

**Figure 5.** Electrochemical performances of the hollow urchinlike CuO microspheres. (a) Cyclic voltammograms (1st, 2nd, 3rd, and 4th), (b) charge–discharge curves (1st, 2nd, 3rd, 4th, and 20th), (c) cycling performance and Coulombic efficiency at 0.1 C rate, and (d) rate performance.
Cu\textsuperscript{II}\textsubscript{1-x}Cu\textsubscript{x}\textsubscript{1}O\textsubscript{1-x/2} + (1 - x)Li\textsuperscript{+} → x/2Cu\textsubscript{2}O + (1 - x)/2Li\textsubscript{2}O - (1 - x)e\textsuperscript{-} (5)

1/2Cu\textsubscript{2}O + Li\textsuperscript{+} → Cu + 1/2Li\textsubscript{2}O - e\textsuperscript{-} (6)

Furthermore, two oxidation peaks at 2.45 V (strong) and 2.74 V (weak) appeared during the first anodic scan process because of the formation of Cu\textsubscript{2}O and CuO, respectively, corresponding to the following two reactions\textsuperscript{58}

Cu + 1/2Li\textsubscript{2}O → 1/2Cu\textsubscript{2}O + Li + e\textsuperscript{-} (7)

1/2Cu\textsubscript{2}O + 1/2Li\textsubscript{2}O → CuO + Li + e\textsuperscript{-} (8)

Both Cu and Li\textsubscript{2}O were produced during the cathodic scan process, resulting in the formation of solid electrolyte interface film on the surface of hollow urchinlike CuO materials. Correspondingly, the irreversible cathodic peaks between 0.5 and 1.5 V appeared in the following charge–discharge process, which was also observed from the galvanostatic discharge–charge curves of hollow urchinlike CuO microspheres (Figure 5b) recorded at a rate of 0.1 C in the voltage range of 0.02–3.0 V. Figure 5b showed three typical plateaus in different voltage ranges from 2.5 to 1.5, 2.5 to 1.0, and 1.0 to 0.2 V, respectively, corresponding to the formation of Cu\textsubscript{3}O\textsubscript{2}, Cu\textsubscript{2}O, and Cu and Li\textsubscript{2}O, according to the above-mentioned reactions (eqs 7 and 8). The cycling performance and Coulombic efficiency results (Figure 5c) showed that the initial charge and discharge capacities were 1019 and 525 mA h g\textsuperscript{-1}, respectively, with a Coulombic efficiency of 51.5%. Afterward, both charge and discharge capacities slightly varied around 530 mA h g\textsuperscript{-1} reversibly with the Coulombic efficiency of nearly 100%. The reversible capacity of hollow urchinlike CuO microspheres remained as high as 511 mA h g\textsuperscript{-1} after 40 cycle processes, suggesting their excellent cyclic stability. The rate-performance results (Figure 5d) showed that the capability was decreased gradually upon increasing the current density from 0.1 to 0.2, 0.5, and 1 C, whereas the capability returned reversibly to its original one, once the current density was decreased to 0.1 C, suggesting its excellent rate capability. It should be mentioned that the value of 511 mA h g\textsuperscript{-1} is one of the highest capabilities reported for CuO materials under similar conditions,\textsuperscript{20,21,59,60} which evidently confirmed the application potential of hollow urchinlike CuO microspheres in the lithium-ion batteries.

**CONCLUSIONS**

In summary, structurally novel 3D hierarchical CuO microspheres with hollow urchinlike microstructures were successfully developed by employing BS surfactants as templates. It was noticed that the BS-assisted formation of hollow urchinlike CuO microspheres was common regardless of the reaction temperature and time and the source of copper ions. However, the molar ratio of [Cu\textsuperscript{II}]/[BS] and the hydrophobic chain length of BS affected the morphologies of CuO particles much. Generally speaking, high concentrations of BS and BS with longer chain length strongly favored the formation of hollow urchinlike CuO microspheres obviously. Moreover, the corresponding formation mechanism was also proposed based on the selective adsorption of BS surfactants on the CuO crystal facets. Attributing to their particular characteristics, these hollow urchinlike CuO microspheres showed excellent performance in lithium-ion batteries as anode materials. In particular, the reversible capability was as high as 511 mA h g\textsuperscript{-1} under the current density of 0.1 C after 40 charge–discharge cycles, which was one of the best values for CuO materials in this field.\textsuperscript{20,21,59,60} The present work not only provided important fundamental information in developing surfactant-assisted 3D hierarchical CuO but also showed a promising application potential in the energy field with better performance. According to our work and other related works on the photocatalyst of CuO materials,\textsuperscript{40,42} the developed hollow urchinlike CuO microspheres might also show excellent potential in the field of environmental conservation.

**EXPERIMENTAL SECTION**

**Materials.** BS surfactants including BS-10, BS-12, and BS-14 were synthesized according to the same procedure, as described previously.\textsuperscript{20} Chemicals including CuCl\textsubscript{2}·2H\textsubscript{2}O (99%), Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O (99%), CuSO\textsubscript{4}·5H\textsubscript{2}O (99%), Cu(CH\textsubscript{3}COO)\textsubscript{2}·H\textsubscript{2}O (99%), and NH\textsubscript{4}H\textsubscript{2}O (17%) were obtained from Sinopharm Chemical Reagent Corporation. All other solvents and reagents were obtained from commercial sources and were used as received.

**Synthesis of Hollow Urchinlike CuO Microspheres.** All CuO microspheres were synthesized by the same procedure in this work. Typically, 0.25 mmol (0.04275 g) CuCl\textsubscript{2}·2H\textsubscript{2}O and 0.5 mmol (0.01648 g) BS-12 were dissolved in 15 ml of water and stirred for 30 min to form a uniform blue solution. Afterward, 0.5 mL of ammonium hydroxide was added into the solution and stirred for additional 20 min. Then, the dispersion was transferred into a Teflon-lined stainless autoclave and sealed, which was maintained at 130 °C for 12 h. The crude products were isolated by centrifugation after cooling to room temperature and washed with water and absolute ethanol for several times. Finally, the products were dried in vacuum at 50 °C for 24 h.

**Characterizations.** XRD patterns of CuO powders were recorded on a Bruker D8 Focus X-ray diffractometer (Germany) using Cu Ka radiation (λ = 0.1542 nm) operated at 40 kV and 40 mA. SEM was carried out on a Zeiss Sigma field-emission SEM. FTIR spectra were recorded on a Nicolet Nexus 670 spectrometer in the range from 4000 to 400 cm\textsuperscript{-1}. TEM and HRTEM were performed on a JEM-2100 TEM at an acceleration voltage of 200 kV. The surface atomic concentration and chemical bonding energy of the sample were obtained by XPS (K-Alpha, Thermo Fisher Scientific) using microfocused monochromatized Al Kα radiation. Spectra were collected under the residual pressure of the analysis chamber, which was 1 × 10\textsuperscript{-9} mbar. XPS spectra were corrected with respect to the C 1s peak (at a binding energy of 284.6 eV) and fitted using the Gaussian–Lorentzian line shape. The equilibrium surface tensions were measured by the du Noüy ring method (Krüss K100, Germany) at 25 °C. UV–vis spectrum measurements were carried out on a UV–vis Tu-1901 spectrophotometer (Pigenral, China) using ultrapure deionized water (Millipore) as a blank at 25 °C.

**Electrochemical Measurements.** Electrochemical testing was performed using coin-type (CR-2016) testing cells, using the CuO active materials as the working electrode and metallic lithium foil as the reference and counter electrodes. The CuO working electrodes were prepared by a slurry coating procedure. The slurry was prepared by dispersing the active material, acetylene black, and polyvinylidene fluoride binder with a weight ratio of 80:10:10 in N-methyl-2-pyrrolidone solvent by stirring overnight. The mass of each working electrode was precisely measured with an electronic analytical microbalance. Testing cells were assembled in an argon-filled
glovebox, where the moisture content and oxygen levels were controlled below 1 ppm (20 °C). The electrolyte was 1 M LiPF₆ in a mixture of ethylene carbonate and dimethyl carbonate with a volumetric ratio of 1:1, and the polypropylene microporous membrane (Celgard 2326) was used as the separator. Cyclic voltammetry was conducted from an electrochemical workstation at 0.02–3.0 V (vs Li⁺/Li) with a scan rate of 0.2 mV s⁻¹.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01299.

FTIR spectra of BS-12 and hollow urchinlike CuO powders and TG curve of hollow urchinlike CuO powders; SEM images of CuO microspheres formed at 100 and 160 °C for 12 h in the presence of BS-12 with [CuCl₂]/[BS-12] = 1/2, respectively, and the inset image in each SEM image showing the corresponding single CuO microsphere; SEM images of CuO microspheres formed after 4, 8, 16, and 20 h, respectively, at 130 °C in the presence of BS-12 with [CuCl₂]/[BS-12] = 1/2, respectively, and the inset image in each SEM image showing the corresponding single CuO microsphere; SEM images of CuO microspheres synthesized from CuSO₄, Cu(NO₃)₂, and Cu(OAc)₂, respectively, after 12 h at 130 °C in the presence of BS-12 with [CuCl₂]/[BS-12] = 1/2; and UV–vis spectra of CuCl₂ and BS mixtures in aqueous solutions at 25 °C, [CuCl₂] + [BS] = 0.1 M (PDF)

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**Notes**

The authors declare no competing financial interest.

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