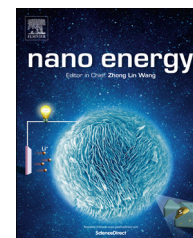




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RAPID COMMUNICATION

Carbon cage encapsulating nano-cluster Li_2S by ionic liquid polymerization and pyrolysis for high performance Li-S batteries



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Abstract

The reversibility and stability of Li_2S electrode can be improved by carbon coating on nano sized Li_2S . However, how to uniformly coat a dense layer of carbon on nano sized Li_2S is still challenge so far. Here, we utilized a novel flowable ionic liquid (1-Ethyl-3-methylimidazolium dicyanamide) as a carbon precursor to uniformly coat a dense carbon on Li_2S nano-clusters. The carbon coated nano- Li_2S cathode displays not only much high active material utilization (826 mAh/g at 0.1 C) due to short lithium ion diffusion distance and low charge transfer resistance, but also long cycling stability (82% of capacity retention after 500 cycles at 1 C) with near 100% Coulombic efficiency due to encapsulation of the lithium polysulfide within the carbon cage.

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Introduction

During the last two decades, lithium-ion batteries (LIBs) have achieved a great success in portable electronic devices due to their high energy density. However, with the rapidly expanding demand on high energy density batteries from clean energy storage, low emission transportation (e.g., electric vehicles),

current state-of-the-art LIBs could hardly keep up with those ever-growing requirements [1–3]. The sluggish progress is attributed to the relatively low capacity of cathode materials (<300 mAh/g) [4]. In the efforts of developing the next generation cathode, sulfur has attracted more and more attention due to its high theoretical capacity (1672 mAh/g S), low cost and environmental benignity [5–15]. Since there is no lithium in pristine sulfur, lithium metal had to be used as the anode. Once employing metallic lithium anode, it is inevitable to face the safety issues caused by lithium dendrite formation during cycling, which limits the practical

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application of metallic lithium-sulfur batteries. One alternative method is to use lithium sulfide (Li_2S) as the cathode which not only can provide a high theoretical specific capacity (1166 mAh/g) but also, in contrast to sulfur electrode, can be paired with a diversity of lithium-free anodes (e.g., graphite, Si, Sn), alleviating the safety issues induced by using metallic lithium [16,17]. Nevertheless, the micro sized Li_2S suffers from fast capacity decay, low capacity and low Coulombic efficiency due to the long ion diffusion distance in commercial micro sized Li_2S and slow charge transfer between electrolyte and active materials [18]. Several previous studies have demonstrated that the reversibility and cycling stability of micro-sized Li_2S electrode could be improved by reducing particle size to nano-scale to shorten lithium ion diffusion distance or by carbon coating to improve electronic conductivity and enhance charge transfer [18–31]. However, it is much challenged to achieve a uniform and dense carbon coating on nano sized Li_2S , which is critical to ensure the electronic conductivity of insulating Li_2S and structure stability during long cycle. Traditional carbon coating normally uses carbohydrate or polymer as the carbon precursor. The water is generated during decomposition of carbon precursor, which could react with Nano- Li_2S . In addition, the carbonization of polymeric precursors usually breaks down the polymeric chain and generates large amount of volatile species, resulting in porous carbon coating with impurity [32]. Recently, we successfully used an ionic liquid as a carbon precursor to form a conformal carbon coating in porous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles due to the excellent fluidic properties of ionic liquid [33,34]. As a matter of fact, the high flow ability of ionic liquid and wettability to sulfides make the ionic liquid unique carbon source for carbon coating on nano- Li_2S .

In this work, a high fluid ionic liquid (IL) (1-Ethyl-3-methylimidazolium dicyanamide) $[\text{Emim}][\text{N}(\text{CN})_2]$ is utilized as a novel carbon precursor to form uniform and dense carbon cage coating on Li_2S nano-cluster. Firstly, the ionic liquid is penetrated into agglomerated Nano- Li_2S particle and is polymerized at low temperature and then carbonized at a high temperature. Due to the oxygen-free nature of $[\text{Emim}][\text{N}(\text{CN})_2]$ (with chemical formula of $\text{C}_8\text{H}_{11}\text{N}_5$), H_2O will not generate during its decompositions in inert atmosphere, which effectively avoids the side reaction between Li_2S and H_2O in pyrolysis process. Secondly, strong Coulombic interaction between cation and anion makes IL nearly non-volatile, thus, which is favorable for crosslinking reaction under pyrolysis conditions and thereby increasing carbon yield and carbon density [35,36], meanwhile the high mobility of $[\text{Emim}][\text{N}(\text{CN})_2]$ is easy to achieve sufficient immersion with Li_2S particle and IL, which is beneficial to form an uniform carbon coating on Li_2S subsequently. The high fluid, non-volatile IL carbon precursor for carbon coating combines the advantages of simple operation, easy obtainment and high yield in solid-state carbonization reaction and conformal coating in chemical vapor deposition (CVD) [20].

Experimental section

Material synthesis

Nano- Li_2S was prepared by a one step in-situ chemical reduction method and the whole experiment was conducted

in an argon (Ar)-filled glove box [37]. Firstly, sulfur is dispersed into tetrahydrofura (THF) solvent by strong mechanical agitation to make a 0.5 mol/L (20 mL) suspension. Then 1/8 (2.5 mL) of reductant (1 mol/L $\text{Li}(\text{CH}_2\text{CH}_3)_3\text{BH}$ in THF) was slowly introduced into the suspension under magnetic stirring and the solution became dark-brown. And, after waiting for 10 min, the residual 7/8 (17.5 mL) of reductant was slowly added into the solution drop by drop. After 24 h of reaction, the solution was centrifuged, and the precipitate was collected and washed for three times. The final nano- Li_2S was prepared by vacuuming above precipitate for one hour at room temperature and then heating at 90 °C for two hours in Ar atmosphere. A proportion of ILs ($[\text{Emim}][\text{N}(\text{CN})_2]$) from BASF corporation and Nano- Li_2S (50 μL :100 mg) is shocked by vortex mixer to make high viscosity IL and Li_2S mixing uniformly, then heat the mixture by two steps (350 °C for 0.5 h and 600 °C for 0.5 h) in Ar atmosphere to carbonize the IL.

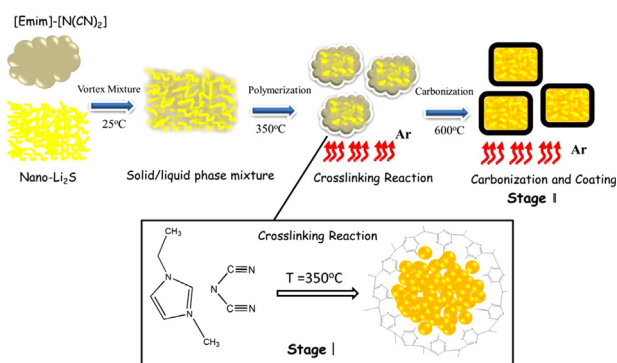
Characterizations and electrochemical measurements

X-ray diffraction patterns were recorded on D8 Advance X-ray diffraction (Bruker), with Cu K-alpha radiation in the 2-theta ranging from 10 to 90 and all samples were assembled in airtight specimen holder ring (Bruker) in Ar filled glove box. Raman measurements were performed on a Horiba Jobin Yvon Labram Aramis using a 532 nm diode-pumped solid-state laser, attenuated to give $\sim 900 \mu\text{W}$ power at the sample surface and all samples were placed between two slide glasses and sealed by adhesive tape in Ar filled glove-box. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were examined in a Hitachi S-4700 (Japan) operating at 10 kV and in a JEOL (Japan) 2100F field emission respectively.

The electrode was fabricated by compressing cathode (Micro- Li_2S , Nano- Li_2S and C-Nano- Li_2S), carbon black, poly (vinylidene difluoride) (PTFE) in weight ratio of 6:3:1 onto a stainless steel grid (200 mesh) for electrochemical performance measurement and the mass load of electrode is about 2.5–3 mg/cm^2 . The CR2032-type coin cells were assembled with the electrode, pure lithium foil as counter electrode and a glass fiber separator in an Ar-filled glove box. The electrolyte is LiTFSI in DOL (50 vol%)-DME (50 vol%) with the ratio of salt (mol):solvent (L) of 7 mol/1 L as our previous paper [15]. The galvanostatic measurements were carried out on a Land BT2000 battery test system (Wuhan, China) at room-temperature. The Cyclic voltammetry (CV) was carried out on CHI 600E electrochemical workstation.

Results and discussion

Scheme 1 schematically shows the detailed preparation of carbon coating nano-sized Li_2S (C-Nano- Li_2S). First, the as-synthesized Nano- Li_2S is mixed with $[\text{Emim}][\text{N}(\text{CN})_2]$ at room temperature by vortex mixer. Then, the homogeneous mixture is heated to 350 °C and 600 °C under Ar atmosphere to realize the carbonization of $[\text{Emim}][\text{N}(\text{CN})_2]$ through the two stages of polymerization and carbonization process. During the polymerization of cation $[\text{N}(\text{CN})_2]^+$ at low temperature of 350 °C, the $[\text{Emim}][\text{N}(\text{CN})_2]$ shrinks and



Scheme 1 The schematic of preparing carbon cage encapsulating nano-clusters Li_2S composite.

breaks the agglomerated nano- Li_2S into a few nano- Li_2S clusters, while the amorphous polytriazine networks are dynamically formed on the surface of nano- Li_2S clusters at the same time. When the temperature further increases to 600°C (the second stage), the amorphous polytriazine out-layer pyrolysis into rectangular dense carbon cage and encapsulate the inner Li_2S nano-clusters.

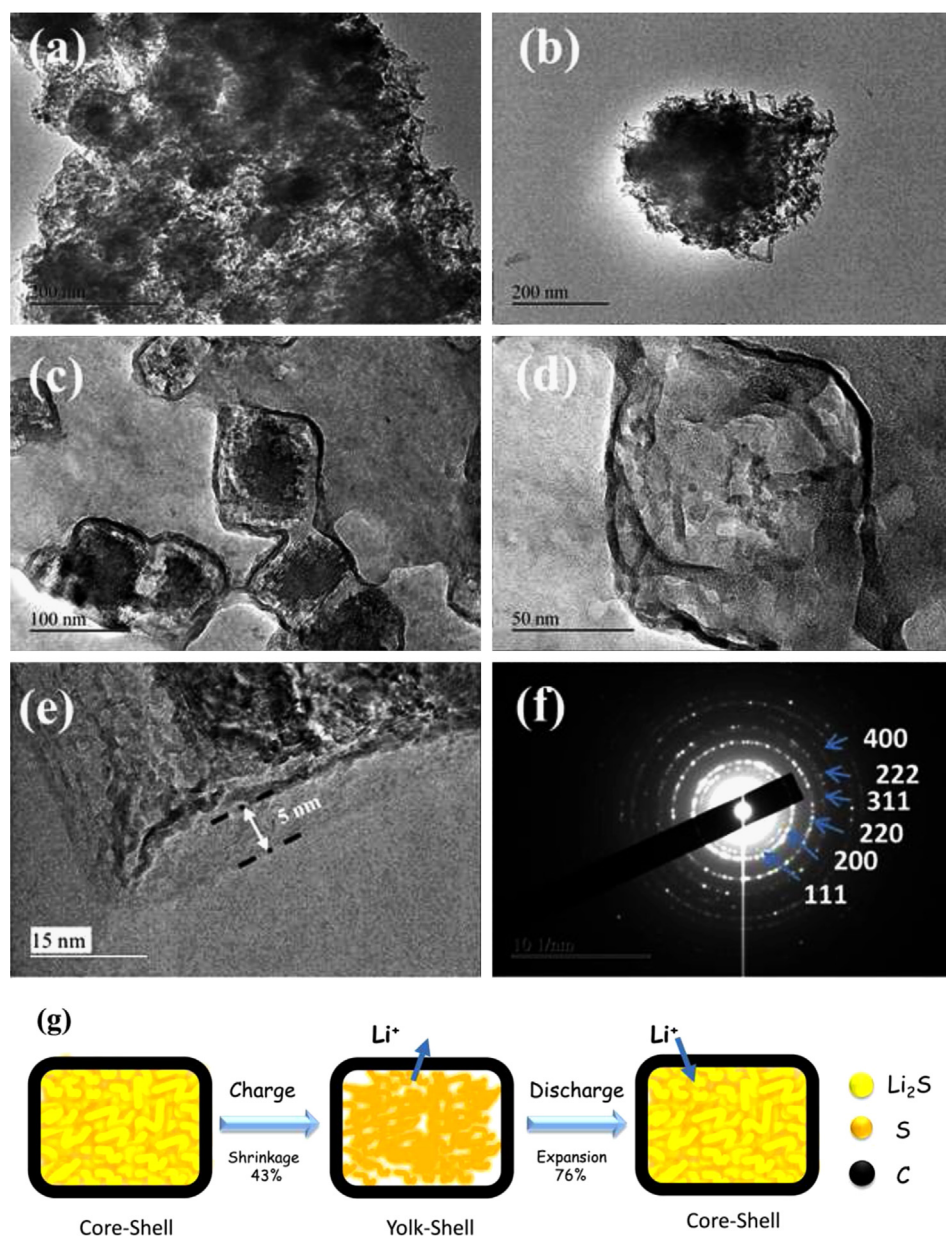
The carbon coating are confirmed by TEM images of nano-sized Li_2S (Nano- Li_2S) and carbon coated nano-sized Li_2S (C-Nano- Li_2S) (Figure 1). The Nano- Li_2S has needle-like morphology and has aggregated into large particles (Figure 1a and b). After carbon coating, the aggregated Nano- Li_2S breaks into about 100 nm with rectangular shape and is confined by the carbon cage (Figure 1c and d). The thickness of carbon coating is about 5 nm as shown in Figure 1e. The SAED pattern in Figure 1f reveals the crystal structure of Li_2S , with the first six rings are indexed to the (111), (200), (220), (311), (222), (400) reflections of Li_2S phase. For carbon coated S nanoparticles, yolk-shell structure is required since the enough free space has to be reserved for 76% volume expansion during initial lithiation [8,38]. However C-Nano- Li_2S is in full lithiation (expanded) state, simple conformal carbon coating rather than complicated yolk-shell is enough for maintaining the structure stability due to no stress/strain generating in whole lithiation/delithiation process (Figure 1g). Thus, the electrochemical performance of Nano- Li_2S coated by IL-pyrolysis is expected to have stable cycling stability.

Figure 2a shows the XRD patterns of Nano- Li_2S , C-Nano- Li_2S and commercial Micro- Li_2S (50 μm particle size). The SEM image of commercial Micro- Li_2S is shown in Figure S1. As shown in Figure 2a, Nano- Li_2S is in crystal structure without any detectable impurity (the bump at $\sim 20^\circ$ is due to the airtight sample holder). The XRD pattern of C-Nano- Li_2S is the same as that of Nano- Li_2S , confirming that no any side reaction between Li_2S and products generated from the pyrolysis process of the oxygen-free [Emim]-[N(CN) $_2$] ($\text{C}_8\text{H}_{11}\text{N}_5$) precursor. As expected, the half-peak widths of Nano- Li_2S and C-Nano- Li_2S significantly increase compared to the XRD pattern of commercial Micro- Li_2S due to the size effects. The natures of coated carbon and lithium sulfide were characterized using Raman spectra (Figure 2b). The Raman spectra of C-Nano- Li_2S in the range of $200\text{--}1200\text{ cm}^{-1}$ is the same as commercial Micro- Li_2S and Nano- Li_2S . The two additional broad peaks at 1334 cm^{-1} and 1600 cm^{-1} for C-Nano- Li_2S is attributed to carbon since the carbon produced by pyrolysis of IL also shows similar peaks. The peak at 1334 cm^{-1} (D-band) is usually associated with the

vibrations of carbon atoms with dangling bonds forth in-plane terminations of disordered graphite, and the peak at 1600 cm^{-1} (G-band) (corresponding to the E_{2g} mode) is closely related to the vibration in all sp^2 bonded carbon atoms in a two-dimensional hexagonal lattice, such as in a graphene layer. The intensity ratio of the D- to G- band (I_D/I_G) could further reflect the relative disorder and degree of graphitization of carbon. In this case, the intensity of D-band peak is stronger than G-band, indicating that the generated carbon is more disordered. To detail understand the nature of coated carbon, a bulk carbon synthesized by pyrolysis of IL was characterized using scanning electron microscopy (SEM) (Figure S2) and XRD (Figure S3). As shown in Figure S2, the pyrolysis of IL can form a dense carbon without any noticeable cracks, which could effectively encapsulate the inside intermediate lithium polysulfide and avoid the shuttle effect when it coated on nano- Li_2S particles. XRD pattern in Figure S3 shows that the pyrolysis-generated carbon is partially graphitized, in which the broad peaks at 26° and 44° were corresponding to (002) and (100) of graphite. The carbon-yield during the pyrolysis of [Emim]-[N(CN) $_2$] was estimated by measuring the weight difference before and after carbonization of [Emim]-[N(CN) $_2$] in Ar under the same heat treatment condition as for [Emim]-[N(CN) $_2$]/Nano- Li_2S composite. The carbon-yield of [Emim]-[N(CN) $_2$] is 20 wt%. Since the ratio of ILs ([Emim]-[N(CN) $_2$]) to Nano- Li_2S is $50\text{ }\mu\text{L}:100\text{ mg}$, we can estimated the carbon content in C-Nano- Li_2S composite using equation below:

Carbon content = carbon yield \times IL volume \times IL density / carbon yield \times IL volume \times IL density + Li_2S . The carbon content was determined as 10% ($20\% \times 50\text{ }\mu\text{L} \times 1.06\text{ g/cm}^3 / 20\% \times 50 \times 1.06 + 100\text{ mg} = 9.6\%$).

In order to further prove the effect of carbon coating by [Emim]-[N(CN) $_2$], we tested the electrochemical performances of commercial Micro- Li_2S , Nano- Li_2S and C-Nano- Li_2S (Figure 3). Figure 3a shows the charge-discharge curves of commercial Micro- Li_2S , Nano- Li_2S and C-Nano- Li_2S at a rate of 0.1 C (117 mA/g- Li_2S) after the first cycle activation process (0.02 C) ($\sim 23\text{ mA/g-Li}_2\text{S}$), and the first charge-discharge profile of C-Nano- Li_2S at 0.02 C is presented in Figure S4. Compared with Micro- Li_2S and Nano- Li_2S , C-Nano- Li_2S shows a much higher utilization of active material, as indicated by the large difference in lithiation capacities, which are 826.1 mAh/g for C-Nano- Li_2S , 608.4 mAh/g for Nano- Li_2S and 162 mAh/g for micro-sized commercial Li_2S . The capacity of C-Nano- Li_2S is calculated by the total weight of cathode. The significant increase in capacity for C-Nano- Li_2S could be contributed to much high specific surface area, high electronic conductivity and short lithium diffusion distance, which facilitate the lithiation/delithiation kinetics and increase the utilization of Li_2S . Figure 3b shows the cycling stability of C-Nano- Li_2S , Nano- Li_2S and Micro- Li_2S at 0.1 C ($\sim 117\text{ mA/g}$), which presents that C-Nano- Li_2S maintains 78.5% of initial capacity after 50 charge/discharge cycles which is much higher than that (51.8%) of Nano- Li_2S . Meanwhile, the long-term cycling stability of C-Nano- Li_2S at a high rate of 1 C (1166 mA/g- Li_2S) is also shown in Figure 3c. As shown in Figure 3c, a reversible capacity of 439.5 mAh/g- Li_2S (calculated based on Li_2S) or 630.8 mAh/g-S (calculated based on S) could be achieved even at a high rate of 1 C after the initial activation process (0.1 C). Moreover, high capacity retention of 82% could be achieved after 500 cycles with a Coulombic efficiency near 100%. C-Nano- Li_2S also shows high rate capacity as demonstrated in Figure 3d. It exhibits



Carbon cage encapsulating Nano-clusters Li_2S

Figure 1 TEM images of (a) and (b) Nano- Li_2S ; (c), (d) and (e) C-Nano- Li_2S ; (f) selected area electron diffraction (SAED) pattern of the particle shown in (d); (g) schematic of the delithiation and lithiation process in carbon-coated Nano- Li_2S with cage-like structure.

capacities of 856 mAh/g, 691 mAh/g, 537 mAh/g, 365 mAh/g, and 251 mAh/g at current rates of 0.1, 0.2, 0.5, 1, and 2 C. When the current density is reduced back from 2 C to 0.1 C, the capacity is almost fully recovered, indicating the robust rate stability of the C-Nano- Li_2S electrode. This significant improvement on electrochemical performances of C-Nano- Li_2S is attributed to the unique core-shell structure of C-Nano- Li_2S , which could effectively reduce cycling decay caused by large volume change between Li_2S and S and inhibit the shuttle reaction induced from the dissolution of high-order polysulfide. Meanwhile, carbon coating-layer as a cage inhibits nanoparticle agglomeration induced by redistribution of active material during the cycles.

Conclusion

In summary, we developed a facile and effective carbon coating method by utilizing high fluid ionic liquid (IL) (1-Ethyl-3-methylimidazolium dicyanamide) [Emim]-[N(CN) $_2$] as a novel liquid phase carbon precursor. In virtue of the unique oxygen-free chemical formula and physicochemical properties of [Emim]-[N(CN) $_2$], we successfully prepare to achieve nano-scale carbon cage encapsulating Li_2S nano-clusters (Nano- Li_2S) by designing two heat treatment steps. This method combines the advantages of solid-state reaction (simple operation, easy obtainment and high yield) and

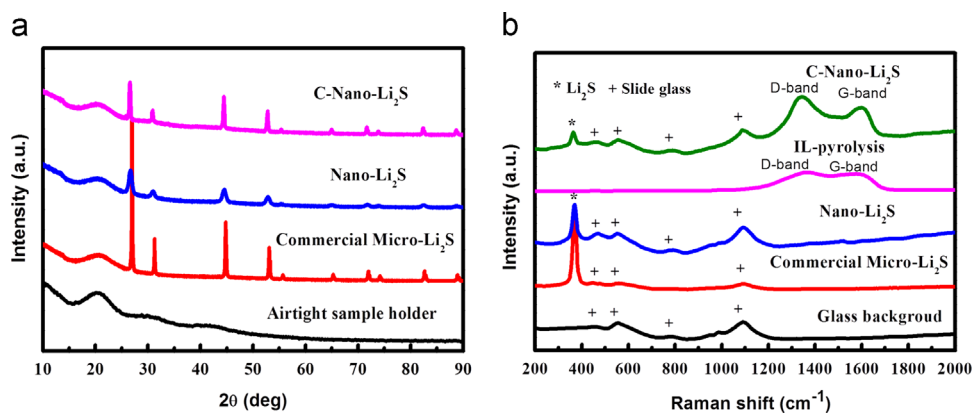


Figure 2 (a) X-ray diffraction patterns and (b) Raman spectra.

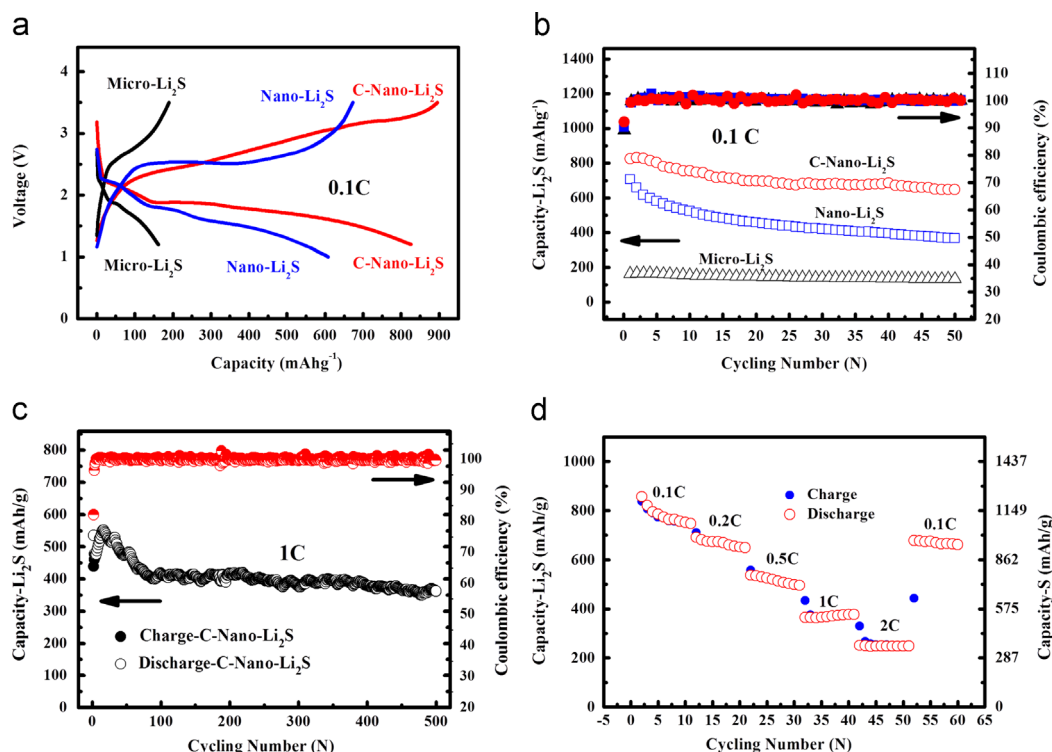


Figure 3 Comparison of electrochemical performance of different Li₂S samples (Micro-sized Li₂S purchasing from Aldrich, Nano-Li₂S, and C-Nano-Li₂S), all the capacity calculated based on the weight of C/Li₂S. (a) the typical charge-discharge profiles at 0.1 C after the first cycle activation (charge to 3.8 V) at 0.02C; (b) cycling life and Coulombic efficiencies at C/10 after activation for 1 cycle at 0.02 C; (c) long cycling life and Coulombic efficiency of C-Nano-Li₂S at a high rate (1 C) after the first cycle at 0.1 C; (d) rate capability of C-Nano-Li₂S.

chemical vapor deposition (CVD) approach (coating uniformity and entirety). Compared with commercial Micro-Li₂S and pure Nano-Li₂S, C-Nano-Li₂S electrode displays much higher Li₂S utilization in virtue of short lithium ion diffusion distance in nano-sized particle and low charge transfer by carbon coating. More importantly, the formed core-shell structure is able to enhance electrode stability for long-term cycling by entrapping the lithium polysulfide within the carbon cage. The nano-clusters Li₂S encapsulated in carbon cage exhibited a high capacity (826 mAh/g at 0.1 C) and high capacity retention after 500 cycles (82% at 1 C) with near 100% Coulombic efficiency.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2015.02.021>.

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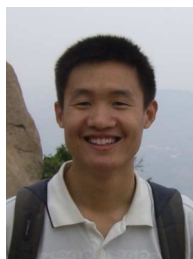


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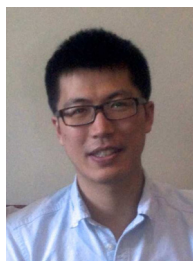


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