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Nanoparticle-assembled interconnected $\text{PbO}_{1.44}$ hollow spheres enabled by PVP-driven transformation of $\beta\text{-PbO}_2$ and self-sacrificial templating for superior lithium storage†

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Lead oxides (PbO_x , $1 \leq x \leq 2$) are promising high-capacity and low-cost anodes for lithium ion batteries (LIBs). However, the huge lithiation-induced volume expansion of conventional large-sized PbO_x particles leads to severe electrode pulverization with poor cycling stability. Herein, a rare mixed-valence $\text{PbO}_{1.44}$ with a unique hierarchical architecture of nanoparticle-assembled interconnected hollow spheres (denoted $\text{PbO}_{1.44}$ NAHSs) is crafted by

introducing polyvinylpyrrolidone (PVP) into the solution of generating $\beta\text{-PbO}_2$ microspheres (MSs), which is exploited for the first time as a potential advanced anode material for LIBs. Notably, an intriguing PVP-driven dissolution–recrystallization transformation process converting $\beta\text{-PbO}_2$ MSs into $\text{PbO}_{1.44}$ NAHSs is revealed by PVP-concentration and reaction-time control experiments, demonstrating the dual function of PVP as a mild reducing agent combined with it being a morphology regulator for the construction of $\text{PbO}_{1.44}$ NAHSs. Furthermore, a self-sacrificial templating mechanism is demonstrated for yielding the interconnected hollow structure of $\text{PbO}_{1.44}$ NAHSs. Remarkably, $\text{PbO}_{1.44}$ NAHSs deliver stable capacities of 561 and 453 mA h g^{-1} after 100 and 200 cycles at 50 and 500 mA g^{-1} , respectively, in sharp contrast to the performance of $\beta\text{-PbO}_2$ MSs (52 and 43 mA h g^{-1}). Structural and electrochemical measurements of the cycled electrodes indicate that the hollow and nanoarchitectural structure of $\text{PbO}_{1.44}$ NAHSs enables their superior cycling and rate capabilities, benefiting from the effectively buffered volume expansion and shortened lithium storage distance, respectively. As such, this work highlights a robust PVP-assisted strategy to fabricate rare mixed-valence $\text{PbO}_{1.44}$ NAHSs with outstanding electrochemical reactivity and mechanical robustness for lithium storage and various potential applications.

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1. Introduction

The ever-increasing demand for portable electronics with long service life and high power density has triggered the rapid development of high-performance energy storage technologies.^{1,2} Among all of the commercial electrochemical power sources, lithium ion batteries (LIBs) have achieved great success due to their higher energy density, longer cycle life, and better environmental friendliness in contrast to most of the popular secondary batteries.^{3,4} However, the low theoretical mass and volume capacities of commercial graphite anodes (*i.e.*, 372 mA h g^{-1} and 830 mA h cm^{-3}) seriously restrict the property improvement of next-generation LIBs.^{5,6}

In recent decades, elements in Group IVA (*i.e.*, Si, Ge, Sn and Pb) and their compounds have attracted wide attention as promising high-capacity anodes for LIBs based on their alloying–dealloying reaction mechanisms with the advantages of suitable low-voltage plateaus (~ 0.5 V *vs.* Li⁺/Li), low cost and abundance.^{7,8} Therein, lead oxides (PbO_{*x*}, $1 \leq x \leq 2$) possess higher theoretical mass and especially volumetric specific capacities (*e.g.*, PbO (769 mA h g⁻¹ and 7329 mA h cm⁻³) and PbO₂ (941 mA h g⁻¹ and 8827 mA h cm⁻³)) than graphite, based on the conversion-combined alloying–dealloying reactions of PbO_{*x*} + 2*x*Li⁺ + 2*x*e⁻ \rightleftharpoons Pb + *x*Li₂O ($1 \leq x \leq 2$) and Pb + *y*Li⁺ + *y*e⁻ \rightleftharpoons Li_{*y*}Pb ($0 \leq y \leq 4.4$), respectively.^{9–12} Nevertheless, due to the sluggish electrochemical reaction kinetics and huge volume expansion, the conventionally fabricated PbO_{*x*} particles with large-sized bulk structures usually exhibit poor cycling stability and rate capability.^{13–15} Therefore, rational approaches to the design of structures and compositions of PbO_{*x*}-based materials are crucial to enhance their lithium storage performances for realizing their practical application as anodes of LIBs.^{16–19}

As a post-transition metal with the electronic configuration of 6s²6p², Pb has many types of oxides including PbO, PbO₂ and various mixed-valence compounds (*i.e.*, Pb₂O₃, Pb₃O₄ and non-stoichiometric PbO_{*x*} ($1 < x < 2$)). Due to their outstanding properties in optical, ferroelectric, dielectric, energy-storage and oxygen-sensing fields, PbO_{*x*}-based materials have been widely used in the industrial fields of lead acid batteries, paints, glasses and so on.^{20–22} As a result, the fabrication strategies and crystallization behaviors of PbO_{*x*} have always been hot research topics.^{23,24} For electrochemical syntheses, orthorhombic α -PbO₂ and tetragonal β -PbO₂ can be generally obtained in a strong acidic medium and an alkaline or neutral medium, respectively.²⁵ In contrast to electrochemical methods, solution-based chemical routes for synthesizing PbO_{*x*} are more controllable in terms of the structure–composition design and easier to scale up.^{26–28} However, up to now, the preparation of phase-pure non-stoichiometric PbO_{*x*} ($1 < x < 2$) by the more popular solution-based methods has rarely been reported, limiting their structural analysis, property investigation and application exploration.^{20–28}

As for the mixed-valence oxides of PbO_{*x*} (*e.g.*, Pb₂O₃, Pb₃O₄ and non-stoichiometric PbO_{*x*} ($1 < x < 2$)), the non-integral *x* value can be regarded as an incomplete oxidation of Pb²⁺ or a partial reduction of Pb⁴⁺ in the crystallization process of PbO_{*x*} ($1 < x < 2$), occasionally found in the heat-treatment process of solid-state precursors of PbO₂ or PbO. For example, PbO_{1.55} has been captured during the heat-treatment of chemically produced β -PbO₂ at 400 °C, which is recognized as one of the crystalline intermediates of partially reduced β -PbO₂.²⁹ Similarly, serial crystalline phases of PbO_{*x*} ($1 < x < 2$) have also been detected during the air-oxidizing of tetragonal PbO, resulting in PbO_{1.548} and PbO_{1.333} at 286 and 351 °C, respectively.³⁰ Therein, the created PbO_{*x*} series ($1.41 < x < 1.57$) exhibited similar X-ray diffraction (XRD) patterns to that of cubic PbO_{1.44} (*a* = 4.9525 Å, JCPDS no. 27-1201) obtained after annealing PbO at 293 °C for 180 h in an air atmosphere. A thin

film of well-defined PbO_{1.44} was prepared by reactive direct current magnetron sputtering from a metallic lead target onto Si (100) wafers and glass substrates in a precisely controlled flow of an oxygen–argon mixture.³¹ Nevertheless, there has been no report concerning the fabrication of PbO_{1.44} with high purity, high crystallinity and fine structure *via* a facile solution-based method until now. The solution-based method is widely used for the synthesis of ultra-fine powders in research and industry due to its significant advantages of high controllability, low cost and high reaction efficiency.^{3,5,7,8} First, the solution-based method can control the reaction rate, particle size distribution and morphology by adjusting the reaction conditions and additives, thus achieving precise control of the products. Second, compared with other synthesis methods (*e.g.* gas-phase method and solid-phase method), the equipment cost for solution reaction is relatively low with simple operation, so it is easier to achieve large-scale industrial production. Third, the reaction speed of solution-based synthesis is generally fast with high reaction efficiency to quickly obtain the desired products.

In this work, a facile polyvinyl pyrrolidone (PVP)-assisted hydrothermal route has been rationally developed to produce pure-phase cubic PbO_{1.44} particles (~ 1 μ m in diameter) with high crystallinity and a unique structure of nanoparticles (~ 50 nm in diameter) assembled into interconnected hollow spheres (denoted PbO_{1.44} NAHSs), which have been studied for the first time as promising anode materials for LIBs. As a polymeric surfactant, PVP generally acts as a soft-templating and capping agent for the crystallization and self-assembly of inorganic particles.^{32–34} Besides, PVP has also been successfully used for the controllable synthesis of noble metal particles (*e.g.*, Ag, Au, Pd and Pt) by serving as a mild reductant for the slow reduction of water-soluble metal salts.^{35–37} As expected, by introducing PVP as a mild reductant into the hydrothermal reaction solution for the preparation of β -PbO₂ microspheres (denoted β -PbO₂ MSs), an intriguing PVP-driven dissolution–recrystallization transformation process converting β -PbO₂ MSs into PbO_{1.44} NAHSs has been discovered and well proven by a PVP-concentration control experiment. More importantly, time-dependent experiments demonstrate a self-sacrificial templating mechanism for the formation of the unique interconnected structure of PbO_{1.44} NAHSs. Therefore, PVP serves as both a mild reductant and a morphology regulator for the formation of nanostructured PbO_{1.44} NAHSs.

Notably, PbO_{1.44} NAHSs exhibit outstanding cycling and rate capabilities with stable capacities of 561 and 453 mA h g⁻¹ after 100 and 200 cycles at 50 and 500 mA g⁻¹, respectively, in sharp contrast to the performance of β -PbO₂ MSs (52 and 43 mA h g⁻¹). As uncovered by systematic structural and electrochemical investigations, the superior electrochemical properties of PbO_{1.44} NAHSs can be attributed to the unique interconnected hollow structure assembled from nanoparticles. First, the secondary nanoparticles shorten the lithium storage distance and enlarge the contact area with the electrolyte for sufficient lithium storage reaction and fast electrochemical kinetics, giving rise to the high capacity and

excellent rate capability, respectively. Second, the interconnected hollow structure effectively buffers the lithiation–delithiation-induced volume expansion–shrinkage of $\text{PbO}_{1.44}$ NAHSs, enabling the ultra-high structural robustness of the electrode and thus the outstanding cycling performance. As such, this study underscores a robust PVP-assisted hydrothermal route to prepare high-quality $\text{PbO}_{1.44}$ NAHSs with excellent electrochemical reactivity and mechanical robustness for a wide range of diverse potential applications including lithium-ion batteries, lead-acid batteries, catalysis, sensing, and so on.

2. Results and discussion

2.1. PVP-driven transformation of $\beta\text{-PbO}_2$ MSs into $\text{PbO}_{1.44}$ NAHSs

Scanning electron microscopy (SEM, Fig. 1a–d and S1†) and transmission electron microscopy (TEM, Fig. 1e–h) images reveal that the 7 h hydrothermal reaction of lead acetate, sodium hydroxide and ammonium persulfate in the presence of polyvinylpyrrolidone K30 (PVP, 3 g L^{-1}) at 120°C gave rise to a product with a unique structure of nanoparticle-assembled hollow spheres (NAHSs). Notably, all the hollow

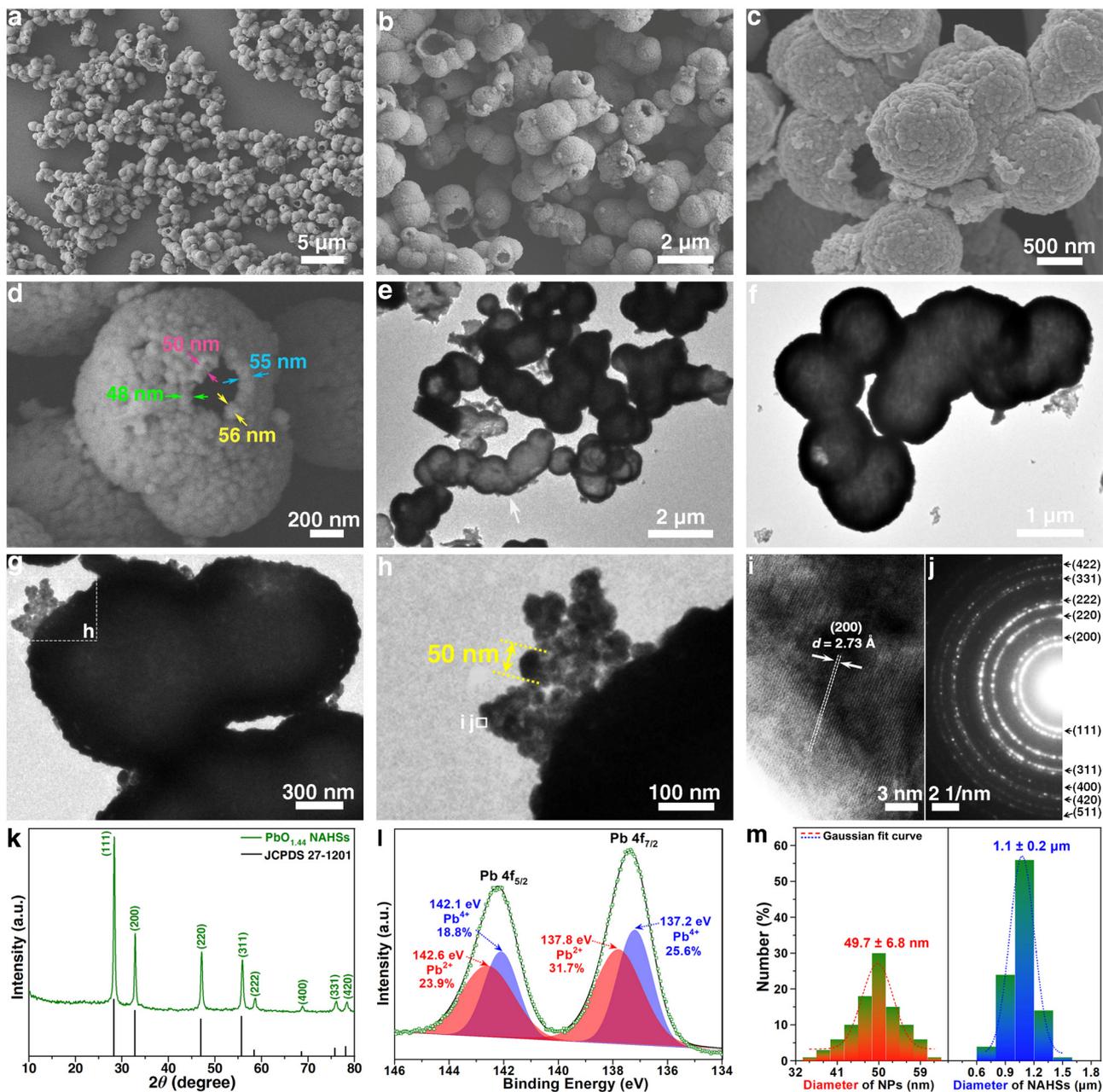


Fig. 1 Structural characterization of $\text{PbO}_{1.44}$ NAHSs. (a–d) SEM and (e–i) TEM images. (j) SAED pattern, (k) XRD pattern and (l) XPS spectrum of $\text{PbO}_{1.44}$ NAHSs. (m) Diameter distributions of secondary $\text{PbO}_{1.44}$ nanoparticles (left panel) and $\text{PbO}_{1.44}$ NAHSs (right panel).

spheres are interconnected with adjacent ones, as distinctly demonstrated by the TEM images of Fig. 1e–g. The high magnification SEM images (Fig. 1d and S1c–f†) clearly show that the hollow spheres are assembled from ultra-fine nanoparticles. The high-resolution TEM (HRTEM) image (Fig. 1i), selected area electron diffraction (SAED) pattern (Fig. 1j) and powder X-ray diffraction (XRD) pattern (Fig. 1k) of the product indicate the pure-phase, high-crystallinity and polycrystalline character of cubic $\text{PbO}_{1.44}$ crystals ($a = 5.469 \text{ \AA}$, JCPDS no. 27-1201). In the X-ray photoelectron spectroscopy (XPS) spectrum of Pb 4f of the $\text{PbO}_{1.44}$ NAHSSs (Fig. 1l), the Pb 4f_{5/2} and Pb 4f_{7/2} peaks can be divided into two pairs of peaks at 142.6 and 137.8 eV corresponding to Pb^{2+} and at 142.1 and 137.2 eV corresponding to Pb^{4+} , respectively. According to the relative area percentages of the Pb 4f peaks of $\text{PbO}_{1.44}$ NAHSSs (*i.e.*, Pb^{2+} (55.6%) and Pb^{4+} (44.4%)), a chemical formula of $\text{PbO}_{1.444}$ can be estimated, which is almost identical to the stoichiometric ratio of $\text{PbO}_{1.44}$. From the particle size statistics based on the SEM and TEM images (Fig. 1a–h and S1†), the average diameters of $\text{PbO}_{1.44}$ NAHSSs and secondary nanoparticles that are assembled into $\text{PbO}_{1.44}$ NAHSSs are $1.1 \pm 0.2 \mu\text{m}$ and $49.7 \pm 6.8 \text{ nm}$ (Fig. 1m), respectively.

As a well-known dispersant or colloidal stabilizer of nanoparticles, the polymeric surfactant PVP has been popularly involved in the size and morphology controllable syntheses of a variety of functional micro/nano particles.^{38–42} Besides, it has been proved that the abundant carbonyl groups of PVP can be oxidized to carboxyl or ester groups, endowing PVP with mild reducibility.³⁵ In order to clarify the crucial roles of PVP in the formation of $\text{PbO}_{1.44}$ NAHSSs, a series of control experiments that involve regulating PVP concentrations (*i.e.*, 0, 0.5, 1.0, 1.5, 2.0 and 2.5 g L^{-1}) were performed (Fig. 2 and S2–S8†). As a blank experiment in the absence of PVP, the reaction of lead acetate, sodium hydroxide and ammonium persulfate resulted in the generation of inhomogeneous large-sized solid $\beta\text{-PbO}_2$ microspheres (denoted $\beta\text{-PbO}_2$ MSs) (Fig. 2a, b, l and S2†) with an average diameter of $3.9 \pm 1.5 \mu\text{m}$ (Fig. S2f†). The Pb 4f XPS spectrum of $\beta\text{-PbO}_2$ MSs (Fig. S3†) shows Pb 4f_{5/2} and Pb 4f_{7/2} peaks at 142.1 and 137.2 eV, corresponding to Pb^{4+} in $\beta\text{-PbO}_2$.

Interestingly, after introducing a small amount of PVP (0.5 g L^{-1}) into the reaction solution for producing $\beta\text{-PbO}_2$, a mixture of $\beta\text{-PbO}_2$ MSs (primary) and $\text{PbO}_{1.44}$ NAHSSs (secondary) was created (Fig. 2c, l and S4†). Moreover, along with the gradually increased concentrations of PVP to 1.0, 1.5, 2.0, and 2.5 g L^{-1} , the amount ratios of $\text{PbO}_{1.44}$ NAHSSs in the mixed products keep on increasing (Fig. 2d–k and S5–S8†), in accordance with the continuously strengthening XRD peaks of $\text{PbO}_{1.44}$ and weakening XRD peaks of $\beta\text{-PbO}_2$ (Fig. 2l). It is noteworthy that some $\text{PbO}_{1.44}$ NAHSSs grow *in situ* on the $\beta\text{-PbO}_2$ MSs, as indicated by the white arrows in Fig. 2d and e, implying the close relationship between $\text{PbO}_{1.44}$ NAHSSs and $\beta\text{-PbO}_2$ MSs. In addition, the fragmentary particles of $\beta\text{-PbO}_2$ MSs can be observed in the mixtures as indicated by the white arrows in Fig. 2g, i and k, suggesting a PVP-driven reduction combined dissolution process of $\beta\text{-PbO}_2$ causing the trans-

formation of $\beta\text{-PbO}_2$ MSs into $\text{PbO}_{1.44}$ NAHSSs. Therefore, it can be concluded that PVP serves as a dual-functional additive acting as a mild reducing agent combined with being a morphology regulator to induce the conversion of $\beta\text{-PbO}_2$ MSs into $\text{PbO}_{1.44}$ NAHSSs.

2.2. Self-sacrificial templating formation of the interconnected hollow structure of $\text{PbO}_{1.44}$ NAHSSs

To elucidate the formation mechanism of the unique architecture of nanoparticle-assembled interconnected hollow spheres of $\text{PbO}_{1.44}$ NAHSSs, time-dependent experiments were performed over designated incubation times of 1, 3 and 5 h (Fig. 3 and S9–S11†). After reaction for 1 h, amorphous mixed particles were obtained (Fig. 3a–c, l and S9†), including a large amount of randomly aggregated solid spheres assembled from nanoparticles (Fig. 3c and S9b†) and a small amount of large irregular particles (as indicated by the white arrows in Fig. 3a and b). Then, after 3 h of reaction (Fig. 3d–h, l and S10†), the hydrothermal solution-mediated dissolution–recrystallization took place from the inside to the outside of the amorphous solid spheres formed after 1 h, generating interconnected $\text{PbO}_{1.44}$ hollow spheres with thick shells (Fig. 3f and g). Notably, the SAED pattern of a solid microsphere from the 3 h product confirms that the microspheres in the intermediate mixtures are $\beta\text{-PbO}_2$. Due to the gradual PVP-driven reduction and dissolution of $\beta\text{-PbO}_2$ MSs and hydrothermal-induced dissolution–recrystallization from the inside out of $\text{PbO}_{1.44}$ NAHSSs, a mixture of highly crystalline $\text{PbO}_{1.44}$ NAHSSs (primary) with thinner shells and a small amount of small irregular crumbs of $\beta\text{-PbO}_2$ MSs (secondary, as indicated by the white arrows in Fig. 3i and j) were obtained after 5 h (Fig. 3i–l and S11†). Finally, pure phase $\text{PbO}_{1.44}$ NAHSSs were produced after 7 h of the hydrothermal reaction (Fig. 1 and S1†).

SEM images of the representative intermediate particles obtained after 1, 3 and 5 h visually demonstrate the structural evolution of $\text{PbO}_{1.44}$ NAHSSs (Fig. 4a–c) and $\beta\text{-PbO}_2$ MSs (Fig. 4d–f). A typical hydrothermal-driven Ostwald ripening combined with a self-sacrificial templating mechanism accounts for the formation of $\text{PbO}_{1.44}$ NAHSSs.⁴³ Aggregated amorphous solid spheres assembled from nanoparticles (denoted amorphous $\text{PbO}_{1.44}$ NASSs) were formed after 1 h (Fig. 4a). Then, the hydrothermal environment induced the dissolution of the inner smaller nanoparticles, which were initially deposited from the solution, and then the recrystallization on the surfaces of later deposited larger nanoparticles, giving rise to the formation of $\text{PbO}_{1.44}$ NAHSSs with thick shells ($\sim 250\text{--}320 \text{ nm}$) after 3 h of reaction (Fig. 4b).^{43,44} As the Ostwald ripening process continued, the shell thicknesses of the $\text{PbO}_{1.44}$ NAHSSs continued to decrease to $\sim 110\text{--}140 \text{ nm}$ for the 5 h intermediate (Fig. 4c) and then $\sim 50 \text{ nm}$ for the 7 h product (Fig. 1d). Therein, due to the dissolution of the nanoparticles at the contact areas of randomly aggregated spheres formed after 1 h, the unique interconnected hollow structure is created.⁴⁴ As for the $\beta\text{-PbO}_2$ MSs, a PVP-driven progressive dissolution process was observed along with extended reaction

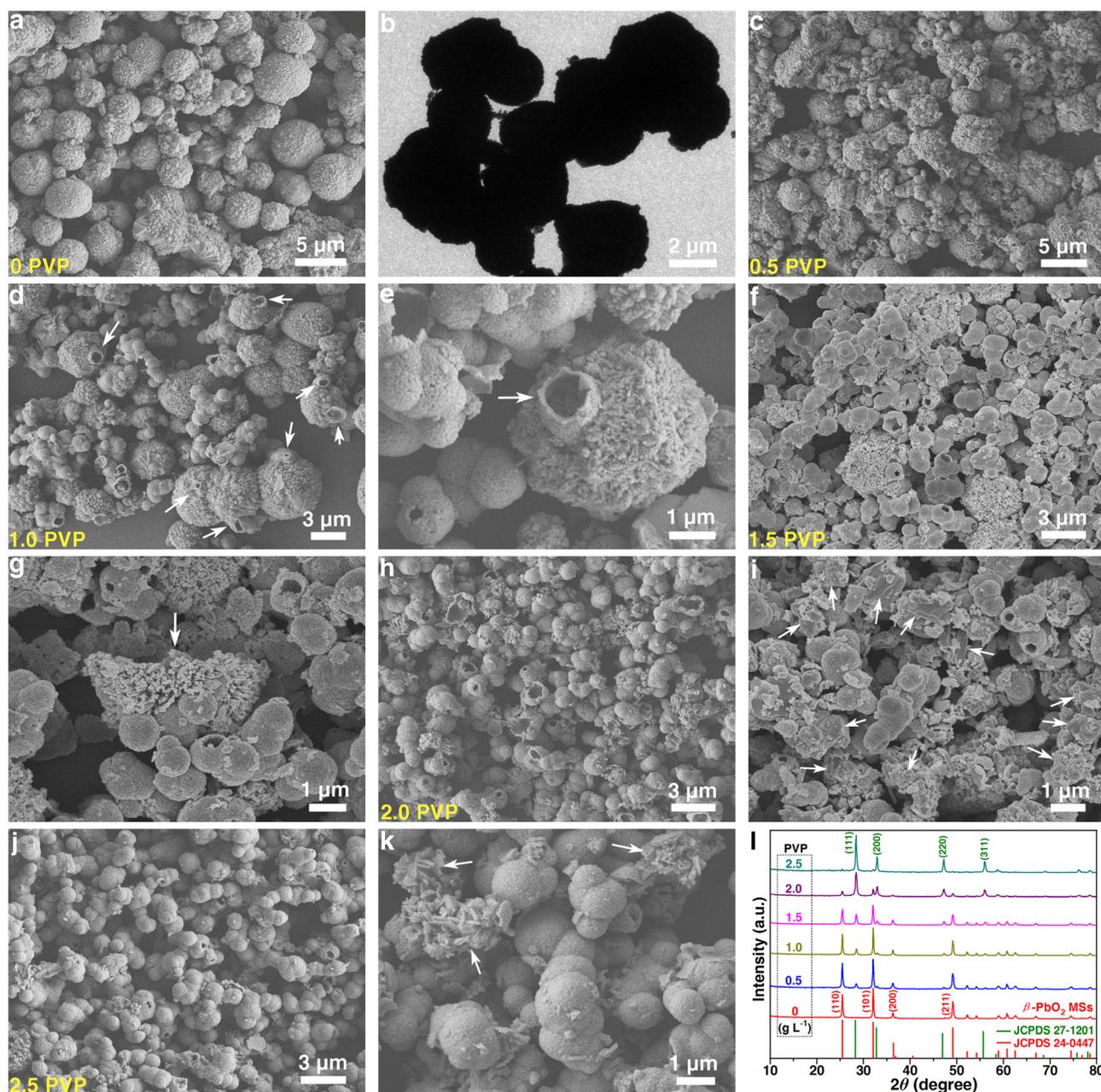


Fig. 2 Effect of PVP concentrations on the formation of $\text{PbO}_{1.44}$ NAHSs. (a) SEM and (b) TEM images of $\beta\text{-PbO}_2$ MSs. (c–k) SEM images and (l) XRD patterns of the mixtures of $\beta\text{-PbO}_2$ MSs and $\text{PbO}_{1.44}$ NAHSs obtained in the presence of (c) 0.5, (d and e) 1.0, (f and g) 1.5, (h and i) 2.0 and (j and k) 2.5 g L^{-1} PVP.

times, that is, from complete MSs (1 h, Fig. 4d) to incomplete MSs (3 h, Fig. 4e) and then to irregular fragments (5 h, Fig. 4f), which finally disappeared at 7 h (Fig. 1a, k and 3l). The structure formation mechanism of $\text{PbO}_{1.44}$ NAHSs is concisely illustrated in Fig. 4g. The weak reducing agent of PVP induces the progressive reduction and dissolution of $\beta\text{-PbO}_2$ MSs and simultaneous recrystallization on the $\text{PbO}_{1.44}$ NAHSs. Furthermore, the Ostwald ripening process from the inside outwards of the aggregated spheres generated after 1 h triggers

a self-sacrificial templating mechanism that constructs the interconnected hollow structure of $\text{PbO}_{1.44}$ NAHSs.^{43,44}

2.3. Superior lithium storage capability of $\text{PbO}_{1.44}$ NAHSs

The electrochemical properties of $\text{PbO}_{1.44}$ NAHSs and $\beta\text{-PbO}_2$ MSs were examined using lithium cell models within a potential window of 0.01–3.0 V vs. Li^+/Li .^{45,46} As an anode material of LIBs, $\text{PbO}_{1.44}$ NAHSs exhibited outstanding cycling stability at 50 (Fig. 5a) and 500 mA g^{-1} (Fig. 5b) with ultra-stable

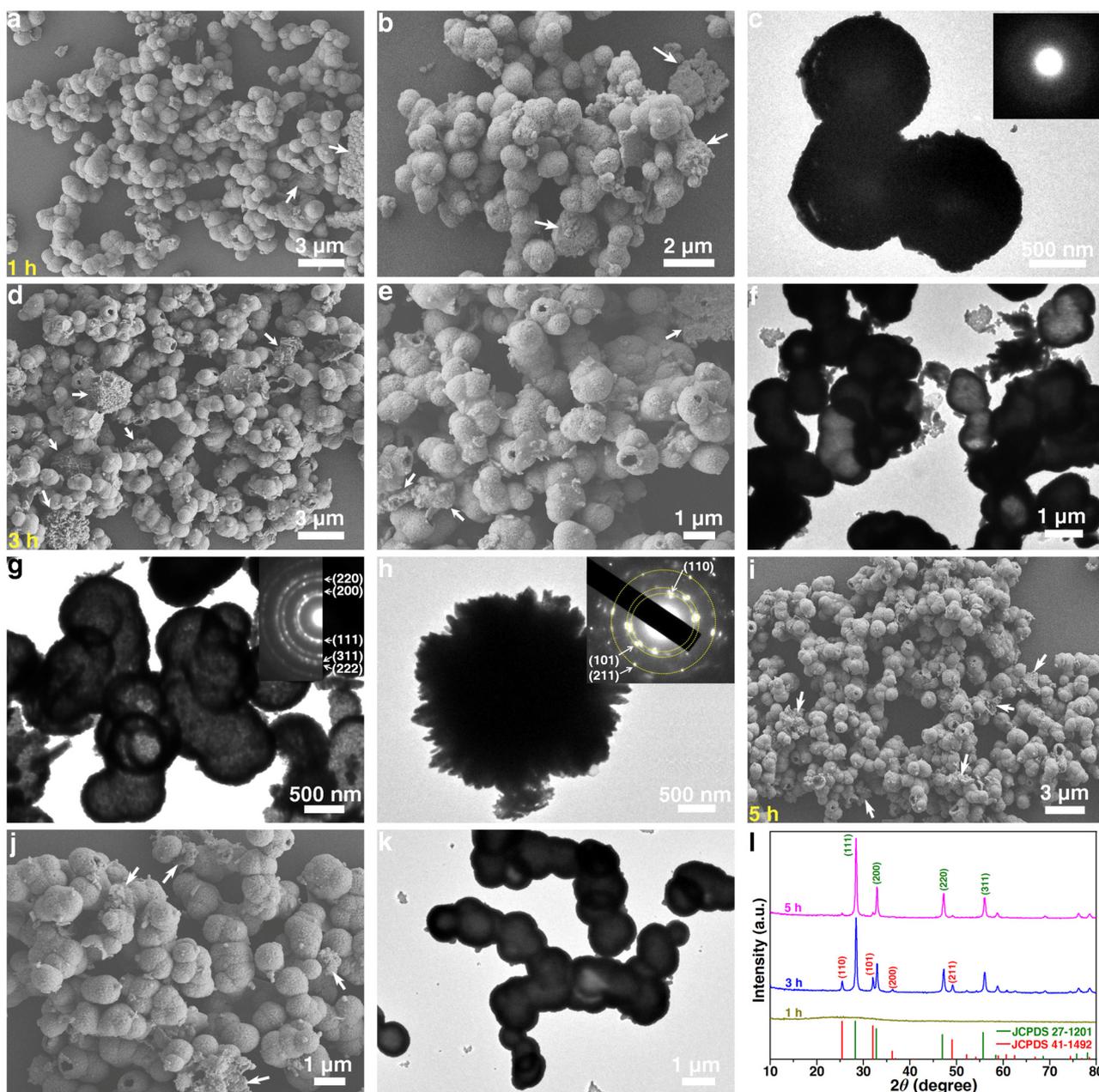


Fig. 3 Effect of reaction time on the formation of $\text{PbO}_{1.44}$ NAHSs. (a, b, d, e, i, j) SEM and (c, f, g, h, k) TEM images and (l) XRD patterns of the intermediate mixtures of $\text{PbO}_{1.44}$ NAHSs and $\beta\text{-PbO}_2$ MSs obtained after different reaction times of (a–c) 1, (d–h) 3 and (i–k) 5 h. Insets in (c, g, and h) are the corresponding SAED patterns of the samples.

capacities of 561 and 453 mA h g^{-1} after 100 and 200 cycles, respectively, in sharp contrast to the $\beta\text{-PbO}_2$ MSs (52 and 43 mA h g^{-1}). It is noteworthy that the capacities of $\text{PbO}_{1.44}$ NAHSs at the high current rate (C-rate) of 500 mA g^{-1} show a continuously increasing trend, from 412 mA h g^{-1} at the second discharge to 453 mA h g^{-1} at the 200th discharge. This can reasonably be attributed to the electrochemical activation of the electrode along with increased cycle numbers, due to the gradual perfection of the SEI layer and the progressive full penetration of the electrolyte with improved ionic conductivity

for enhanced reaction kinetics.^{5–8} As expected, $\text{PbO}_{1.44}$ NAHSs also exhibited markedly enhanced rate capability at various C-rates compared with that of $\beta\text{-PbO}_2$ MSs (Fig. 5c). At a C-rate of 50 mA g^{-1} , $\text{PbO}_{1.44}$ NAHSs yielded an initial Coulomb efficiency (ICE) of 69.5%, with initial discharge/charge capacities of 893/621 mA h g^{-1} , respectively, which is much higher than the ICE of $\beta\text{-PbO}_2$ (54.4%). Even at a high C-rate of 1000 mA g^{-1} , $\text{PbO}_{1.44}$ NAHSs delivered a satisfactory capacity of 351 mA h g^{-1} on the 50th cycle, 4.4 times higher than that of $\beta\text{-PbO}_2$ MSs (79 mA h g^{-1}). When the C-rate was returned to

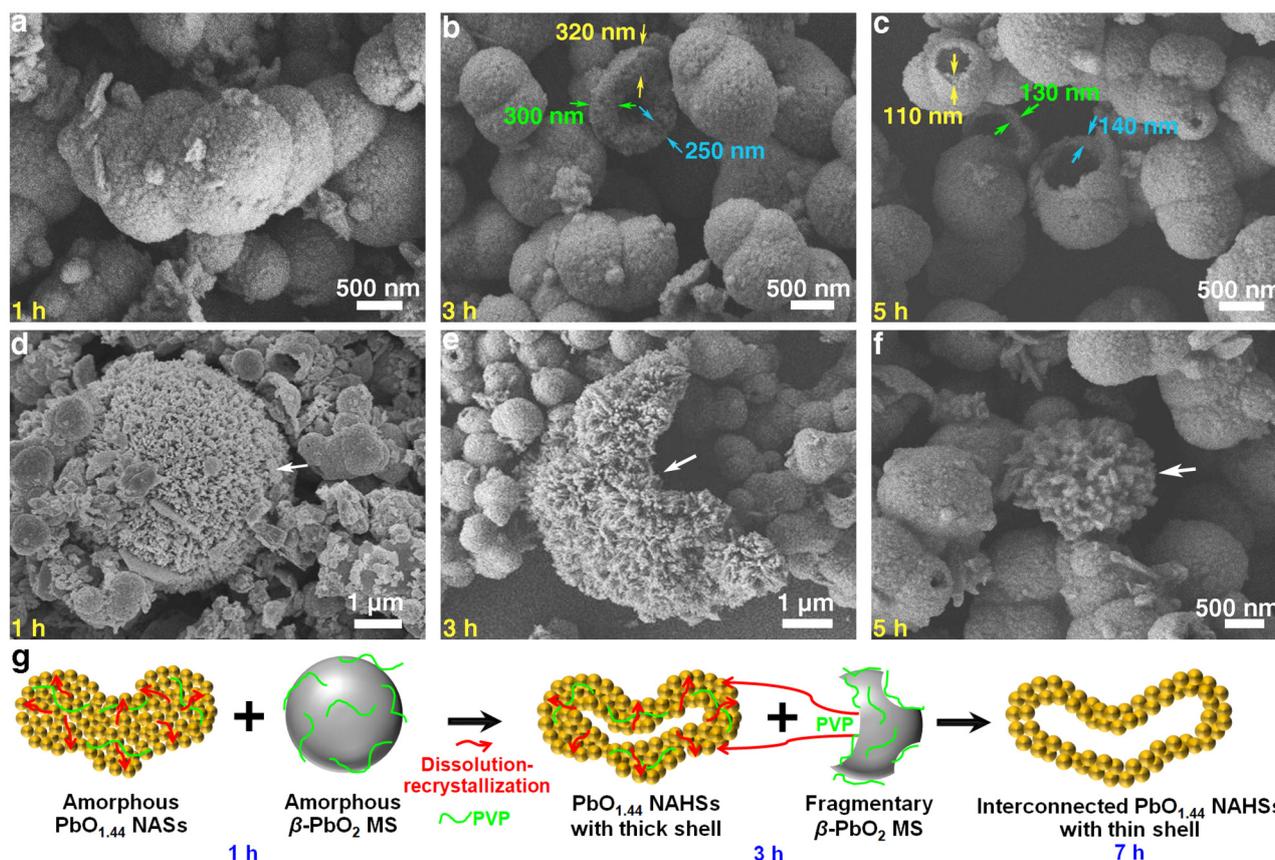


Fig. 4 Formation mechanism of $\text{PbO}_{1.44}$ NAHSs. SEM images of representative intermediate particles of (a–c) $\text{PbO}_{1.44}$ NAHSs and (d–f) $\beta\text{-PbO}_2$ MSs obtained after different reaction times of (a and d) 1, (b and e) 3 and (c and f) 5 h. (g) Schematic illustration of the formation mechanism of $\text{PbO}_{1.44}$ NAHSs.

50 mA g^{-1} after 60 cycles, the capacity of $\text{PbO}_{1.44}$ NAHSs successfully recovered to a high value of 623 mA h g^{-1} on the 90th cycle, which is almost the same as the first charge capacity (*i.e.*, 621 mA h g^{-1}), demonstrating the excellent capacity retention ability of $\text{PbO}_{1.44}$ NAHSs even after cycling at various C-rates.

To understand the electrochemical behaviors of $\text{PbO}_{1.44}$ NAHSs and $\beta\text{-PbO}_2$ MSs, the charge–discharge profiles (Fig. 5d and e) and cyclic voltammetry (CV) curves (Fig. 5f and g) were comparatively investigated. During the first cycles, the discharge capacities being higher than the charge capacities for both $\text{PbO}_{1.44}$ NAHSs and $\beta\text{-PbO}_2$ MSs can be primarily attributed to the irreversible formation of solid electrolyte interphase (SEI) layers on the electrodes, in agreement with the significant degradation of the discharge plateaus at 1.3 and 0.1 V (Fig. 5d) and the corresponding anodic peaks at 1.22 and 0.11 V (Fig. 5f) of $\text{PbO}_{1.44}$ NAHSs in the first lithiation process.⁴⁷ Similar decay trends in the related discharge plateaus and anodic peaks also occurred in the case of $\beta\text{-PbO}_2$ MSs (Fig. 5e and g). Remarkably, after the first discharge process, the charge–discharge profiles (Fig. 5d) and CV curves (Fig. 5f) of $\text{PbO}_{1.44}$ NAHSs are almost overlapped with each other, indicating the excellent reversibility of the lithiation–delithiation reac-

tions on the $\text{PbO}_{1.44}$ NAHSs electrode. According to the reports about PbO_x -based anodes for LIBs, the three pairs of discharge/charge plateaus (0.5/0.6, 0.4/0.5 and 0.3/0.4 V) and anodic/cathodic peaks below 0.7 V (*i.e.*, 0.53/0.63, 0.35/0.51 and 0.28/0.42 V) for $\text{PbO}_{1.44}$ NAHSs can be assigned to the reversible alloying/dealloying reactions in Pb .^{9,10} In addition, the discharge plateau (1.5 V)/anodic peak (1.52 V) and charge plateaus (1.2 and 1.6 V)/cathodic peaks (1.26 and 1.61 V) in the 0.7–1.7 V range (Fig. 5d and f) can be attributed to the conversion reactions between Pb and $\text{PbO}_{1.44}$.^{11,12}

In stark contrast to the outstanding electrochemical reversibility of $\text{PbO}_{1.44}$ NAHSs, the lengths of the discharge/charge plateaus (Fig. 5e) and the intensities of the anodic/cathodic peaks (Fig. 5g) of $\beta\text{-PbO}_2$ MSs continue to decay with increasing cycle numbers. Finally, there is almost no voltage plateau on the 50th cycle at 50 mA g^{-1} for $\beta\text{-PbO}_2$ MSs (Fig. 5e). More importantly, the decay rate of the discharge/charge plateaus of $\beta\text{-PbO}_2$ MSs (Fig. 5i) is much faster than that of $\text{PbO}_{1.44}$ NAHSs (Fig. 5h) along with increased C-rates, as obviously exhibited in the contrasting differential capacity *versus* voltage (dQ/dV) curves of the discharge profiles of $\text{PbO}_{1.44}$ NAHSs (Fig. 5j) and $\beta\text{-PbO}_2$ MSs (Fig. 5k). Notably, for both $\beta\text{-PbO}_2$ MSs and $\text{PbO}_{1.44}$ NAHSs, a faster degradation rate can be observed for

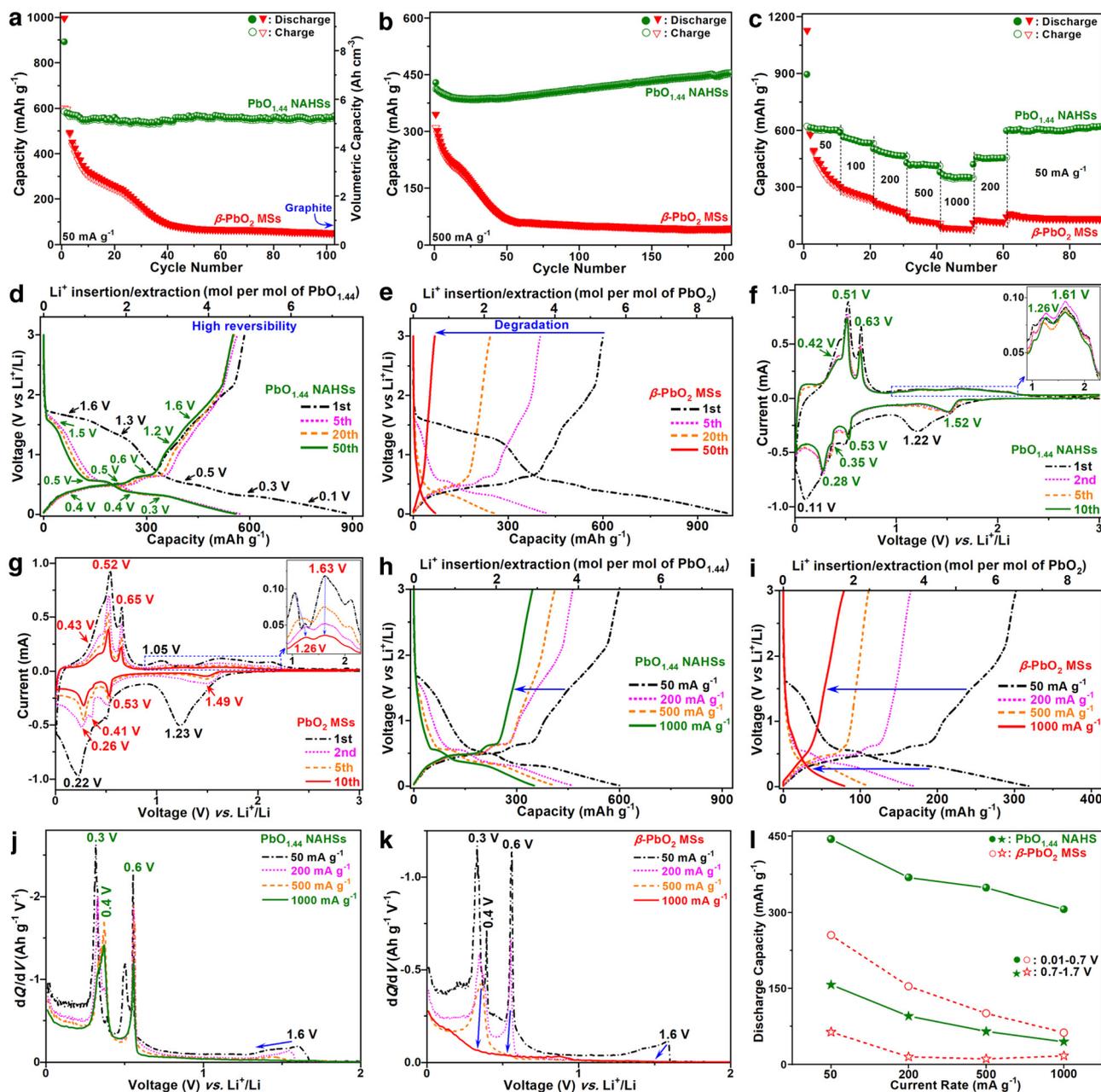


Fig. 5 Superior electrochemical performance of $\text{PbO}_{1.44}$ NAHSs compared to that of $\beta\text{-PbO}_2$ MSs. (a and b) Cycling and (c) rate performances of $\text{PbO}_{1.44}$ NAHSs and $\beta\text{-PbO}_2$ MSs as anodes of LIBs at designated C-rates. (d and e) Discharge–charge profiles at 50 mA g^{-1} and (f and g) CV curves at 0.2 mV s^{-1} of (d and f) $\text{PbO}_{1.44}$ NAHSs and (e and g) $\beta\text{-PbO}_2$ MSs. (h and i) Discharge–charge profiles, (j and k) dQ/dV curves of the discharge profiles and (l) comparison of the discharge capacities in the different voltage ranges of 0.01–0.6 and 0.6–1.7 V at different C-rates of (h and j) $\text{PbO}_{1.44}$ NAHSs and (i and k) $\beta\text{-PbO}_2$ MSs.

the plateaus in the voltage range of 0.7–1.7 V than that in the 0.01–0.7 V range along with increased C-rates, corresponding to the conversion reaction of PbO_x and the alloying–dealloying reaction of Pb, respectively. This suggests that the kinetics of the conversion reaction is slower than that of the alloying–dealloying reaction.^{7,9} The capacities at different C-rates of the discharge profiles in the two voltage ranges of 0.01–0.7 V and 0.7–1.7 V are statistically analyzed as shown in Fig. 5l. The

long Li^+/e^- transport distance of large-sized bulk-structured $\beta\text{-PbO}_2$ MSs leads to the poor kinetics in both conversion and alloying–dealloying reactions with rapidly decaying capacities along with increasing C-rates (Fig. 5l). Remarkably, $\text{PbO}_{1.44}$ NAHSs demonstrate an apparently improved stability in the discharge capacities from the plateaus over the voltage range of 0.01–0.7 V, corresponding to the alloying reaction of Pb, which contributes the major capacity at low and especially

high C-rates. Namely, the superior lithium storage capability of $\text{PbO}_{1.44}$ NAHSs can be primarily attributed to the much higher alloying–dealloying reaction kinetics than that of $\beta\text{-PbO}_2$ MSs, benefiting from the nanoparticle-assembled hollow structure with rich channels and short distances for the fast Li^+ transfer.

To clarify the performance enhancement mechanisms of $\text{PbO}_{1.44}$ NAHSs, systematic characterization studies of the cycled electrodes were performed, such as galvanostatic intermittent titration (GITT) measurements (Fig. 6a–d), electrochemical impedance spectroscopy (EIS) measurements (Fig. 6e), capturing SEM (Fig. 6f, k, S12 and S13†) and TEM (Fig. 6g and h) images, an SAED pattern (Fig. 6i) and the XPS spectrum (Fig. 6j). Fig. 6a and c show the potential response curves of $\text{PbO}_{1.44}$ NAHSs and $\beta\text{-PbO}_2$ MSs from the GITT measurements taken during the 10th discharge–charge processes at 50 mA g^{-1} as anodes of LIBs, respectively. Notably, the overpotentials of $\text{PbO}_{1.44}$ NAHSs remain at a lower level than those of $\beta\text{-PbO}_2$ MSs at the same discharge/charge state, especially in the high voltage ranges for the conversion reaction, suggesting a higher Li^+ ion conductivity and a lower polarization of $\text{PbO}_{1.44}$ NAHSs than those of $\beta\text{-PbO}_2$ MSs. Assuming that the Li^+ transfer satisfies Fick's second law, the Li^+ diffusion coefficient (D_{Li^+}) can be calculated by the equation of $D = \frac{4}{\pi\tau} \left(\frac{m_{\text{B}} V_{\text{m}}}{M_{\text{B}} S} \right)^2 \left[\frac{\Delta E_{\text{s}}}{\Delta E_{\tau}} \right]^2$, ($\tau \ll \frac{L^2}{D}$), where τ , L and S represent the constant current titration time, diffusion length and electrode surface area, ΔE_{s} and ΔE_{τ} refer to the steady-state voltage change after a current disturbance and voltage change during the constant current titration, and m_{B} , V_{m} and M_{B} are the molar mass, volume and molecular mass of $\text{PbO}_{1.44}$ or $\beta\text{-PbO}_2$, respectively.⁴⁸ The average D_{Li^+} values of $1.2 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ and $1.7 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ of $\text{PbO}_{1.44}$ NAHSs for the alloying and dealloying reaction processes (Fig. 6b and d) are approximately one order of magnitude higher than those of $\beta\text{-PbO}_2$ MSs (1.6×10^{-12} and $1.9 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$), respectively. This firmly demonstrates the excellent alloying–dealloying reaction kinetics of $\text{PbO}_{1.44}$ NAHSs, which accounts for the high capacity and outstanding rate capability. The Nyquist plots of the freshly assembled cells of $\text{PbO}_{1.44}$ NAHSs and $\beta\text{-PbO}_2$ MSs are fitted according to the equivalent circuit (inset in Fig. 6e), where R_{s} , R_{ct} , Z_{w} and CPE represent the electrolyte resistance, charge transfer resistance, Warburg impedance and constant phase element, respectively.⁴⁹ The estimated R_{ct} of $\text{PbO}_{1.44}$ NAHSs (118 Ω) is about a quarter of that of $\beta\text{-PbO}_2$ MSs (426 Ω), demonstrating the strengthened charge transfer conductivity of $\text{PbO}_{1.44}$ NAHSs with their special hierarchical hollow nanoarchitecture.^{43,44}

To verify the electrode stability enhancement mechanism, the contrasting structures of cycled electrodes of $\text{PbO}_{1.44}$ NAHSs and $\beta\text{-PbO}_2$ MSs (Fig. 6f–k, S12 and S13†) were investigated after the rate performance tests (Fig. 5c). Encouragingly, the cycled electrode of $\text{PbO}_{1.44}$ NAHSs is flat and compact (Fig. 6f, S12, S14a and S15a†). The interconnected hollow interior of $\text{PbO}_{1.44}$ NAHSs can robustly buffer the volume expansion and shrinkage induced by the repeated lithiation and delithiation processes, respectively, to stabilize the struc-

ture of $\text{PbO}_{1.44}$ NAHSs (Fig. 6f and g) and enhance the robustness of the whole electrode. The HRTEM image (Fig. 6h) and SAED pattern (Fig. 6i) of the cycled $\text{PbO}_{1.44}$ NAHSs show the reversible generation of the $\text{PbO}_{1.44}$ phase after the 90th charging process, with distinguished lattice fringes of the $\text{PbO}_{1.44}$ -based (111) facet ($d = 3.16 \text{ \AA}$) and diffraction rings of the (111), (200), (220), (222) and (311) facets of the $\text{PbO}_{1.44}$ crystal (JCPDS card no. 27-1201). The Pb 4f XPS spectrum of the cycled $\text{PbO}_{1.44}$ NAHSs (Fig. 6j) is similar to that of the pristine $\text{PbO}_{1.44}$ NAHSs (Fig. 1l). Therein, the Pb 4f_{5/2} and Pb 4f_{7/2} peaks can be split into two pairs of peaks at 142.7 and 137.9 eV corresponding to Pb^{2+} and at 142.0 and 137.2 eV corresponding to Pb^{4+} , respectively. A chemical formula of $\text{PbO}_{1.563}$ can be estimated from the relative area percentages of the Pb 4f XPS peaks (*i.e.*, Pb^{4+} (56.3%) and Pb^{2+} (43.7%)) of cycled $\text{PbO}_{1.44}$ NAHSs, which is close to the stoichiometric ratio of $\text{PbO}_{1.44}$.

In sharp contrast, severe pulverization of the cycled $\beta\text{-PbO}_2$ MSs electrode (Fig. 6k, S13, S14b and S15b†) was visually detected, as revealed in the upper right inset SEM image of representative cracked $\beta\text{-PbO}_2$ MSs. More seriously, the huge volume expansion of lithiated $\beta\text{-PbO}_2$ MSs caused the peeling off of active materials from the current collector (*i.e.*, Cu foil), as indicated by the yellow arrows in Fig. 6k for the exposed areas of the current collector, resulting in the rapid degradation of the capacities of $\beta\text{-PbO}_2$ MSs with a short cycle life (Fig. 5a–c). As shown in the cross-sectional view SEM images of the pristine and cycled electrodes, the electrode of $\beta\text{-PbO}_2$ MSs (Fig. S14b and S15b†) underwent a thickness variation of 40% (*i.e.*, from ~ 30 to 42 μm), which is much higher than the 14% (*i.e.*, from ~ 28 to 32 μm) of the electrode of $\text{PbO}_{1.44}$ NAHSs (Fig. S14a and S15a†). To clarify the larger specific surface area of $\text{PbO}_{1.44}$ NAHSs compared to that of $\beta\text{-PbO}_2$ MSs, nitrogen adsorption–desorption measurements were performed. The adsorption–desorption isotherms of $\text{PbO}_{1.44}$ NAHSs and $\beta\text{-PbO}_2$ MSs (Fig. 6l) can be classified as type IV isotherms with a type H3 hysteresis loop. The calculated specific surface area (*i.e.*, Brunauer–Emmett–Teller (BET) surface area) and pore volume of $\text{PbO}_{1.44}$ NAHSs (32 $\text{m}^2 \text{ g}^{-1}$ and 0.12 $\text{cm}^3 \text{ g}^{-1}$) are significantly higher than those of $\beta\text{-PbO}_2$ MSs (2 $\text{m}^2 \text{ g}^{-1}$ and 0.01 $\text{cm}^3 \text{ g}^{-1}$), respectively. More importantly, in contrast to $\beta\text{-PbO}_2$ MSs, the higher specific surface area of $\text{PbO}_{1.44}$ NAHSs can induce their more homogeneous mixing with the conductive agent (acetylene black) and binder (sodium alginate), thus allowing them to attach more firmly to the current collector (copper foil) (Fig. S14†). This improves the robustness of the macrostructure of the $\text{PbO}_{1.44}$ NAHSs electrode.

As illustrated comparatively in the schematic image (Fig. 6m), the drastic increase in electrode thickness, caused by the severe volume expansion of lithiated $\beta\text{-PbO}_2$ MSs, induces the electrode to pulverize (Fig. S15b†) and the active material to peel off from the current collector (Fig. 6k), resulting in a rapid capacity decline. In sharp contrast, the superior cycling stability and rate capability of $\text{PbO}_{1.44}$ NAHSs (Fig. 6n) can be reasonably assigned to the excellent structural features

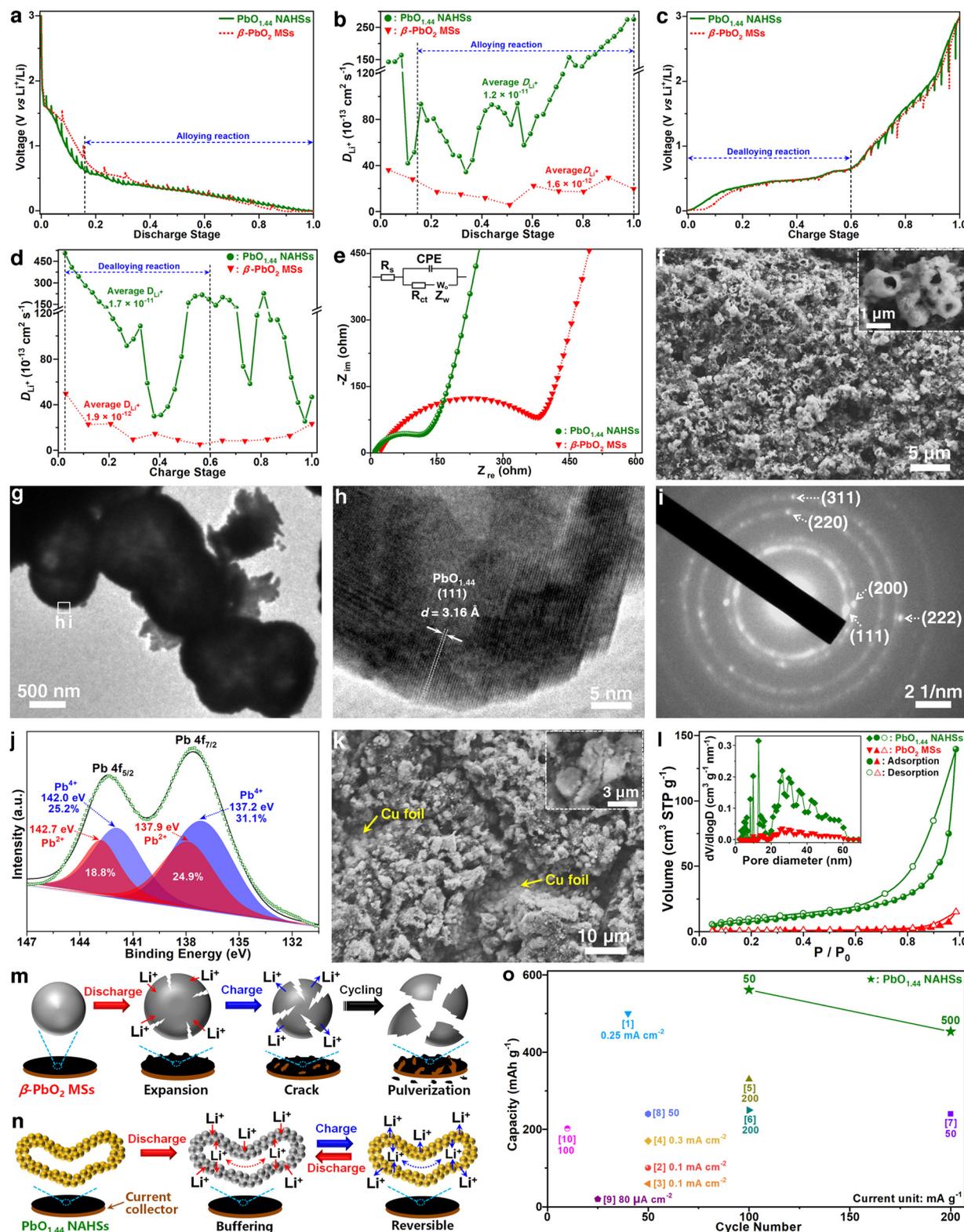


Fig. 6 Performance enhancement mechanism of $\text{PbO}_{1.44}$ NAHSs. (a and c) GITT voltage profiles and (b and d) the calculated Li^+ chemical diffusion coefficients based on stoichiometry from GITT of $\text{PbO}_{1.44}$ NAHSs and $\beta\text{-PbO}_2$ MSs during the 10th cycle at 50 mA g^{-1} . (e) Nyquist plots (inset, equivalent circuit) of cells with $\text{PbO}_{1.44}$ NAHSs and $\beta\text{-PbO}_2$ MSs used as anodes. (f) SEM and (g and h) TEM images, (i) SAED pattern and (j) XPS spectrum of (f–i) cycled $\text{PbO}_{1.44}$ NAHSs and (k) SEM image of cycled $\beta\text{-PbO}_2$ MSs after the 90th cycle in the rate performance tests. (l) Nitrogen adsorption–desorption isotherms and (inset) the pore size distributions of $\text{PbO}_{1.44}$ NAHSs and $\beta\text{-PbO}_2$ MSs. Schematic illustrations of (m) lithiation-induced volume expansion and pulverization of $\beta\text{-PbO}_2$ MSs and (n) effectively buffered volume changes combined with shortened ion transfer distance of $\text{PbO}_{1.44}$ NAHSs. (o) Performance comparison of $\text{PbO}_{1.44}$ NAHSs and reported PbO_x -based anodes as listed in Table S1.†

described as follows: (1) the interconnected hollow interior (Fig. 1e–g, 6f and g) with excellent volume change buffering efficiency enhances the electrode robustness for splendid cycling stability (Fig. 5a and b); (2) the short Li^+/e^- transfer distance of the secondary nanoparticles (~ 50 nm in diameter, Fig. 1d, h and S1a–S1f†) promotes the fast and adequate electrochemical reaction for high capacity at various C-rates (Fig. 5c); (3) the thin shells constructed from ultra-fine nanoparticles (Fig. 1d) effectively reduce the volume expansion–shrinkage of the particles caused by lithium insertion–extraction, to decrease the electrode thickness variation and improve the structural stability of the entire electrode. Owing to the excellent structural features of the nanoparticle assembly and its interconnected hollow interior, the $\text{PbO}_{1.44}$ NAHSs manifests enhanced lithium storage capability in contrast to the recently reported PbO_x -based materials (Fig. 6o and Table S1†).^{10–19}

3. Conclusions

In summary, we have developed a robust strategy for the PVP-driven transformation of $\beta\text{-PbO}_2$ microspheres (MSs) to craft unique nanoparticle-assembled interconnected $\text{PbO}_{1.44}$ hollow spheres (NAHSs), which have been explored for the first time as an advanced anode material for LIBs. In particular, an intriguing PVP-driven reduction combined dissolution–recrystallization transformation process of converting $\beta\text{-PbO}_2$ MSs into $\text{PbO}_{1.44}$ NAHSs is demonstrated by PVP concentration regulation experiments. Moreover, PVP also serves as a capping agent to stabilize the $\text{PbO}_{1.44}$ solid spheres aggregated from the nanoparticles formed after 1 h of reaction and guides their inside-out Ostwald ripening to construct the interconnected hollow structure. Remarkably, $\text{PbO}_{1.44}$ NAHSs demonstrated dramatically enhanced cycling stability and rate capability in stark contrast to the performance of $\beta\text{-PbO}_2$ MSs. Based on the electrochemical analyses of the voltage plateaus and CV peaks, the superior lithium storage capability of $\text{PbO}_{1.44}$ NAHSs is primarily attributed to the effectively enhanced alloying–dealloying reaction kinetics of Pb, which is dramatically boosted by the short ion/electron transfer distance of the ultra-fine secondary $\text{PbO}_{1.44}$ nanoparticles (~ 50 nm in diameter). Furthermore, the ample space of the interconnected hollow interiors of $\text{PbO}_{1.44}$ NAHSs provides superb volume expansion buffering efficiency to reinforce the structural robustness of the electrode for distinguished cycling durability. As such, $\text{PbO}_{1.44}$ NAHSs with excellent lithiation–delithiation reaction kinetics and reversibility may stand out as promising low-cost and high mass/volume capacity (*i.e.*, $561 \text{ mA h g}^{-1}/5262 \text{ mA h cm}^{-3}$) anode candidates for LIBs. Moreover, the proposed reductant and capping dual functions of PVP and the self-sacrificial templating mechanism in the construction of the rare mixed-valence $\text{PbO}_{1.44}$ NAHSs provide new insights into the rational design of novel hollow-structured functional materials with excellent mechanical and electrochemical characteristics for various potential applications.

Author contributions

X. B. and J. Z. contributed equally to this work. All authors have given approval to the final version of the manuscript.

Data availability

All relevant data are within the manuscript and its ESI,† which are also available from the corresponding author on reasonable request.

Conflicts of interest

There are no conflicts to declare.

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