Bi–Sb Nanocrystals Embedded in Phosphorus as High-Performance Potassium Ion Battery Electrodes

Kuan-Ting Chen and Hsing-Yu Tuan*

ABSTRACT: The development of high-performance potassium ion battery (KIB) electrodes requires a nanoengineering design aimed at optimizing the construction of active material/buffer material nanocomposites. These nanocomposites will alleviate the stress resulting from large volume changes induced by K⁺ ion insertion/extraction and enhance the electrical and ion conductivity. We report the synthesis of phosphorus-embedded ultrasmall bismuth–antimony nanocrystals (BiₓSb₁₋ₓ@P, 0 ≤ x ≤ 1) for KIB anodes via a facile solution precipitation at room temperature. BiₓSb₁₋ₓ@P nanocomposites can enhance potassiation–depotassiation reactions with K⁺ ions, owing to several attributes. First, by adjusting the feed ratios of the Bi/Sb reactants, the composition of BiₓSb₁₋ₓ nanocrystals can be systematically tuned for the best KIB anode performance. Second, extremely small (diameter ≈ 3 nm) BiₓSb₁₋ₓ nanocrystals were obtained after cycling and were fixed firmly inside the P matrix. These nanocrystals were effective in buffering the large volume change and preventing the collapse of the electrode. Third, the P matrix served as a good medium for both electron and K⁺ ion transport to enable rapid charge and discharge processes. Fourth, thin and stable solid electrolyte interface (SEI) layers that formed on the surface of the cycled BiₓSb₁₋ₓ@P electrodes resulted in low resistance of the overall battery electrode. Lastly, in situ X-ray diffraction analysis of K⁺ ion insertion/extraction into/from the BiₓSb₁₋ₓ@P electrodes revealed that the potassium storage mechanism involves a simple, direct, and reversible reaction pathway: (Bi, Sb) ↔ K(Bi, Sb) ↔ Kₓ(Bi, Sb). Therefore, electrodes with the optimized composition, i.e., Bi₀.₅Sb₀.₅@P, exhibited excellent electrochemical performance (in terms of specific capacity, rate capacities, and cycling stability) as KIB anodes. Bi₀.₅Sb₀.₅@P anodes retained specific capacities of 295.4 mA h g⁻¹ at 500 mA g⁻¹ and 339.1 mA h g⁻¹ at 1 A g⁻¹ after 800 and 550 cycles, respectively. Furthermore, a capacity of 258.5 mA h g⁻¹ even at 6.5 A g⁻¹ revealed the outstanding rate capability of the Sb-based KIB anodes. Proof-of-concept KIBs utilizing Bi₀.₅Sb₀.₅@P as an anode and PTCDA (peryleneetetracarboxylic dianhydride) as a cathode were used to demonstrate the applicability of Bi₀.₅Sb₀.₅@P electrodes to full cells. This study shows that BiₓSb₁₋ₓ@P nanocomposites are promising carbon-free anode materials for KIB anodes and are readily compatible with the commercial slurry-coating process applied in the battery manufacturing industry.

KEYWORDS: potassium, battery, phosphorus, nanotechnology, nanocrystals

Potassium ion batteries (KIBs) may replace lithium ion batteries (LIBs) as energy storage systems for large-scale stationary energy, owing to several intrinsic advantages. These include high-earth-abundance reserves of K (2.09 wt % in the earth’s crust, i.e., 1000 times more abundant than that of Li (0.0017 wt %)), a lower standard reduction potential (−2.93 V) for K⁴⁺/K⁺ than that for Na⁺/Na⁺ (−2.71 V) in a nonaqueous electrolyte, and a smaller Stokes radius of K ions (3.6 Å in polycarbonate) than that of Li ions (4.8 Å), thereby enabling higher mobility and diffusion kinetics between the electrolyte and electrode. However, it has been challenging to develop electrode materials for high-performance KIBs, especially for anode materials. K belongs to a family of alkali metals, and the corresponding ion radius (1.38 Å) is nearly twice as large as that of the Li ion (0.76 Å). Therefore, K⁺ ion insertion/extraction into/from the electrode

**Cite This:** ACS Nano 2020, 14, 11648–11661
is more difficult relative to Li⁺ and Na⁺ ions, leading to slower transport dynamics and a large volume change during potassiation–depotassiation reactions. This resulted in an undesirable cycling performance and a rapid capacity decay. For example, the maximum potassium storage of graphite (KC₆: 279 mAh g⁻¹), a widely used LIB anode, is too low for KIBs.6–11 Unfortunately, only a few materials exhibit the high specific capacities (>300 mAh g⁻¹) required for KIB anodes.12–14

Antimony (Sb) is considered a promising KIB anode, owing to its extremely high theoretical capacity of 660 mAh g⁻¹ while alloying with K to form K₃Sb at room temperatures. However, Sb undergoes a large volume expansion (~407%) when fully alloyed with K, and bulk Sb cannot endure such high stresses with repeated potassiation–depotassiation cycles, resulting in battery failure and electrode material pulverization.15–19 The methods developed to address this problem can be grouped into the following three categories. (i) The first category is utilizing carbon materials as a soft and ductile matrix with a minor volume fraction to buffer mechanical stresses/strains and maintain the electrode structure integrity during the alloying and dealloying processes. For example, Sb–C composite materials, such as Sb@G@C,²⁰ Sb@NPCM,²¹ Mxene@Sb,²² Sb@HCT,²³ and SnSb–G–C,²⁴ have been reported as Sb–C KIB anodes. (ii) The second category is using Sb–X (X = Sb-based alloy element) compounds as anodes. Sb–X compounds may yield enhanced structural integrity or increased theoretical capacity depending on the intrinsic characteristics of X.²⁵–²⁸ Among these alloys, the intermetallic Bi–Sb alloy has received particular attention due to the following advantages. (1) Bi and Sb form a solid solution (BiₓSb₁₋ₓ) over the entire composition range, and hence, a tunable composition can be adjusted to optimize the electrode performance.²⁹–³² (2) The theoretical capacity of Bi is 385 mAh g⁻¹ for K⁺ ion storage, ensuring high specific capacities of BiₓSb₁₋ₓ alloys. (3) The volume expansion of KₓBi (Bi, Sb), 384%³³ (based on the space group Fm3m with a cubic crystal system), is smaller than that of Bi to KₓBi (406%)³¹ and Sb to KₓSb (407%).³³ Additionally, recent reports suggested that the introduction of Bi into Sb yields high toughness for antipulverization and long-term durability for Na⁺ ion insertion and extraction. This results from the higher Bi/Na ratios and Poisson ratios of Bi relative to those of Sb metal, which induces considerable lattice softening of Sb, through the so-called lattice softening effect.³³ (iii) The third category is that rational designs of nanostructures can enable enhanced structural integrity and electron transport for improved battery performance.³⁴ For example, Wang et al. reported the synthesis of Bi₁₁₋ₓSbₓS₃ nanotubes as KIB anodes to improve cycling performance and maintain the electrode structure integrity during the alloying and dealloying processes.12 They developed a solution-phase precipitation method for stable cycling KIB anodes.³³

Herein, we demonstrate a solution-phase precipitation approach to synthesizing phosphorus-embedded BiₓSb₁₋ₓ(0 ≤ x ≤ 1) nanocrystals as KIB anodes at room temperature. The reactions occur within several seconds in the presence of BiCl₃, SbCl₅, and P(SiMe₃)₃ via reactions involving the elimination of a silyl halide Me₃SiCl. As-synthesized BiₓSb₁₋ₓ nanocrystals (average diameter = 6.35 nm) were embedded in the phosphorus matrix, thereby yielding BiₓSb₁₋ₓ@P nanocomposites. BiₓSb₁₋ₓ nanocrystals with complete stoichiometry tuning can be obtained via the developed synthetic route and used for KIB anode examination without forming P–C composites. Therefore, BiₓSb₁₋ₓ@P nanocomposites exhibit very good battery performance with capacities of 295.4 mAh g⁻¹ (cycling rate = 500 mA g⁻¹) and 339.1 mAh g⁻¹ (cycling rate = 1 A g⁻¹) after 800 and 550 cycles, respectively. Furthermore, an excellent rate capability with a capacity of 258.5 mAh g⁻¹ at 6.5 A g⁻¹ is obtained, which is the highest among the values reported for Sb-based KIB anodes. TEM images of cycled Bi₅.5Sb₅.5@P electrodes reveal dense ultra-small Bi₅.5Sb₅.5 nanocrystals (diameter = 3.39 nm) were formed and were firmly fixed within the P matrix, thus providing reliable structural integrity as well as efficient electron and K⁺ ion transport. In situ operando XRD of Bi₅.5Sb₅.5@P electrodes indicates that the storage mechanism proceeds through a highly reversible alloying–dealloying reaction: (Bi, Sb) ⇌ K(Bi, Sb) ⇌ Kₓ(Bi, Sb). Finally, the performance of the full cell assembled by using BiₓSb₁₋ₓ@P as the anode and PTCDI (perylenetetracarboxylic dihydride) as the cathode was evaluated to demonstrate their feasibility for KIBs.

RESULTS AND DISCUSSION

BiₓSb₁₋ₓ@P nanocrystals were synthesized via a solution precipitation route (see Figure 1). A combination of metal BiCl₃ and SbCl₅ precursors with a desired individual mole ratio is dissolved in toluene. P(SiMe₃)₃ is used as the P precursor.³⁶,³⁷ The reaction is illustrated in Figure 1a. P(SiMe₃)₃ in hexane is added dropwise from the buret into a stirred solution of BiCl₃ and SbCl₅ in the lower bottle at room temperature. As shown in Figure 1b,c, the reactions occur at 3.2 s when the color of the solution starts to change from yellow to dark black precipitates. BiₓSb₁₋ₓ@P alloy particles form via the reactions involving the elimination of a silyl halide Me₃SiX (X = Cl, Br, I). P(SiMe₃)₃ is the key reagent that controls the overall reactions and enables the formation of the P matrix. The synthetic protocol may be
applied to the synthesis of various nanocrystals embedded in the matrix and is quite advantageous for the large-scale production of nanocrystals. Figure 1d shows an experimental setup, where a 300 mL glass beaker is used as a reactor to synthesize ~1 g of Bi$_{0.5}$Sb$_{0.5}$@P nanocrystals in one batch reaction (see Figure 1e).

A representative synthesis result of Bi$_x$Sb$_{1-x}$@P nanocrystals obtained by reacting 1.72 mmol of individual Bi and Sb reactants for the formation of Bi$_{0.5}$Sb$_{0.5}$ alloy nanocrystals is shown in Figure 2. The XRD pattern of the product and the Rietveld-refined results (shown in Figure 2a) can be due to a rhombohedral phase with the R$ar{3}$m (166) space group. The lattice parameters are calculated based on the fitting curve by utilizing the TOPAS V6 software (see Table S1 in the Supporting Information). Furthermore, the diffraction peak positions of the Bi$_{0.5}$Sb$_{0.5}$@P nanocomposites are slightly lower than the standard peak positions corresponding to Sb powder in the database (PDF# 851324), since larger Bi atoms substitute for the smaller Sb atoms.$^{29}$ Through the Scherrer equation, $D = K \lambda / (B \cos \theta)$, the crystal domain size is estimated from the XRD pattern.$^{48}$ The peaks occurring at 27.83, 49.94, and 57.30° correspond to $D = 8.86$, 7.35, and 6.76 nm, respectively. No other peaks except the indexed Bi$_{0.5}$Sb$_{0.5}$ pattern peaks are observed, indicating that the P matrix is amorphous. An average crystal size of 7.76 nm is determined from the three peaks considered in the Scherrer equation. An FESEM image of the nanoparticle composite is shown in Figure 2b. The TEM images shown in Figure 2c,d reveal the Bi$_{0.5}$Sb$_{0.5}$@P nanocrystals with uniformly dispersed Bi$_{0.5}$Sb$_{0.5}$ alloy nanocrystals embedded in the P matrix. A
polydispersity of the nanocrystals (average diameter = 6.35 nm) is observed. Figure 2e shows a high-resolution TEM image of a nanocrystal with a single-crystal structure and interplanar d-spacings of 3.26 Å corresponding to the (012) plane of Bi$_{0.5}$Sb$_{0.5}$. The selected-area electron diffraction pattern obtained for a field of the nanocrystals consists of three diffraction rings corresponding to the (202), (110), and (012) planes of Bi$_{0.5}$Sb$_{0.5}$. Furthermore, EDS of these nanocrystals (see Figure S2g,h in the Supporting Information) reveals an average Bi/Sb composition that corresponds closely to the target atomic ratio of 1:1. The P content of Bi$_{0.5}$Sb$_{0.5}@P$ is $\sim$ 9.59 wt %. The elemental mapping spectra further confirm the homogeneous distribution of Sb and Bi in the alloy particles (Figure 2g), consistent with a material of composition close to Bi$_{0.5}$Sb$_{0.5}$.

The developed synthetic route can lead to obtaining Bi$_{x}$Sb$_{1−x}@P$ nanocrystals with a stoichiometry-adjusted composition tuning from $x = 0$ to 1 by varying the molar ratios of the Bi/Sb feed reactants. Sb and Bi belong to the same space group (R3m) and form a completely mixed solid solution (since they are isostructural), as revealed by the phase diagram. The synthesis produces no other measurable phases. Figure 3a shows the XRD patterns of Bi$_{x}$Sb$_{1−x}@P$ nanocrystals synthesized from separate Bi/Sb molar ratios of 3:1, 1:1, and 1:3. At $x = 0$, the spectrum corresponds to that of Sb (PDF# 851324). As the Bi content increases, the diffraction peaks gradually shift toward a lower 2$\theta$ angle due to the substitution of Bi atoms (radius = 2.3 Å), which are smaller than the Sb atoms (radius = 2.06 Å). The lattice parameters ($a$ and $c$) calculated from XRD patterns are listed in Table S2 in the Supporting Information. The lattice spacing increases along the $a$-axis (from 4.3 Å (Sb) to 4.53 Å (Bi)) and $c$-axis (from 11.22 Å (Sb) to 11.79 Å (Bi)) with decreasing Sb content of the nanocrystals. At $x = 1$, the XRD data can be indexed to Bi (PDF# 851331). The lattice parameters are linearly related to the Sb content, which is consistent with Vegard’s law, i.e., Bi–Sb is homogeneously distributed in the alloyed nanocrystals. Furthermore, EDS conducted for a field of Bi$_{x}$Sb$_{1−x}@P$ nanocomposites (Figure 3d) with varying compositions reveals a linear trend similar to that observed from the XRD pattern. The obtained elemental Sb ratio of the Bi$_{x}$Sb$_{1−x}@P$ nanocrystals is very close to that of the initial Bi/Sb molar ratio of the feed reactants. Figure 3e shows the Brunauer–Emmett–Teller measurements of the Bi$_{0.5}$Sb$_{0.5}@P$ nanocomposites. The specific surface area (13.14 m$^2$ g$^{-1}$) is determined from the Kelvin equation associated with the Barrett–Joyner–Halenda method based on the adsorption
branches of the isotherms, and characteristics of a typical nanocrystal surface area are observed. The TGA (Figure 3f) result reveals a first sharp weight loss (2.18 wt %) at 150 to 200 °C, corresponding to residue Me3SiX in the product. A second sharp weight loss (9.35 wt %) at 300 °C corresponding to the weight loss of P in the nanocrystals is also observed. The P weight loss is very close to the P content of Bi0.5Sb0.5@P (∼9.59 wt %) detected from the EDS spectrum (Figure S2).

The chemical electronic state of the Bi0.5Sb0.5@P nanocrystals is investigated using X-ray photoelectron spectroscopy (XPS). All binding energies have been corrected by referencing the C 1s (284.6 eV). Figure 3 shows the XPS spectra of the Bi0.5Sb0.5@P powder. Figure 3g shows the Bi 4f5/2 and Bi 4f7/2; 4f core splitting into Bi 4f5/2 (161.6 eV) and Bi 4f7/2 (156.3 eV) peaks with a peak separation of 5.3 eV is also observed. Moreover, Bi2O3 4f7/2 (159.4 eV) and Bi2O3 4f5/2 (164.7 eV) are generated by the formation of oxides. The peaks located at 536.8 and 527.3 eV with a peak separation of 6.2 eV (Figure 3h) are due to Sb 3d3/2 and Sb 3d5/2, respectively. The binding energies of Sb 3d3/2 and Sb 3d5/2 are lower than the standard Sb2O3 3d3/2 (539.9 eV) and Sb2O3 3d5/2 (530.6 eV) values. This reconfirms the formation of oxides (Bi2O3 and Sb2O3) on the surface of the Bi0.5Sb0.5@P composites. However, no oxides are detected via the XRD measurement, indicating that only a few amorphous surface oxides are formed. The P 2p (Figure 3i) spectrum consists of peaks corresponding to P 2p3/2 (133.1 eV) for PO3, P 2p1/2 (130 eV) for P, and P 2p3/2 (129.16 eV) for P.

The results in Figure 4a–c show the cyclic voltammetry (CV) plots of Bi@P, Bi0.5Sb0.5@P, and Sb@P nanocomposites, respectively, for the initial three cycles at a scan rate of 0.1 mV s⁻¹ between 0.01 and 2.5 V (vs K+/K). In the first cathodic scan, the initial cathodic process is characterized by a peak at ~0.7 V and a broad curve from 0.30 to 0.08 V, which is weakened during the subsequent cycles. The peaks can be attributed to the potassiation of Bi and the formation of a solid electrolyte interface (SEI) layer on the electrode surface via electrolyte decomposition. The irreversible cathodic peak near 0.1 V can be attributed to the irreversible reaction of the oxides (Bi2O3 and Sb2O3) on the surface of the Bi0.5Sb0.5 alloy nanocrystals. In the second and third scans, two cathodic peaks occur at 0.68 and 0.15 V, indicating the formation of K(Bi, Sb) and K3(Bi, Sb) phases, respectively, which are due to K(Bi, Sb) alloy reactions. In the anodic scans, three peaks at 0.72, 0.85, and 1.22 V correspond to the depotassiation reactions of K3(Bi, Sb) → K(Bi, Sb) → (Bi, Sb). The CV curves obtained for the second and third scans overlap strongly, indicating the high reversibility and stability of the Bi0.5Sb0.5@P composite anode. Furthermore, the two clear peaks at 0.17 and 0.27 V in the homologous differential capacity (dQ/dV) diagram of the Bi0.5Sb0.5@P nanocrystals during the first discharge suggests a two-step reduction process (Figure 4e). The peak voltage at 0.17 V is slightly right shifted.
to the voltage of Sb@C (Figure 4f) at 0.15 V, whereas the other voltage at 0.27 V is slightly left shifted to the peak voltage of Bi@C at 0.29 V (Figure 4d). This indicates a two-step potassiation reaction of Bi and Sb: \((\text{Bi, Sb}) \rightarrow \text{K(Bi, Sb)} \rightarrow \text{K_3(Bi, Sb)}\). In the second cycle (Figure 4g), a similar two-step potassiation reaction is observed. The two oxidation peaks at 0.62 and 1.18 V in the first two cycles correspond to a two-step depotassiation reaction: \(\text{K_3(Bi, Sb)} \rightarrow \text{K(Bi, Sb)} \rightarrow (\text{Bi, Sb})\).32,33

In the half cell test, metal potassium and 4 M bis-(fluorosulfonyl)imide (KFSI) potassium are used as the counter electrode and the electrolyte in dimethyl ether (DME), respectively. A high concentration of electrolytes (e.g., 5 M KFSI in DME) can form a more stable SEI membrane (than that formed by a low concentration), allowing \(K^+\) ion electrodes to maintain long-term stability.36 Recent reports have shown that the synergistic interaction between Bi atoms and Sb atoms can produce a buffering effect that mitigates structural changes induced by volume changes during the potassiation–depotassiation process and improve cycle stability.31 Through the developed synthetic approach that allows stoichiometric control of nanocrystals, the optimally tuned Bi–Sb composition can maximize the synergistic effect of Bi–Sb.29,36 The initial discharge/charge curves of the Bi@P, Bi_{0.25}Sb_{0.75}@P, Bi_{0.5}Sb_{0.5}@P, and Sb@P electrodes at 50 mA g\(^{-1}\) (first discharge capacities: 341.4, 439.9, 444.7, 371.4, and 490.1 mA h g\(^{-1}\), respectively) are shown in Figure 5a. The irreversible capacities of the first cycle result from the formation of an SEI film on the electrode surface. After three cycles at 50 mA g\(^{-1}\), the current rate is changed to 500 mA g\(^{-1}\) to examine the cycling stability of the five electrodes. After the 50 cycles, all five electrodes exhibit fairly stable capacity performance (Figure 5a, inset). The capacities of Bi_{0.5}Sb_{0.5}@P and Bi_{0.75}Sb_{0.25}@P (393.6 and 397.6 mA h g\(^{-1}\), respectively) are higher than those of Bi_{0.5}Sb_{0.5}@P (291.1 mA h g\(^{-1}\)) and Sb@P (312.4 mA h g\(^{-1}\)). If 800 cycles are considered, quite different cycling stability is observed. That is, Bi_{0.5}Sb_{0.5}@P and Bi_{0.75}Sb_{0.25}@P exhibit a very stable 800th-cycle cycling performance with respective capacities of 295.4 and 195.5 mA h g\(^{-1}\), corresponding to capacity decays of only 0.12 and 0.13 per cycle. This behavior differs remarkably from that of the other three electrodes where a significant decline occurs after around the 100th cycle. In fact, another Bi_{0.5}Sb_{0.5}@P electrode retains cycling stability up to 1000 cycles but delivers a slightly decreased capacity of 192 mA h g\(^{-1}\) (see Figure S8 in the Supporting Information). The 1000th-cycle stability is comparable with those recently reported for \(K^+\) ion electrodes using Bi_{1.11}Sb_{0.89}S\(_3\) nanotube and Bi_{0.51}Sb_{0.49}OCl/rGO composites.32,36 (See Figure S5d in the Supporting Information for the corresponding discharge/charge curves of Bi_{0.5}Sb_{0.5}@P.)

![Figure 5](https://dx.doi.org/10.1021/acsnano.0c04203)

ACS Nano 2020, 14, 11648–11661

Figure 5. Electrochemical performance of Bi\(_x\)Sb\(_{1-x}\)@P nanocomposites. Cycling performance of Bi\(_x\)Sb\(_{1-x}\)@P electrodes at rates of (a) 500 mA g\(^{-1}\) and (b) 1 A g\(^{-1}\). (c,d) Rate performance and corresponding voltage profiles of Bi\(_x\)Sb\(_{1-x}\)@P electrode at rates increased from 0.05 to 6.5 A and then reduced to 0.5 A. (e) Rate capabilities of Bi\(_x\)Sb\(_{1-x}\)@P compared with those of Sb-based KIB anode materials reported in the literature.17,18,23,26,31–33,36,55
maintain a capacity of \( \sim 258.5 \text{ mA h g}^{-1} \) even at a current density of \( 6.5 \text{ A g}^{-1} \). However, \( \text{Bi}_{0.25}\text{Sb}_{0.75}@P \) and \( \text{Bi}_{0.75}\text{Sb}_{0.25}@P \) can only deliver capacities at current rates of up to \( 3.5 \text{ A g}^{-1} \). When the current density is returned to 0.5 \text{ A g}^{-1}, all three electrodes return to their original capacity (\( \sim 375 \text{ mA h g}^{-1} \)) and maintain a stable performance for the subsequent cycles.

Figures 5d and S7 show the corresponding discharge/charge curves of the \( \text{Bi}_{0.5}\text{Sb}_{0.5}@P \) electrode at various current densities. At higher currents, voltage polarization will be more pronounced (than at lower currents) because of rapid K\(^+\) ion transport into the electrode. The specific capacities at various current densities of the \( \text{Bi}_{0.5}\text{Sb}_{0.5}@P \) and other Sb-based anodes evaluated in a nonaqueous potassium ion system are compared in Figure 5e. As shown in the figure, the rate capacity of \( \text{Bi}_{0.5}\text{Sb}_{0.5}@P \) surpasses all the capacities reported in the literature (see Table S3 for further details).\(^{17,18,23,26,31,33,36,55}\) The above electrochemical testing results indicate that the \( \text{Bi}_{0.5}\text{Sb}_{0.5} \) is the optimal chemical component for obtaining the best electrochemical performance of our system.

The high rate capability of the \( \text{Bi}_{0.5}\text{Sb}_{0.5}@P \) electrode was investigated via electrochemical kinetic analysis. The CV electrode of \( \text{Bi}_{0.5}\text{Sb}_{0.5}@P \) operated from 0.1 to 1.2 mV s\(^{-1}\) is shown in Figure 6a. The CV curve remains unchanged with changes in the scan rate. The capacitance effect can be determined from the relationship between the measured peak current \( i \) and the scan rate, \( \nu \), i.e., \( i = a\nu^b \), where \( a \) and \( b \) are adjustable constants. Furthermore, the value of \( b \) approaches 0.5 or 1.0, depending on the slope of the logarithmic \( i \) versus logarithmic \( \nu \) curve (Figure 6b). For \( b \) values close to 0.5 and 1.0 are obtained for a diffusion-controlled capacitive process and a surface-capacitance-based capacitive process, respectively.\(^{56,57}\) The \( b \) values obtained for the \( \text{Bi}_{0.5}\text{Sb}_{0.5}@P \) electrode (0.82 and 0.83) indicate that the capacitance dynamics of the electrode is dominated by the surface capacitance. Analyzed using the equation derived by Dunn et al.,\(^{58}\) the scan-rate-dependent CV curve was used to quantify the contribution of capacitive effects (surface pseudocapacitance and double-layer capacitance) and diffusion-controlled K\(^+\) ion insertion. The current equation is given as follows:

\[
\nu = \frac{i}{k_1 + k_2 \nu^{1/2}}
\]

This equation can be rewritten as

\[
\frac{i}{\nu^{1/2}} = k_1 \nu^{1/2} + k_2
\]
where \( i(V), k_1, \) and \( k_2 \sqrt{\nu} \) represent the capacitive reaction (current-capacitance effect due to the surface) and diffusion-controlled reaction (the current insertion process due to diffusion-controlled \( K^+ \)) at a given potential \( V \). By plotting \( i(V)/\nu^{1/2} \) and \( \nu^{1/2} \) at different potentials, a straight line for the values of \( k_1 \) (slope) and \( k_2 \) (intercept) can be obtained from the above formula. This allows quantification of the insertion current for capacitive effects and diffusion control at a given potential (Figure 6c,d). After the closed CV region is integrated, the number of stored charges in different energy storage modes can be distinguished. A CV curve of 0.4 mV s\(^{-1}\) is used for comparison. In Figure 6e, the potential curve (pink area) of the capacitance effect current response is compared with the total measured current area. The Bi\(_{0.5}\)Sb\(_{0.5}@P\) nanocomposites are characterized by a large amount of pseudocapacitive charge. The percentage of capacitance contribution relative to the total area is 67% at 0.4 mV s\(^{-1}\), and the total capacitance is mainly a capacitive contribution. Furthermore, capacitive percentages of 40, 58, 67, 70, 71, and 73% are obtained for scan rates of 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 mV s\(^{-1}\), respectively (Figure 6f). This result shows that the major portion of the capacitance from the Bi\(_{0.5}\)Sb\(_{0.5}@P\) composite electrode is induced by the surface-capacitance effect, which may be due to the P matrix. That is, the matrix yields significant improvement in the capacitance effect of the entire electrode surface, thereby improving the reactivity of Bi\(_{0.5}\)Sb\(_{0.5}@P\) with \( K^+ \) ions and the charge collection efficiency. Electrochemical impedance spectroscopy was conducted during cycling to understand the inherent properties of the Bi\(_{0.5}\)Sb\(_{0.5}@P\) composites. The Nyquist plots of Bi\(_{0.5}\)Sb\(_{0.5}@P\) at different cycles are shown in Figure S9 in the Supporting Information. The resistance of Bi\(_{0.5}\)Sb\(_{0.5}@P\) decreases gradually with a gradually decreasing size of the Bi\(_{0.5}\)Sb\(_{0.5}\) nanoparticles after 10, 50, and 100 cycles. The decreased resistance can enhance the ionic conductivity of the composite, which is beneficial for the insertion/extraction of \( K^+ \) ions into/from the anodes.\(^5\)

Additionally, we also investigate the morphology and crystal structure of the Bi\(_{0.5}\)Sb\(_{0.5}@P\) composite after 550 cycles. Figure 7a,b shows SEM images of the electrode after the cycles. These images reveal that the structures are still very compact and are almost identical to those of the electrode before the cycle (Figure S10 in the Supporting Information). In Figure 7b, the electrode surface is uniformly covered by a very thin SEI layer even after hundreds of cycles, indicating considerable SEI stability at the interface between the Bi\(_{0.5}\)Sb\(_{0.5}@P\) and the liquid electrolyte. The SEI layer is not only an electronic insulator but also a conductor for \( K^+ \) ion transport, and hence, a stable SEI layer is critical for achieving a long cycle life. A thick SEI generally results in the consumption of the

![Image](https://example.com/image.png)
electrolyte and K+ ions, a large electrical contact resistance between the current collector and anode materials, and a long K+ ion diffusion distance. This leads to electrode material degradation due to a large mechanical stress. Furthermore, TEM images (Figure 7c,d) show that the Bi0.5Sb0.5 alloy nanocrystals (average size is only 3.39 nm smaller than that of the original nanocrystals (6.35 nm)) are still densely distributed in the P matrix. The size variation of the nanocrystals is also narrower than that of the noncycled electrode. The size variation of the nanocrystals is also narrower than that of the noncycled electrode (Figure S11). This result shows that, when K+ ions react with nanocrystals, the stress resulting from the volume change leads to no cracking of the Bi0.5Sb0.5 particles, thereby yielding well-distributed nanocrystals embedded in the P matrix. The derived structure is very stable for hundreds of cycles during the alloying−dealloying process. Additionally, the nanocrystals after cycling are single crystalline. The HRTEM image clearly shows that the lattice fringes with a pitch of 0.323 nm correspond to the (012) surface facet of the Bi0.5Sb0.5 phase (Figure 7e). Furthermore, EDS mapping of the cycled Bi0.5Sb0.5@P nanostructures (see Figure 7f) reveals an even distribution of Bi, Sb, P, and K elements in this electrode. This distribution is very similar to that of the original Bi0.5Sb0.5@P composite materials.

Therefore, the P matrix plays an important role in the excellent electrochemical performance of the Bi0.5Sb0.5@P nanocomposites. The matrix controls and limits the growth of Bi0.5Sb0.5 nanocrystals to sizes of <10 nm. Despite the large volume change occurring during potassium and depotassium processes, these nanocrystals are firmly immobilized inside the matrix, and the derived Bi0.5Sb0.5@P nanocomposites, i.e., P-embedded ultrasmall Bi0.5Sb0.5 nanoparticles, provide excellent structural advantages for achieving electrochemical stability. Such small nanocrystals (diameters = 3−4 nm) play a critical role in buffering the volume changes, thereby increasing the electrode cycle life and allowing rapid reaction of K+ ions with Bi0.5Sb0.5. Furthermore, the P matrix is an efficient medium for both electron and K+ ion transport and hence enables good rate capability. Additionally, the controlled growth of a thin and stable SEI layer grown on the surface of the matrix also reduces the overall electrode resistance.

The structural advantages of Bi0.5Sb0.5@P as KIB electrodes compared with other Bi0.5Sb0.5 materials are investigated. We prepared Bi0.5Sb0.5 powders using a ball milling method (SEM image and XRD pattern are shown in Figures S12 and S13 in the Supporting Information) and conducted electrochemical characterization, including CV and half cell tests. From the CV diagram (see Figure S14), the shoulders at peak 1 (~0.75 V) and peak 2 (~1.25 V) are relatively wide. Additionally, many unrecognizable peaks appear in the first-cycle dQ/dV diagram of the ball-milled Bi0.5Sb0.5. The electrochemical reaction of
Bi$_{0.5}$Sb$_{0.5}@P$ with K$^+$ ions may cause structural instability and these unstable electrochemical reactions of ball-milled Bi$_{0.5}$Sb$_{0.5}@P$ with K$^+$ ions may cause structural instability and pulverization of the electrode and uncontrolled growth of the SEI layer during the charging/discharging process. This results in electrolyte consumption and increased electrode resistance. Figure S15 shows the long-term cyclability of the ball-milled Bi$_{0.5}$Sb$_{0.5}@P$ electrodes. The average Coulombic efficiency of the electrodes is 98.5% per cycle, which is lower than that (99.47% per cycle) of the Bi$_{0.5}$Sb$_{0.5}@P$ electrode. After 50 cycles, the average loss capacity is 1 mA h g$^{-1}$ per cycle, far greater than the 0.12 mA h g$^{-1}$ per cycle of the Bi$_{0.5}$Sb$_{0.5}@P$ electrode. Additionally, the cell is short-circuited after 280 cycles. Figure S16 shows an SEM image of the ball-milled Bi$_{0.5}$Sb$_{0.5}$ after 280 cycles. The morphology of the electrode changes significantly after cycling. The recycled Bi$_{0.5}$Sb$_{0.5}@P$ electrode exhibits good structural integrity (Figure 7). However, the cycled electrode material exhibits poor integrity, as evidenced by the breakage of the material into small pieces and coverage (of the material) with a thick SEI layer. These results show that the electrode stability of the ball-milled Bi$_{0.5}$Sb$_{0.5}@P$ is poor. Therefore, in terms of electrochemical stability, Bi$_{0.5}$Sb$_{0.5}@P$ exhibits superior structural advantage over the ball-milled Bi$_{0.5}$Sb$_{0.5}$ materials and excellent behavioral cycling characteristics.

To explain the potassium storage mechanism upon K$^+$ ion insertion and extraction, in situ contour mapping and XRD line plots are used to observe the structural transition and phase evolution of Bi$_{0.5}$Sb$_{0.5}@P$ during the first three discharge/charge processes. Figure 8a shows the in situ mapping XRD pattern of a live Bi$_{0.5}$Sb$_{0.5}@P$ half cell (left column) and the corresponding charge–discharge profile (right column). The proposed potassiation–depotassiation mechanism and the line plots of the operando XRD results obtained for the first three cycles are shown in Figures 8b and 8c–e, respectively. The experimental and calculation results of the (Bi, Sb), K(Bi, Sb), and K$_3$(Bi, Sb) phases are compared in Figures 8f–h. When the electrodes discharge from 2.0 V, the peak occurring at 27.7$^\circ$ associated with (Bi, Sb) becomes weaker than the strong peaks corresponding to the pristine material and moves slightly toward smaller angles. This indicates that K$^+$ ion insertion into (Bi, Sb) crystals has started. When discharged to 0.6 V, the alloying reaction occurs. Two new peak positions at $\sim$1.2 and 32.6$^\circ$, which can be indexed to the (311) facet and (222) facet, respectively, of K(Bi, Sb), are observed. This confirms that the electrode was transformed from (Bi, Sb) to K(Bi, Sb) at this stage. During the discharge process, when the voltage further drops to 0.15 V, two peaks occur at 29.8 and 34.7$^\circ$ corresponding to the (220) and (311) planes of K$_3$(Bi, Sb), respectively. However, the intensity of the K(Bi, Sb) phase decreases, thereby confirming that the alloy reaction transforming K(Bi, Sb) to K$_3$(Bi, Sb) occurs at this stage. The lattice parameters (a and c) calculated from XRD patterns are listed in Table S1 (Supporting Information). The potassium alloy reaction is completed through the above-mentioned processes. During the charging process, the depotassiation reaction proceeds when the voltage increases from 0.15 V. The intensity of K$_3$(Bi, Sb) decreases gradually and shifts slightly to a larger angle (than the initial angle), indicating that the K$^+$ ions exit the (Bi, Sb) crystal at this stage. When the voltage increases to 0.6 V, the peak corresponding to K$_3$(Bi, Sb) disappears completely, and the peak of K(Bi, Sb) reappears. When the voltage increases further to 1.3 V, the peak corresponding to the (012) facet of (Bi, Sb) reappears. The overall charging process and the discharging process are completely reversed. During the second and third cycles, the relationship between the changes in the peaks and the positions of the voltage is exactly the same as that of the curve obtained for the first cycle. Therefore, the potassiation–depotassiation process of the (Bi, Sb) alloys is also a reversible reaction during the second and third cycles. The weak peak appearing at an angle of 25.4$^\circ$ may correspond to the (112) facet of KP. The peak intensity of KP is very weak during the three cycles, indicating that this reaction is irreversible. Therefore, the results of in situ XRD and the elemental analysis ($\sim$9 wt % in the whole electrode) conducted via TGA and EDS indicate that phosphorus contributes an irreversible
and negligible capacity in the first discharge process. Thus, the resulting capacity obtained from the Bi0.5Sb0.5@P electrode is mainly due to the reversible reaction of Bi0.5Sb0.5 with K+ ions.

According to the results of the in situ XRD combined battery cycle in the above three cycles, the overall process of potassiation–depotassiation can be divided into five stages, as summarized below

\[
\text{Stage I:}\ P + K^+ + e^- \rightarrow KP + SEI\ formation
\]

\[
\text{Stage II:}\ (Bi, Sb) + K^+ + e^- \rightarrow K(Bi, Sb)\ (\sim 0.6\ V)
\]

\[
\text{Stage III:}\ K(Bi, Sb) + K^+ + e^- \rightarrow K_3(Bi, Sb)\ (\sim 0.15\ V)
\]

\[
\text{Stage IV:}\ K_3(Bi, Sb) - K^+ - e^- \rightarrow K(Bi, Sb)\ (\sim 0.6\ V)
\]

\[
\text{Stage V:}\ K(Bi, Sb) - K^+ - e^- \rightarrow (Bi, Sb)\ (\sim 1.3\ V)
\]

Based on the above results, the proposed stages and corresponding capacities are summarized in Figure 8b. Irreversible reactions including the response of SEI and the response of P to KP occur in stage I, the very beginning of the discharge process from 2 V. In stage II, i.e., for discharge voltages ranging from 2 to 0.6 V, K+ ions become incorporated into the (Bi, Sb) crystal, and the initial process of alloying reaction begins. When the discharge reaches 0.6 V, (Bi, Sb) is completely transformed to K(Bi, Sb) with potassium ion alloying. An interval voltage range of 0.6 to 0.15 V in stage III leads to an alloying reaction, which, upon continuous K+ ion insertion, completely transforms K(Bi, Sb) into K3(Bi, Sb). In stage IV in the charging reaction, the voltage increased from 0.15 to 0.6 V, and the depotassiation of K3(Bi, Sb) was ionized to form K(Bi, Sb). (Bi, Sb) crystals are reformed at ~1.3 V in this stage. The in situ XRD patterns corresponding to the first three cycles reveal that the potassiation–depotassiation reactions occurring in stages II to V are reversible reactions. Furthermore, regarding the potassiation–depotassiation process of K+ ions reacting with Bi1.11Sb0.89S3 nanotubes and BiSb@C nanocomposites, the reported reaction pathway of K+ ions with BiSb@C is simpler than previously reported pathways. For example, the potassiation–depotassiation process of Bi1.11Sb0.89S3 nanotubes involves six successive stages where involved irreversible reactions induce the decomposition of (BiSb)3S3 into Bi, Sb, and K2S4. This decomposition is followed by in situ alloying of Bi and Sb. BiSb@C nanocomposites undergo seven steps of the potassiation–depotassiation processes, which involve irreversible reactions of (Bi, Sb) to K(Bi, Sb) and K(Bi, Sb).

We paired a PTCDA cathode with a Bi0.5Sb0.5@P anode to construct a potassium ion full cell for demonstrating the feasibility as a KIB full cell anode. Figure 9a shows a schematic of the full cell configuration, and Figure S18 (Supporting Information) provides a detailed analysis of PTCDA, including electrochemical evaluation of the half cell. Based on the charge/discharge curve, a PTCDA cathode provides 119.7 mA h g−1 at 500 mA g−1 and working voltages ranging from 1.5 to 3.5 V. The electrolyte solution used in the full cell is 4 M KFSI in DME, and the charge/discharge voltage interval ranges from 0.5 to 3.4 V. The charging curve of the Bi0.5Sb0.5@P/PTCDA full cell should occur in this interval, as revealed by the individual half cell charge and discharge profiles of Bi0.5Sb0.5@P and PTCDA. Two plateaus ranging from 2.0 to 2.5 V and 2.7 to 2.9 V occur in this curve (Figure 9b), i.e., the voltage curve of the Bi0.5Sb0.5@P/PTCDA full cell corresponding to Figure 9d. The voltage curve reveals two prominent plateaus in the charge and discharge curves. The difference between the voltage values obtained from the charging/discharging voltage profile of the full cell is ~2.9 V, which is similar to the difference between the voltage of the PTCDA cathode (3.5 V) and the charging voltage of Bi0.5Sb0.5@P (0.55 V). A pair of different redox versus CV curves show 2.5/2.85 V in the third and fourth cycles, and the overlapping shape in the cycles indicates the good reversibility and stability of Bi0.5Sb0.5@P/PTCDA full cell (Figure 9c).

The cell exhibits a long-term cycle life (Figure 9e), where an initial specific discharge capacity of 280 mA h g−1 (based on the mass of active materials) is provided. Furthermore, a reversible discharge specific capacity of 154 mA h g−1 after 100 cycles at 400 mA g−1 is maintained. The lower capacity (154 mA h g−1) shows that the Bi0.5Sb0.5@P specific capacity of the full cell is lower than that of the half cell. This results from the mismatching between the lower charging voltage in the full cell (~1.0 V relative to K+/K) and the positive and negative capacities. The performance of the full cells can be further improved by optimizing the capacity balance between anode and cathode materials. The above full battery results indicate that Bi0.5Sb0.5@P anodes are quite promising for future KIBs.

**CONCLUSIONS**

A solution precipitation method is used to synthesize Bi8Sb5@P nanocomposites with the entire stoichiometry of the Bi/Sb ratio inside the P matrix. The optimally tuned Bi–Sb composition can maximize a buffering effect for large volume changes during the potassiation–depotassiation process. Bi8Sb5@P nanocrystal electrodes exhibit 1000-cycle stability and allow ultrafast potassium ion insertion and extraction of (Bi, Sb). The potassium storage mechanism of these electrodes occurs via a simple, direct, and reversible reaction pathway: (Bi, Sb) ↔ K(Bi, Sb) ↔ K3(Bi, Sb). The ultrasmall Bi8Sb5 nanocrystals evolved after cycling provided excellent structural advantages for outstanding electrochemical performance. The P matrix plays an important role in the excellent electrochemical performance of the Bi0.5Sb0.5@P nanocomposites. The matrix can limit the growth of Bi8Sb5 nanocrystals to sizes of <10 nm and immobilizes nanocrystals inside the composites during cycling. Furthermore, the matrix serves both as a good electron transport medium for a very high rate capability and a good intermediate layer for uniform and thin SEI layer growth. This study shows that P is a carbon-alternative buffer material for KIB anodes accounting for a low content of the active materials and is well-mixed with additive materials for high compatibility with commercial fabrication procedures.

**MATERIALS AND METHODS**

**Materials.** Bismuth(III) chloride (BiCl3, 99.9%) was purchased from Alfa Aesar. Antimony(III) chloride (SbCl3, 99%), perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), potassium metal (98%), 1,2-dimethoxyethane (DME, anhydrous, 99.5%), toluene (anhydrous, 99.99%), and sodium carboxymethyl cellulose (NaCMC, average Mn ≈ 700 000) were purchased from Sigma-Aldrich. Tris(trimethylsilyl)phosphine, min. 98% (P(SiMe3)3, 10 w% in hexanes), was purchased from STREM. Potassium bis[(fluorosulfonyl)imide (KFSI, 97%) was purchased from Chemical Block. The Celgard membrane was purchased from Advantec. Super P and the coin-type cell CR2032 were purchased from Shining Energy.

**Material Synthesis.** Bi8Sb5@P nanocrystals were synthesized by colloid chemical reactions under an atmosphere of argon. First, 1.72 mmol of SbCl3 and 1.72 mmol of BiCl3 were dispersed in 40 mL
of toluene and stirred for 1 h. Then, 3.34 mmol of P(SiMe3)3 was added dropwise into a stirred solution at room temperature. After the solution was stirred for 3 h, the black precipitate was washed with ethanol and toluene several times and thereafter separated by centrifugation. Finally, the obtained sample was dried by rotary evaporation and subjected to a tube furnace and annealed at 200 °C for 2 h with a ramp rate of 5 °C/min under Ar flow. For comparison, the Bi0.5Sb0.5@P samples with different Bi/Sb ratios (1:3 and 3:1) were synthesized using the same method as Bi0.5Sb0.5@P and are denoted as Bi0.25Sb0.75@P and Bi0.75Sb0.25@P, respectively. Bi0.5P and Sb0.5P were also synthesized using the same method and corresponding metal sources. Bi0.5Sb0.5P prepared by a ball milling method. Bi powder (99.5%, 325 mesh, Alfa Aesar) and Sb powder (99.5%, 100 mesh, Alfa Aesar) in a mole ratio of 1:1 were mixed and sealed in a stainless steel jar with stainless steel balls inside an argon-filled glovebox. After that, the stainless steel jar was put into the Planetary Ball Mill PM 100 machine and rotated at 500 rpm for 12 h.

Material Characterizations. The morphology and the microstructure of the prepared samples were investigated using scanning electron microscopy (HTACHIT-SU8010) with energy-dispersive X-ray spectroscopy (HORIBA, EX-250) and spherical aberration corrected scanning transmission electron microscopy (JEOL, ARM200F). The structure and composition were characterized using X-ray diffraction (Bruker, D8 ADVANCE) with Cu Kα radiation, and the valence states of the samples were identified by a high-resolution X-ray photoelectron spectrometer (ULYAC-PH, PHI QuantaneraII). Thermogravimetric analysis was carried out using a thermogravimetric analyzer (TA, Q50) from 50 to 800 °C with a heating rate of 10 °C/min in N2. The Brunauer–Emmett–Teller surface area and pore distribution plots were measured by a Micromeritics ASAP 2060. The analysis of the XRD pattern was conducted using EVA software.

Electrochemical Measurements. Bi0.5Sb0.5@P, Bi@P, and Sb@P were mixed with Super P and carboxymethyl cellulose (CMC) binder in a weight ratio of 8:1:1, which was blended with Super P and carboxymethyl cellulose (CMC) binder in a weight ratio of 8:1:1, which was spread on an aluminum foil. The electrochemical properties of the as-prepared electrodes were evaluated by assembling CR 2032-type coin cells. The half-cell was assembled using the Bi0.5Sb0.5@P anode, PTCDA cathode, and the electrolyte sandwiched between 0.05 and 2 V (vs K+/K). Galvanostatic charge/discharge tests were performed in a voltage range of 0.05 to 2 V for Bi0.5Sb0.5@P and 1.5 to 3.5 V for PTCDA at a current density of 50 mA g−1 for a few times to obtain densely packed SEI films before the stability tests at 500 mA g−1. Galvanostatic charge/discharge tests were performed in a voltage range of 0.05 to 2 V for Bi0.5Sb0.5@P and 1.5 to 3.5 V for PTCDA at different current densities on a Maccor Series 4000 battery test system. Full cells were obtained with CR-2032-type coin cells in the argon-filled glovebox. For the half-cell measurement, the investigated sample was used as the working electrode, potassium metal foil was used as the counter electrode, and glass fiber was used as the separator, and 4 M KFSI in DME was used as the electrolyte. The cells were cycled at 50 mA g−1 for 3 cycles. The operando XRD patterns of Bi0.5Sb0.5@P were collected on Bruker D8 ADVANCE diffractometer (Cu Kα) for three cycles. The investigation sample was used as the working electrode, potassium metal foil was used as the counter electrode and reference electrode, and 4 M KFSI in DME was used as the electrolyte. A current density of 50 mA g−1 is selected for charging and discharging processes between 0.05−2 V (vs K+/K).

ASSOCIATED CONTENT

Supporting Information

Crystal structure parameters of Bi, Sb, Bi0.5Sb0.5, K(Bi,Sb), and K5(Bi,Sb); calculated lattice parameters of Bi0.5Sb0.5@P nanocomposites; TEM images, Raman spectra, and EDS analysis of Bi0.5Sb0.5@P nanocomposites; TGA analysis, XPS spectrum, and BET measurement of Bi0.5Sb0.5@P and Bi0.75Sb0.25@P nanocomposites; the voltage profiles of the electrochemical performance of Bi0.5Sb0.5@P nanocomposites; Nyquist plots of Bi0.5Sb0.5@P composites; SEM images of the Bi0.5Sb0.5@P electrode before cycling; electrochemical cycling performance of PTCDA KIB cathodes (PDF)

AUTHOR INFORMATION

Corresponding Author

Hsing-Yu Tuan — Department of Chemical Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan; orcid.org/0000-0003-2819-2270; Phone: (866)3-571-5131 ext: 42509; Email: hytuan@che.nthu.edu

Author

Kuan-Ting Chen — Department of Chemical Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan

Complete contact information is available at: https://pubs.acs.org/10.1021/acsnano.0c04203

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported from the Young Scholar Fellowship Program by the Ministry of Science and Technology in Taiwan, under the Grants of MOST 108-2636-E-007-013, MOST 108-2622-8-007-016, and MOST 109-2636-E-007-001. The authors also acknowledge the financial support of National Tsing Hua University through the grant of 107Q2708E1.

REFERENCES


An, Y.; Tian, Y.; Wei, H.; Xi, B.; Xiong, S.; Feng, J.; Qian, Y. Porosity-and Graphitization-Controlled Fabrication of Nanoporous...


