Advanced Hybrid Supercapacitor Based on a Mesoporous Niobium Pentoxide/Carbon as High-Performance Anode

Eunho Lim,†* Haegyeom Kim,§ Changshin Jo,‡ Jinyoung Chun,§ Kyojin Ku,§ Seongseop Kim,‡ Hyung Ik Lee,† In-Sik Nam,*§ Songhun Yoon,* Kisuk Kang,§,#,* and Jinwoo Lee†,‡,*

†School of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang, Kyungbuk 790-784, Republic of Korea, §Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang, Kyungbuk 790-784, Republic of Korea, ‡Department of Materials Science and Engineering, Research Institute of Advanced Materials (RIMa), Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul 151-742, Republic of Korea, ^4-3, Agency for Defense Development, Yuseong, P.O. Box 35-4, 305-600 Daejeon, Republic of Korea, †Department of Integrative Engineering, Chung-Ang University, 221, Heukseok-Dong, Dongjak-Gu, Seoul 156-756, Republic of Korea, and #Center for Nanoparticle Research, Institute for Basic Science (IBS), Seoul National University, Seoul 151-742, Republic of Korea.†* E. Lim, H. Kim, and C. Jo contributed equally to this work.

The range of energy-storage device applications has expanded from portable electronics to large-scale energy-storage systems, including renewable energy storage and electricity transportation.1 To fulfill the energy and power density requirements of energy applications, much research has been devoted to improving the performances of energy-storage devices such as lithium-ion batteries (LIBs) and supercapacitors (SCs). Moreover, despite their high energy densities (~150 W h kg⁻¹), LIBs have fundamental limitations such as low power densities and poor cycling lifetimes because they operate using faradaic reactions that involve ionic diffusion in a crystal framework.5,10 In contrast, it is well-known that SCs provide high power (2–5 kW kg⁻¹) and have long cycling stabilities because they are based on fast physical adsorption/desorption of solvated ions at the electrode-electrolyte interface; however, they usually suffer from limited energy densities (3–6 Wh kg⁻¹).11,12 Recently, novel energy-storage

**ABSTRACT** Recently, hybrid supercapacitors (HSCs), which combine the use of battery and supercapacitor, have been extensively studied in order to satisfy increasing demands for large energy density and high power capability in energy-storage devices. For this purpose, the requirement for anode materials that provide enhanced charge storage sites (high capacity) and accommodate fast charge transport (high rate capability) has increased. Herein, therefore, a preparation of nanocomposite as anode material is presented and an advanced HSC using it is thoroughly analyzed. The HSC comprises a mesoporous Nb₂O₅/carbon (m-Nb₂O₅-C) nanocomposite anode synthesized by a simple one-pot method using a block copolymer assisted self-assembly and commercial activated carbon (MSP-20) cathode under organic electrolyte. The m-Nb₂O₅-C anode provides high specific capacity with outstanding rate performance and cyclability, mainly stemming from its enhanced pseudocapacitive behavior through introduction of a carbon-coated mesostructure within a voltage range from 3.0 to 1.1 V (vs Li/Li⁺). The HSC using the m-Nb₂O₅-C anode and MSP-20 cathode exhibits excellent energy and power densities (74 W h kg⁻¹ and 18 510 W kg⁻¹), with advanced cycle life (capacity retention: ~90% at 1000 mA g⁻¹ after 1000 cycles) within potential range from 1.0 to 3.5 V. In particular, we note that the highest power density (18 510 W kg⁻¹) of HSC is achieved at 15 W h kg⁻¹, which is the highest level among similar HSC systems previously reported. With further study, the HSCs developed in this work could be a next-generation energy-storage device, bridging the performance gap between conventional batteries and supercapacitors.

**KEYWORDS:** hybrid supercapacitors · Nb₂O₅ · pseudocapacitive properties · mesoporous materials · block copolymer-assisted self-assembly

The range of energy-storage device applications has expanded from portable electronics to large-scale energy-storage systems, including renewable energy storage and electricity transportation.1-4 To fulfill the energy and power density requirements of energy applications, much research has been devoted to improving the performances of energy-storage devices such as lithium-ion batteries (LIBs) and supercapacitors (SCs).5-8 However, despite their high energy densities (~150 W h kg⁻¹), LIBs have fundamental limitations such as low power densities and poor cycling lifetimes because they operate using faradaic reactions that involve ionic diffusion in a crystal framework.9,10 In contrast, it is well-known that SCs provide high power (2–5 kW kg⁻¹) and have long cycling stabilities because they are based on fast physical adsorption/desorption of solvated ions at the electrode-electrolyte interface; however, they usually suffer from limited energy densities (3–6 Wh kg⁻¹).11,12 Recently, novel energy-storage...
systems having the advantages of both LIBs and SCs have been proposed, namely, hybrid supercapacitors (HSCs).\textsuperscript{11,13} The concept of HSC is the combination of both energy-storage systems by using electrode materials of LIBs as anodes and carbonaceous electrodes of SCs as cathodes under organic electrolyte containing lithium salts.\textsuperscript{14–17} Previous studies have shown that the energy and power densities of HSCs are comparable to, or even higher than, those of LIBs and SCs. However, the imbalance between the kinetics of the two electrodes is a problem that needs to be solved for commercial applications because, in general, anode kinetics using the faradaic lithium intercalation reaction is far more sluggish than that of cathodes using physical adsorption/desorption of electrolyte ions.\textsuperscript{18,19} Therefore, it is vital to develop novel high-power anode materials to narrow the kinetics gap between two electrodes. In previous studies, nanostructured titanium-based anode materials such as TiO\textsubscript{2} and Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} have been extensively used in HSC systems because of their fast Li\textsuperscript{+} insertion kinetics.\textsuperscript{19,20} However, the relatively high redox potential (>1.5 V) over titanate electrodes is a major drawback, and leads to unnecessary loss of energy density.\textsuperscript{21,22} Niobium pentoxide (Nb\textsubscript{2}O\textsubscript{5}) is one of the most promising candidates for replacing conventional titanate electrodes. Recently, it has been demonstrated that Nb\textsubscript{2}O\textsubscript{5} can deliver high power through a mainly pseudocapacitive reaction of Li\textsuperscript{+} on the (near) surface of the electrode, accompanied by an intercalation reaction.\textsuperscript{23,24} The Nb\textsubscript{2}O\textsubscript{5} with pseudocapacitive reaction mechanism for charge storage could be very suitable as the anode of HSC systems because of its outstanding high power performance. This unique property of Nb\textsubscript{2}O\textsubscript{5} could result in the harmonious electrochemical performance with electrical double-layer type cathode based on intrinsically fast physical adsorption/desorption of electrolyte ions. The high theoretical capacity (≈200 mAh g\textsuperscript{-1}), which is higher than that of Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} (≈175 mAh g\textsuperscript{-1}), is also advantageous in delivering high energy densities in HSC systems.\textsuperscript{25–27} However, the application of Nb\textsubscript{2}O\textsubscript{5}-based anodes in HSCs has been hampered by both the low electrical conductivity and the difficulty to control optimum crystal structure.\textsuperscript{24,28} The sluggish mobility of electrons in Nb\textsubscript{2}O\textsubscript{5} should be further improved through surface modifications (e.g., carbon coating). Although the nanocomposite of nanosized Nb\textsubscript{2}O\textsubscript{5} nanocrystals and high conductive carbon nanotubes (CNTs) was prepared by Lu et al., the specific capacity of pseudohexagonal Nb\textsubscript{2}O\textsubscript{5}/CNTs composite (calcined at 300 °C) was still not sufficient for the high-performance HSC system.\textsuperscript{29} This low capacity was attributed to strong capacity-dependency on the crystal structure of Nb\textsubscript{2}O\textsubscript{5} material. Among various crystal structures of Nb\textsubscript{2}O\textsubscript{5}, the orthorhombic phase has shown the highest specific capacity compared with other phases such as pseudohexagonal and amorphous phase.\textsuperscript{24} However, nanoparticle aggregation is inevitable due to high calcination temperature (>600 °C) for the orthorhombic phase formation of Nb\textsubscript{2}O\textsubscript{5}. Particularly, HSC systems require the high-power anode materials in order to balance the kinetics gap between the slow faradaic anode and the fast electric double-layer type cathode. For the purpose of kinetics improvement of anode system, nanosized orthorhombic Nb\textsubscript{2}O\textsubscript{5} material is highly advantageous. In spite of this merit, the synthesis of small-sized orthorhombic Nb\textsubscript{2}O\textsubscript{5} has been recognized as one of the major challenges, mainly due to synthetic difficulties. For these reasons, the research on Nb\textsubscript{2}O\textsubscript{5}-based HSC systems has been rarely realized. Hence, one can expect that well-nanostructured orthorhombic Nb\textsubscript{2}O\textsubscript{5} with carbon coating can produce high-performance anode for HSC system.

In addressing this issue, a key strategy is the one-pot synthesis of a mesoporous Nb\textsubscript{2}O\textsubscript{5}/carbon nanocomposite (denoted by m-Nb\textsubscript{2}O\textsubscript{5}–C). The m-Nb\textsubscript{2}O\textsubscript{5}–C is synthesized using a block copolymer (poly(ethylene oxide-b-poly(styrene)), PEO-b-PS) as a structure-directing agent.\textsuperscript{30,31} The mesoporous material comprising nanocrystalline Nb\textsubscript{2}O\textsubscript{5} could enhance the electrochemical activity originated from (i) particles of nanoscale regime, providing a shortened diffusion length and the large electrode—electrolyte interface area compared with the bulk structure; and (ii) enhanced ionic transportation through the mesopores.\textsuperscript{32–34} In addition, (iii) the uniform carbon layers formed by thermal decomposition of the PS block during heat-treatment not only maintain the mesostructure comprising orthorhombic Nb\textsubscript{2}O\textsubscript{5} nanocrystals from high temperature (700 °C) heat-treatment under N\textsubscript{2} atmosphere, but also improve the electrical conductivity of m-Nb\textsubscript{2}O\textsubscript{5}–C with enhanced electron transportation.\textsuperscript{35} Here, we report an advanced HSC with an m-Nb\textsubscript{2}O\textsubscript{5}–C anode combined with an activated carbon (MSP-20) cathode. The novel HSC system described in this paper had superior electrochemical properties, including energy and power densities, because of the synergistic effects of the mesoporous structure and pseudocapacitive properties of Nb\textsubscript{2}O\textsubscript{5}.

**RESULTS AND DISCUSSION**

**Synthesis of m-Nb\textsubscript{2}O\textsubscript{5}–C.** Scheme 1 shows a schematic diagram of m-Nb\textsubscript{2}O\textsubscript{5}–C synthesis and a HSC system. The m-Nb\textsubscript{2}O\textsubscript{5}–C was synthesized by a one-pot synthesis method, which is evaporation-induced self-assembly (EISA), using niobium precursors and a laboratory-synthesized amphiphilic block copolymer (PEO-b-PS).\textsuperscript{30} The niobium precursors undergo a non-evaporation process for self-assembly, heat-treatment via hydrolytic sol–gel reaction to form a niobium oxide sol which interacts with the hydrophilic PEO block via hydrogen bonding, in an organic solvent. After an evaporation process for self-assembly, heat-treatment
of the niobium oxide sol/PEO-b-PS assembled composite at 700 °C under N₂ afforded highly ordered mesoporous structures. The resulting m-Nb₂O₅–C was used as the anode active material in the HSC system. For control experiments, mesoporous Nb₂O₅ (denoted by m-Nb₂O₅) obtained by m-Nb₂O₅/C heat-treatment in air and nanometer-sized bulk Nb₂O₅ (denoted by b-Nb₂O₅) synthesized without a block copolymer were prepared.

The X-ray diffraction (XRD) patterns of Nb₂O₅ samples (Figure 1a) match the orthorhombic phase (JCPDS No. 30-0873) of Nb₂O₅. The crystallite sizes of m-Nb₂O₅–C, m-Nb₂O₅, and b-Nb₂O₅, calculated using the Debye–Scherrer equation, were 12, 12, and 21 nm, respectively. The crystallite sizes of m-Nb₂O₅–C and m-Nb₂O₅ were approximately half that of b-Nb₂O₅; the size was not changed during heat-treatment in air (m-Nb₂O₅/C to m-Nb₂O₅). As confirmed in previous studies, small crystallites favor Li⁺ insertion into Nb₂O₅ electrodes, with an improved surface charge contribution.

Small-angle X-ray scattering (SAXS) patterns show that the as-synthesized Nb₂O₅ (block copolymer/precursors composite annealed at 100 °C), m-Nb₂O₅–C, and m-Nb₂O₅ have long-range ordered structures (Figure 1b). The arrows in the figure represent the relative scattering vector (q) positions 3½ and 4½ from the first-order
maximum, indicating that the hexagonally ordered Nb2O5 structure is well developed. The q value of as-synthesized Nb2O5 compared to that of m-Nb2O5−C and m-Nb2O5 was slightly larger (an increase from 0.17 to 0.19); this is attributed to framework shrinkage during heat-treatment. Notably, the SAXS pattern of m-Nb2O5 shows well preserved patterns compared to that of as-synthesized Nb2O5 and m-Nb2O5−C. It represents that the highly ordered mesostructure with high crystallinity was well developed by block copolymer assisted self-assembly.30 The mesoporous structures of the Nb2O5 samples were further characterized using N2 adsorption—desorption isotherms (Figure 1c) and scanning electron microscope (SEM; Figure 1d). The N2 adsorption curves of mesoporous Nb2O5 materials exhibit type IV curves, with a sharp adsorption at ~0.9 P0/Pc (Figure 1c and Figure S1a). This indicates extensive generation of uniform mesopores, in particular large pores that can be used as appropriate pathways for electrolyte penetration. The main pore size, calculated using the Barrett—Joyner—Halenda (BJH) method, and the Brunauer—Emmett—Teller (BET) surface area of m-Nb2O5−C were 30 nm and 76 m2 g−1, respectively.37 After removal of in situ formed carbon, the pore size and surface area were 50 nm and 40 m2 g−1, respectively. The surface area of the mesostructured material was much higher than that of b-Nb2O5 (<3 m2 g−1). It should be noted that the synthesis of mesoporous material (>30 nm) is only feasible when laboratory-synthesized PEO-b-PS with higher molecular weight and Flory-Huggins interaction parameter is used as a structure-directing agent,38,39 which is not possible to synthesize using Pluronic-based commercial block copolymers. SEM images of m-Nb2O5−C, as-synthesized Nb2O5, and m-Nb2O5 (Figure 1d and Figure S1b) show uniformly generated mesopores with a well-ordered hexagonal array, consistent with the SAXS and the N2 physisorption results.

Raman spectroscopy and thermogravimetric analysis (TGA) were employed to confirm the presence of in situ formed carbon of m-Nb2O5−C as shown in Figure 2. The presence of carbon in m-Nb2O5−C is verified by Raman spectroscopy with two bands around 1600 (graphitic carbon, G-band) and 1350 (disordered carbon, D-band) cm−1, respectively.30,40 TGA result is also in good agreement with the result of Raman spectroscopy, indicating the presence of in situ formed carbon where the carbon content is about 11 wt % as shown Figure 2b. Furthermore, electron energy loss spectroscopy (EELS) analysis image was used to directly confirm the existence of carbon in m-Nb2O5−C. Figure S2 clearly shows that the carbon-coated mesostructure is well synthesized. In this study, the in situ formed carbon plays key roles in not only maintaining the mesostructure from the high heat-treatment under N2 atmosphere, but also improving electronic network in m-Nb2O5−C. When compared with the mesoporous Nb2O5 (main pore size: 13−15 nm) thin film prepared by KLE block copolymer, our method was based on block copolymer (PEO-b-PS) as a structure directing agent to produce the carbon-coated mesoporous Nb2O5 (<30 nm) powder comprising nanosized Nb2O5 particles (m-Nb2O5−C) via one-pot synthesis method without any further treatment.41 Hence, it is expected that our m-Nb2O5−C material has several merits such as simple preparation with easy scale-up and lower cost.

**Electrochemical characterization.** Nb2O5/Li and MSP-20/Li Half-Cell Test. To investigate the electrochemical performance of Nb2O5 electrodes, half-cells were prepared using a 2032-type coin cell with lithium metal as the counter and reference electrodes. Cyclic voltammetry (CV) tests at sweep rates from 0.1 to 4.8 mV s−1 were conducted to examine the pseudocapacitive behavior of m-Nb2O5−C (Figure S3a,b).19,23 The broad cathodic and anodic peaks in the potential ranges of 1.1−2.2 V from the CV data can be attributed to Nb2O5+xLi+ + xe− ↔ LixNb2O5, where x is the degree of lithium insertion from 0 to 2.42 Generally, the current (i) and sweep rates (v) have the relationship i = avb (a and b are appropriate values), obeying the power law.43 It has been well established in previous studies that the b value in pseudocapacitive behavior is usually distinct from that in the case of the Li+ intercalation process;23,33 b = 0.5 represents a diffusion-controlled process caused by cation intercalation and b = 1 symbolizes capacitive behavior via a surface faradaic redox reaction.23,43 As Figure 3a (and Figure S4a) shows, the relationships between i and v for m-Nb2O5−C.
are linear \((b = 1)\), suggesting that its charge-storage behavior is best described as pseudocapacitive behavior.\(^{19,23,24,41}\) The CV measurements for different mass loadings \((0.60/2.23 \text{ mg})\) of \(\text{m-Nb}_2\text{O}_5/\text{C}\) at sweep rates from 0.1 to 50 mV s\(^{-1}\) were also performed to additionally examine its pseudocapacitive property as shown in Figures S3 and S4b. From the relations between \(i\) and \(v\), it should be noted that the charge-storage mechanism trend of \(\text{m-Nb}_2\text{O}_5/\text{C}\) is not changed with respect to various mass loadings of \(\text{m-Nb}_2\text{O}_5/\text{C}\), mainly due to its unique electrochemical property. At high sweep rates, a small deviation of the high mass loading electrode is probably due to the high total internal resistances from the high loading, which is not resulted from the change of charging mechanism.\(^{23}\)

The galvanostatic charge–discharge (delithiation–lithiation) voltage profiles over \(\text{Nb}_2\text{O}_5\) electrodes at a current density of 10 mA g\(^{-1}\) in the potential window 1.1–3.0 V (vs \(\text{Li/Li}^+\)) are displayed in Figure 3b (and Figure S5a,b). The discharge capacities of \(\text{m-Nb}_2\text{O}_5\) electrodes were larger than those of \(\text{b-Nb}_2\text{O}_5\), indicating significant enhancement of electrochemical activity by the mesostructured \(\text{Nb}_2\text{O}_5\). Furthermore, the charge–discharge profiles did not change significantly after the first cycle even though the first irreversible capacity losses of \(\text{m-Nb}_2\text{O}_5–\text{C}, \text{m-Nb}_2\text{O}_5\), and \(\text{b-Nb}_2\text{O}_5\) were 21.4, 27.3, and 15.3%, respectively. In general, nanostructured electrode materials have an irreversible capacity of approximately 20–40%.\(^{44,45}\) Note that the capacity of \(\text{m-Nb}_2\text{O}_5–\text{C}\) electrode was smaller than that of \(\text{m-Nb}_2\text{O}_5\) at low current densities \((10–100 \text{ mA g}^{-1})\); this is caused by small capacity contribution of the \textit{in situ} formed carbon (~11 wt %) in \(\text{m-Nb}_2\text{O}_5–\text{C}\) as shown in Figure S6. The real contribution of \textit{in situ} formed carbon in \(\text{m-Nb}_2\text{O}_5–\text{C}\) for specific capacity may be approximately less than 2 mA h g\(^{-1}\), considering low capacity of ordered mesoporous carbon (<20 mA h g\(^{-1}\)) and the carbon content (~11 wt %) in \(\text{m-Nb}_2\text{O}_5–\text{C}\).

Interestingly, the charge–discharge curves of the \(\text{m-Nb}_2\text{O}_5–\text{C}\) electrode exhibited more sloped patterns compared to that of \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) in the voltage range from 2.2 to 1.1 V, which is in good agreement with the broad cathodic–anodic peaks in the CV results (Figure S3). When compared with the voltage plateau at ~1.55 V in \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) electrode, furthermore, the inclined trend of charge–discharge profiles in \(\text{m-Nb}_2\text{O}_5–\text{C}\) electrode can lead to better prediction of state-of-charge (SOC), which is highly beneficial in high power application.

Figure 3c shows the rate performances of \(\text{m-Nb}_2\text{O}_5–\text{C}, \text{m-Nb}_2\text{O}_5\), and \(\text{b-Nb}_2\text{O}_5\) electrodes for various current densities from 10 to 5000 mA g\(^{-1}\) in the voltage window of 1.1–3.0 V (vs \(\text{Li/Li}^+\)). The charge–discharge capacities and capacity retentions of the mesostructured \(\text{Nb}_2\text{O}_5\) electrodes were much higher than those of the \(\text{b-Nb}_2\text{O}_5\) electrode at all current densities. This shows that the mesoporous structure improves the rate capability, mainly because of improved electrolyte penetration through the mesopores and shortened \(\text{Li}^+\) diffusion.
lengths within the pore walls. A more developed pseudocapacitive contribution in the nanocrystal surface (12 nm) could also be a reason for the improved rate capability. As shown in Figure S4a, the b values of the m-Nb₂O₅—C and m-Nb₂O₅ electrodes were very close to 1, but large deviation from 1 were observed for the b-Nb₂O₅ electrode, which again indicates that the introduction of porous structure comprising nanosized Nb₂O₅ nanocrystals improves kinetics in electrochemical reactions. In previous studies, it was reported that the charge-storage mechanism is changed from the diffusion-limited Li⁺ intercalation process to surface faradaic reactions in the nanosized materials. In particular, the charge–discharge capacity of m-Nb₂O₅—C (115.1 mA h g⁻¹) was far higher than that of m-Nb₂O₅ (84.4 mA h g⁻¹) and b-Nb₂O₅ (12.9 mA h g⁻¹) at very high current density (5000 mA g⁻¹, equivalent to 25 C rate); this might be one of the best rate performances ever reported for titanium or niobium oxide-based anode materials. The excellent rate performance of m-Nb₂O₅—C is clearly shown in Figure S7a–c. The charge–discharge profiles under different current densities show that an improved rate performance of m-Nb₂O₅—C compared with that of the others was observed with increasing current density. Clearly, the high rate performance of the m-Nb₂O₅—C electrode compared with that of m-Nb₂O₅ is attributable to enhanced electrical conductivity owing to the presence of conductive carbon derived from the PS-block. As summarized in Table S1, the electrical conductivity of m-Nb₂O₅—C is much higher than that of m-Nb₂O₅ and pure Nb₂O₅ previously reported. In other words, the carbon layer in m-Nb₂O₅—C provides a fast electronic conduction into insulating Nb₂O₅ nanocrystals, resulting in a reduced internal resistance of Nb₂O₅ electrode. Therefore, this promoted electron supply through the in situ carbon gives rise to a fast response at high current density (at 5000 mA g⁻¹) by maintaining the pseudocapacitive reaction of Nb₂O₅.

Figure 3d shows the cycling performance of the m-Nb₂O₅—C/Li half cell at a current rate of 2000 mA g⁻¹. During prolonged cycling (4000 cycles), ~80% of the initial capacity is retained, i.e., much higher stability than that of other intercalation-based Li⁺ insertion materials is achieved. The cycling stability might be attributed to the unique structure of m-Nb₂O₅—C, which is a uniformly carbon-coated mesostructure. As reported by previous study, amorphous carbon layer on electrode materials has resulted in suppressed surface side reaction during cycling. In this study, the in situ formed carbon in m-Nb₂O₅—C could play an important role in enhancing the surface stability of Nb₂O₅. In the HSC system, electric double-layer type cathodes such as activated and porous carbon electrodes are typically used, which conventionally exhibit much better rate performances and more stable cycle life than battery type anodes. Therefore, the m-Nb₂O₅—C electrode is the most suitable anode for HSC performance improvement, because of its significantly improved rate capability and extended cycling lifetime. Before constructing the HSC, the MSP-20 electrode was also tested in a half-cell at a current rate of 100 mA g⁻¹ in the voltage window 3.0–4.5 V in the HSC system, electric double-layer type cathodes such as activated and porous carbon electrodes are typically used, which conventionally exhibit much better rate performances and more stable cycle life than battery type anodes. Therefore, the m-Nb₂O₅—C electrode is the most suitable anode for HSC performance improvement, because of its significantly improved rate capability and extended cycling lifetime. Before constructing the HSC, the MSP-20 electrode was also tested in a half-cell at a current rate of 100 mA g⁻¹ in the voltage window 3.0–4.5 V in the HSC system, electric double-layer type cathodes such as activated and porous carbon electrodes are typically used, which conventionally exhibit much better rate performances and more stable cycle life than battery type anodes. Therefore, the m-Nb₂O₅—C electrode is the most suitable anode for HSC performance improvement, because of its significantly improved rate capability and extended cycling lifetime. Before constructing the HSC, the MSP-20 electrode was also tested in a half-cell at a current rate of 100 mA g⁻¹ in the voltage window 3.0–4.5 V. This charge–discharge profile of the MSP-20 electrode does not significantly change during repeated cycles, with an acceptably high capacity of ~70 mA h g⁻¹. The characteristic linear profiles reveal that the MSP-20 electrode operates via nonfaradaic capacitive reactions, in which ions are adsorbed and desorbed on the surface. 

Nb₂O₅//MSP-20 Hybrid Supercapacitor Test. To achieve the high-energy and power densities of HSCs, the mass ratio of the electrodes was optimized as shown in Figure S8a. The best mass ratio of cathode and anode active materials was carefully balanced to 3:1 in the voltage range of 0.5–3.0 V for high electrochemical performances of the HSCs. CV was performed to evaluate the electrochemical properties of the HSC in the voltage range 0.5–3.0 V at various scan rates from 2 to 50 mV s⁻¹ (Figure 5). Because of the negligible capacity achieved less than 0.5 V in the HSC, the cutoff voltage was limited to 0.5 V. In this respect, we first optimize the HSC full cells in the voltage window between 0.5 and 3.0 V. In contrast to symmetric SCs with rectangular CV profiles, our HSC

Figure 4. (a) Charge–discharge profiles of MSP-20. (b) Cycling performance of the MSP-20 at 100 mA g⁻¹ between 3.0 and 4.5 V.
has an asymmetric CV profile, indicating introduction of a faradaic reaction into the HSC system.\textsuperscript{18,52} The intrinsic redox active property of Nb$_2$O$_5$ anode materials may contribute to the asymmetric CV profile with deviation from the quasi-broad rectangular CV. In the CV analysis, the cathodic and anodic currents of the HSC based on m-Nb$_2$O$_5$/C increased compared to the HSCs with m-Nb$_2$O$_5$ and b-Nb$_2$O$_5$ anodes, while maintaining the curve shapes, showing that the electrochemical activity of the HSC with the m-Nb$_2$O$_5$–C anode is higher than those of the control groups. In addition, the linear relationship between current response peaks and scan rates, shown in Figure 5c, reveals that the charge-storage reaction in the HSC is mainly based on surface faradaic reactions rather than diffusion-limited reactions.\textsuperscript{12} The electrochemical properties of the HSCs based on the m-Nb$_2$O$_5$–C electrode anode were further investigated by galvanostatic measurements at current rates from 50 to 8000 mA g$^{-1}$, as shown in Figure 6a,b. The charge–discharge profiles of the HSC were not typical triangular shapes, unlike those of symmetric SCs.\textsuperscript{52} This again shows that the charge-storage mechanism in the HSC is based on a combination of a faradaic pseudocapacitive reaction at the anode and nonfaradaic capacitive charge-storage at the cathode. The charge–discharge curves of the HSC using m-Nb$_2$O$_5$–C were measured and compared with those of the HSCs using m-Nb$_2$O$_5$ and b-Nb$_2$O$_5$ at 400 mA g$^{-1}$ as shown in Figure 6c. The charge–discharge time of the HSC using an m-Nb$_2$O$_5$–C anode was much longer than those of the HSCs using m-Nb$_2$O$_5$ and b-Nb$_2$O$_5$ at a current rate of 400 mA g$^{-1}$, again indicating the electrochemical performance of the HSC with m-Nb$_2$O$_5$–C anode is superior compared to those of the control groups. Furthermore, the HSC using m-Nb$_2$O$_5$–C shows stable cyclability over 1000 cycles (~90%) without noticeable capacity fading as shown in Figure 6d.

Figure 7 shows a Ragone plot representing the trade-off between power and energy density, which
Figure 7. Ragone plots of hybrid supercapacitors based on m-Nb2O5–C, m-Nb2O5, and b-Nb2O5 anodes. The energy and power densities were calculated by numerically integrating the galvanostatic discharge curves as follows: \[ E = \int_{t_f}^{t_i} IV dt = \frac{1}{2} C (E_{\text{max}} + E_{\text{min}}) (E_{\text{max}} - E_{\text{min}}) = \Delta V \times \frac{I}{m} \times t \] \[ P = \frac{E}{t} = \Delta V \times \frac{I}{m} \] \[ \Delta V = \frac{E_{\text{max}} + E_{\text{min}}}{2} \] where \( C = \left[ \frac{(I \times \Delta t)/m}{[1/(E_{\text{max}} - E_{\text{min}})]} \right] \) is the specific capacitance \( (F/g) \), \( E_{\text{max}} \) (3.0 or 3.5 V) and \( E_{\text{min}} \) (1.0 V) are the initial and final discharge potentials \( (V) \), \( I \) is the discharge current \( (A) \), \( t \) is the discharge time \( (s) \), and \( m \) is the total mass of active materials in both anode and cathode.

The performance of the HSC using m-Nb2O5–C significantly surpasses that of the control group. In addition, the Ragone plot shows that the specific power and energy densities of the HSC using m-Nb2O5–C is higher compared to similar HSC systems including TiO2(B)/CNT (●), C–Li2Ti3O7/AC (شت), anatase TiO2/AC (●), CNT/Nb2O5//AC (●), LiCrTiO4//AC (●), C–Li2Ti3O7//AC (شت), and Li1.2(Mn0.32Ni0.32Fe0.16)O2//AC (●).29,31,32 The maximum energy and power densities of this system were 48 W h kg\(^{-1}\) and 14 164 W kg\(^{-1}\), respectively. The high energy density of ~15 W h kg\(^{-1}\) was maintained at a 5.5 s discharge rate, delivering 9897 W kg\(^{-1}\), which is better performance compared with other similar HSC systems. To maximize energy and power densities, the cutoff voltage at the end of charging was increased to 3.5 V (Figure S9ab). In the best mass ratio (2.5:1) of cathode and anode active materials (Figure S8b), the maximum energy (74 W h kg\(^{-1}\)) and power (18 510 W kg\(^{-1}\)) densities were achieved, respectively, without significant capacity degradation (Figure S9c). Furthermore, a high energy density of 20 W h kg\(^{-1}\) was achieved at a 6 s discharge rate with 12 137 W kg\(^{-1}\). Even at 15 W h kg\(^{-1}\), the highest power density of 18 510 W kg\(^{-1}\) was achieved, demonstrating that the HSC using m-Nb2O5–C covers the wide energy and power density regions. This is particularly important for HSCs to bridge between LIBs and SCs, because it is generally not easy for LIBs and SCs to achieve such high energy density at high power region. As shown in Figure S10, the HSC system would be recognized as a next-generation energy-storage device, mainly because of its exceptional electrochemical performances. The reasons for the outstanding electrochemical properties of the HSC using m-Nb2O5–C are as follows. (i) Li\(^{+}\) charge storage preferentially happens in outer surface of Nb2O5 rather than Li-intercalation reaction accompanied by slow solid-state diffusion.23,24 (ii) The porous structure improves surface redox reactions via a large electrolyte-electrode interface area.32,57 (iii) The interconnected mesoporous structure can provide enhanced ion transport.32 (iv) The \textit{in situ} formed carbon significantly increases the electrical conductivity throughout the electrode.46

CONCLUSIONS

In conclusion, the electrochemical performances of Nb2O5 electrodes synthesized by a one-pot synthesis method were solidly investigated for use in HSC systems. The results revealed that the synthesized Nb2O5 samples showed high capacities and rate properties, mainly because of their pseudocapacitive properties. In particular, a novel HSC system comprising a m-Nb2O5–C nanocomposite anode with an MSP-20 cathode provided superior energy and power densities (74 W h kg\(^{-1}\) and 18 510 W kg\(^{-1}\)), with excellent cycling stability. The performance of the HSC using m-Nb2O5–C is comparable or even higher than that of other HSC systems reported. In particular, the highest power density (18 510 W kg\(^{-1}\)) of the HSC using m-Nb2O5–C was achieved at 15 W h kg\(^{-1}\), which is a remarkable result compared to other similar HSC systems. With more research, this HSC system could be one of the main energy-storage systems, along with conventional LIBs and SCs.

METHODS

Synthesis of Nb2O5 Samples. The m-Nb2O5–C and m-Nb2O5 were synthesized by a simple one-pot method using block copolymer (PEO-b-PS, \( M_n = 40\,700\) g/mol, and 12.9 wt % of PEO). For the synthesis of m-Nb2O5–C, niobium ethoxide (0.19 mL, 0.75 mmol) and niobium chloride (0.20 g, 0.75 mmol) were
stirred together in 20 mL of chloroform with 0.2 g of PEO-b-PS. The solution was stirred for 5 h at room temperature and then poured onto a Petri-dish. The Petri-dish was heated to 50 °C to obtain the as-synthesized transparent film. The as-synthesized transparent film was dried at 100 °C overnight and carefully collected. The collected resulting material was heat-treated in N₂ condition at 700 °C for 2 h. To obtain m-Nb₂O₅, the in situ formed carbon of m-Nb₂O₅–C was removed by subsequent calcination in air at 450 °C for 2 h. The b-Nb₂O₅ was also prepared by the same method mentioned above without PEO-b-PS.

**Characterization of Nb₂O₅ Samples.** The Bruker DB Advance X-ray diffractometer (Cu Kα radiation) was employed for identifying powder XRD patterns. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449C thermobalance. SAXS measurements were conducted using a Tristar II 3020 instrument (Micromeritics Instrument Corporation). The mesoporous structures were confirmed by SEM with a S-4200 field-emission SEM (Hitachi). The electron energy loss spectroscopy analysis was carried out using energy-filtering transmission electron microscopy (EF-TEM, JEOL JEM-2200FS). For the TEM analysis, the m-Nb₂O₅–C sample was sectioned at a thickness of 100 nm using a Siemens TECNAI XPL. A Raman spectrometer (Horiba Jobin Yvon, LabRam Aramis) was employed with a laser at 514.532 nm (Ar-ion laser) at a power of 100 μW.

**Electrochemical Characterization.** For the preparation of anode of half-cell tests, the active materials (80 wt %), super-P carbon (10 wt %), and polyvinylidene fluoride (PVDF) (10 wt %) were homogeneously mixed in N-methyl-2-pyrrolidone (NMP), and then the mixtures were coated on a piece of Cu foil. The electrodes were dried at 110 °C overnight and then roll-pressed. The 2032-type coin cells with a Li metal were assembled in an Ar-filled glovebox. LIRP 11,0.0 M in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as the electrolyte (EC/DMC, 1:1 volume ratio). Panaxetec Co., Korea, was carefully balanced to 3:1 in the voltage range of 0.5–3.0 V. For the discharge test of Nb₂O₅ samples, the mass loading of active materials was controlled approximately by 0.4–1.4 mg cm⁻². For cathode of half-cell tests, an activated carbon (MSP-20, 90 wt %) with conductive carbon (5 wt %) and polytetrafluoroethylene (PTFE, 5 wt %) were mixed together, and then the cathode cell was assembled by the same method mentioned above. For full-cell tests of the hybrid supercapacitors, the full-cells were assembled using both Nb₂O₅ electrodes via the same method mentioned above without PEO-b-PS.

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