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High-Power and Long-Life Supercapacitive Performance of Hierarchical, 3-D Urchin-Like W$_{18}$O$_{49}$ Nanostructure Electrodes

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Highly uniform 3-D urchin-like W$_{18}$O$_{49}$ nanoarchitectures (U-WO) consisting of 1-D single-crystalline W$_{18}$O$_{49}$ nanowires are demonstrated as superb supercapacitor electrode materials, along with the unique morphological and structural features. The U-WO electrodes exhibit not only high-rate capability but also long-life cycle performance, resulted in ~176 F g$^{-1}$ at an extremely high current density of 40 A g$^{-1}$ for up to 7000 cycles.

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ABSTRACT
We report the facile, one-pot synthesis of 3-D urchin-like $W_{18}O_{49}$ nanostructures (U-WO) via a simple solvothermal approach. An excellent supercapacitive performance is achieved by the U-WO because of its large Brunauer–Emmett–Teller (BET) specific surface area (ca. 123 m² g⁻¹) and unique morphological and structural features. The U-WO electrodes not only exhibit high rate-capability with a specific capacitance ($C_{sp}$) of ~235 F g⁻¹ at 20 A g⁻¹, but also superior long-life performance for 1000 cycles, and even up to 7000 cycles, showing ~176 F g⁻¹ at 40 A g⁻¹.

KEYWORDS
Hierarchical structure, $W_{18}O_{49}$, High-power, Long cycle life, Supercapacitor
1. Introduction

Supercapacitors (SCs, also known as electrochemical capacitors or ultracapacitors) are considered to be one of the most promising energy-storage devices because of many advantages, such as high-power density, faster charge–discharge (CD) processes, very long cycle life, and relatively low costs [1-5]. It is well-known that pseudocapacitors have a higher capacitance because they employ fast and reversible surface Faradaic redox reactions for charge storage, while electrical double-layer capacitors (EDLCs) merely utilize the electrical charge at the electrode/electrolyte interface. Therefore, great effort has been focused on employing redox-active materials, such as various transition metal oxides (TMO; RuO$_2$, MnO$_2$, NiO$_x$, FeO$_x$, CoO$_x$, MoO$_x$, WO$_{3-x}$, etc.) [6-13] and conducting polymers (polyaniline and polypyrrole) [14, 15] that result in a high specific capacitance ($C_p$) and cycling stability of the pseudocapacitors. TMO-based electrode materials demonstrate a high $C_p$; however, owing to their intrinsically slow Faradaic redox reactions and poor electrical conductivity, their low rate-capability is inevitable and this limits their practical applications for SCs [16-19]. To overcome these inherent drawbacks, alternative materials based on more conductive metal oxides with a highly developed surface area and pore structure are urgently required.

Tungsten oxides (WO$_x$, 2 ≤ x ≤ 3) are potential candidates, which exhibit multiple oxidation states because of the intercalation of electrons and protons into the oxide. This results in the formation of hydrogen tungsten bronzes (H$_2$WO$_3$), and/or the reduction of WO$_x$ through the breaking of tungsten–oxygen bonds [20-27]. Recently, WO$_x$ nanostructures have been intensively investigated as one of the most promising semiconductor materials. In particular, of all the various phases in the WO$_x$ system, the nonstoichiometric phase (i.e., WO$_{3-x}$ form) offers distinctive physical and chemical properties. This makes it an effective candidate for various applications, such as gas sensors [28], field-emitting devices [29, 30], photocatalysts [31], and electrochromic devices [32, 33]. Among the WO$_x$ materials, W$_{18}$O$_{49}$ (or WO$_{2.7}$) has attracted great interest because of its unique structural plane and the oxygen defects within its nanostructures [34, 35]. Furthermore, to date, monoclinic W$_{18}$O$_{49}$ with the largest oxygen deficiency in W$_{18}$O$_{27}$–W$_{30}$ is reported to be the only oxide that can be isolated in a stable form. To fabricate high performance WO$_{3-x}$ electrodes, it is necessary to increase the electrical conductivity of WO$_{3-x}$ to achieve a low total internal resistance and to develop a nanostructured WO$_{3-x}$ with a high surface area via a facile synthetic route. Until now, however, few studies have been conducted on the pseudocapacitive performance of WO$_{3-x}$-based materials [19, 36-39]. Furthermore, to apply WO$_{3-x}$ electrode materials in high-performance SCs, it is still a challenge to achieve a long-life cycling stability with a high $C_p$ and high rate-capability.

Herein, we report on high-performance SC electrodes based on highly uniform 3-D urchin-like W$_{18}$O$_{49}$ nanostructures (denoted as U-WO); in this U-WO, the hierarchical formation consists of a number of 1-D single-crystalline W$_{18}$O$_{49}$ nanowires, and this provides a large Brunauer–Emmett–Teller (BET) specific surface area as well as mesoporous characteristics. These factors are important for the exposure of sufficient electroactive species with a large contact area to the electrolyte, and they also provide structural stability and efficient pathways for the diffusion of ions and the transfer of electrons. This U-WO was easily prepared through a facile, one-pot synthesis via a solvothermal method, using ethanol as a solvent and WCl$_6$ as a tungsten precursor. The possible formation mechanism of the U-WO was demonstrated, and the structural and electrochemical properties of the U-WO electrodes for SC applications were systematically characterized. In particular, with their unique morphological and structural features, the U-WO electrodes were superior in several key areas for high-performance SC applications; they featured high-power and
long-life performance with a high $C_{sp}$.

2. Results and discussion

Figure 1a shows a typical FE-SEM image of the U-WO, which indicates that the U-WO is urchin-like, with a highly uniform diameter of ca. 800 nm. Furthermore, the magnified image reveals that the U-WO has a hierarchical formation consisting of a large number of radial nanowires (inset of Figure 1a). Interestingly, some nanowires constituting the individual U-WO can be touched with the neighbor nanowires of another U-WO, which may indicate the formation of a 3-D network of nanowires. The phase identification and purity of the U-WO were also determined using XRD analysis (Figure 1b). It is well-known that $W_{18}O_{49}$ exhibits a monoclinic-type structure (P2/m; $a = 18.318$ Å, $b = 3.782$ Å, and $c = 14.028$ Å), in which the crystal structure is strongly anisotropic and incorporates an ordered 2-D lattice of connected, edge-sharing, and mutually distorted $WO_6$ octahedra [40, 41-43]. Here, the XRD pattern of the U-WO correlates with the monoclinic-phase, $W_{18}O_{49}$ (JCPDS file #05-0392). Especially, the corresponding pattern exhibits two distinct reflections (at $2\theta = 23.3$ and 47.6°) indexed to the (0k0) planes, whereas all the other reflections are much weaker and broader. These sharp (101) and (020) peaks strongly suggest that the crystal growth occurs preferentially along the b-axis, which is coincident with previously reported 1-D $W_{18}O_{49}$ nanostructures, such as nanowires, nanowhiskers, nanofibers, and nanorods [40, 41-43]. In the monoclinic $W_{18}O_{49}$ structure, the close-packed planes are [010]; thus, the $W_{18}O_{49}$ crystal would preferentially grow along the [010] direction [40]. In addition, the (0k0) peak positions seemed to be slightly shifted to a lower angle. According to Tian et al. [37], this tendency may be due to the existence of a large number of surface oxygen vacancies in the $W_{18}O_{49}$ nanostructures. Importantly, the presence of oxygen vacancies or the nonstoichiometric nature of the material would generally enhance the conductivity [19, 37]. In particular, it is well-known that the existence of a number of oxygen vacancies can narrow the bandgap and improve the electrical conductivity by a large degree [44]. Furthermore, those oxygen vacancies within monoclinic $W_{18}O_{49}$ increase the number of W$^{5+}$ or W$^{4+}$ states, favoring the formation of $H_xW_{18}O_{49}$ and consequently enhancing the charge intercalation ability of
**Figure 2** TEM characterization of U-WO; (a) low- and (b) high-magnification micrographs, (c) HR-TEM image taken from the open-square zone (red line) of (b), and (d) corresponding fast Fourier transform (FFT) pattern.

$W_{18}O_{49}$ nanostructures; that is, the oxygen vacancies can serve as the reactive sites for $H^+$ intercalation and electron transfer, and thereby leads to the enhanced conductivity as well as redox process [45].

Further insights into the morphology and microstructure of the U-WO were obtained using TEM observations. Figure 2a and 2b show the low- and high-magnification TEM images, respectively, indicating that the U-WO not only consists of hierarchical structures, but also possesses numerous nanowires. Furthermore, the nanowires in the U-WO are not densely packed together, particularly at the ends of the nanowires. This feature is quite important for SC electrodes because a porous structure provides a large surface area for contact with the electrolyte filling, thereby generating a number of electroactive sites which enhance the electrochemical performance. These nanowires have a relatively uniform diameter of 5 nm, as shown in Figure 2c. Moreover, the HR-TEM image and corresponding FFT pattern (Figure 2d) further confirm the single-crystalline nature of the $W_{18}O_{49}$ nanowires. Importantly, the $d$-spacing between the well-resolved lattice fringes can be determined as 3.78 Å, corresponding to the (010) planes of the monoclinic $W_{18}O_{49}$. This indicates that the $W_{18}O_{49}$ nanowires are grown preferentially along the [010] direction, which correlates with the results of the XRD analysis. In addition, we also investigated the EDX spectra along with the elemental mapping of “W” and “O” to assist a crystal structure of U-WO, as shown in Figure S1 (Electronic Supplementary Material, ESM), which revealed not only the well-matched units of both W and O elements but also a component ratio of W to O showing the atomic percentages of 4.4 and 11.9% in U-WO, respectively.

Here, based on the above results and those of
literature [41, 46-52], the possible formation of the U-WO was illustrated by the TEM and FE-SEM images (Figure 3). In the current study, the U-WO were prepared by solvothermally treating WCl₆ in ethanol at 200 °C; neither surfactants nor templates were introduced to the reaction system. According to Guo et al. [53], the tungsten oxides (WO₃-x) can be mainly formed by ethanolysis, followed by a hydrolysis process, as described below.

\[
\text{WC}_6 + RCH_2OH \rightarrow (RCH_2O)_n-WCl_m + n\text{HCl} \quad (1), \text{ and }
\]
\[
(RCH_2O)_n-WCl_m + \text{H}_2\text{O} \rightarrow \text{WO}_{3-x} + RCH_2OH + \text{HCl} \quad (2)
\]

(R is the alkyl group.)

Considering reaction (1) and (2), the following mechanism can be proposed. Initially, the rapid hydrolysis rate of the W-containing precursors yielded a supersaturated medium and led to the formation of numerous amorphous particles or W₁₈O₄₉ nuclei. Subsequently, they were aggregated by the well-known Gibbs–Tomson law [54], that is, the larger particles grow at the expense of the smaller ones. Given that the surfaces with the lowest energy within the monoclinic W₁₈O₄₉ are likely to be the {010}-type surfaces [29], these W₁₈O₄₉ crystal clusters that were initially formed tended to be bound by {010}-type facets [55]. The W₁₈O₄₉ crystal clusters functioned as seeds for further crystal growth. Thus, crystalline W₁₈O₄₉ nanorods could initially be formed.
Figure 4 Electrochemical characterization of U-WO electrodes; (a) CV behavior at six different scan rates between 10 and 500 mV s\(^{-1}\), and (inset) enlarged CV curves at scan rates of 10 and 20 mV s\(^{-1}\), (b) galvanostatic discharge profiles at various current densities from 0.5 to 20 A g\(^{-1}\), and (inset) enlarged profiles for current densities of 5, 10, and 20 A g\(^{-1}\), (c) the current density dependence of the \(C_{sp}\). The inset illustrates the facile movement of the ions in the electrolyte and the electron pathways of the U-WO electrode. (d) Ragone plot at various current densities, (e) cycling performance at a current density of 20 A g\(^{-1}\) for 1000 cycles and continuously up to 7000 cycles at a current density of 40 A g\(^{-1}\).

Anisotropically along the closed-packed 010 direction to minimize the surface energy, resulting in the formation of primary urchin rudiments which subsequently serve as a template. With a prolonged reaction, the oriented, urchin-like W\textsubscript{18}O\textsubscript{49} nanowires could be grown further and finally expand into fully synthesized 3-D urchin-like hierarchical architectures.

From this morphological feature based on the oriented self-assembly of the W\textsubscript{18}O\textsubscript{49} nanowires, the U-WO form a hierarchical structure with a large surface area, as depicted by the N\textsubscript{2} adsorption–desorption isotherm shown in Figure S2 (Electronic Supplementary Material, ESM). Such a hierarchical structure results in a very large BET\textsubscript{SSA} of ca. 123 m\(^2\) g\(^{-1}\) as well as mesoporous properties (total pore volume: 0.16 cm\(^3\) g\(^{-1}\)) which are favorable for electrode materials.
Figure 4 shows the electrochemical performance of the U-WO electrode measured in 1 M H_{2}SO_{4} aqueous electrolyte using the three-electrode system. The results of the CV were initially evaluated to investigate the electrochemical behavior at six different scan rates (Figure 4a). It is noted that all the CV curves revealed pseudocapacitive characteristics, showing a pair of redox peaks within the potential range of -0.6–0.4 V (vs. Ag/AgCl). This redox pair is owed to the W_{3}O_{8}-related redox reactions, corresponding to the conversion between the different valence states of W, as follows [45]:

\[
WO_{3-x} + yH^{+} + ye^{-} \leftrightarrow H_{2}WO_{3-x} \tag{3}
\]

The anodic peak is due to the oxidation of WO_{3-x} to H_{2}WO_{3-x} (reaction (3)), which corresponds to a hydration process where electrons from the electrode and H^{+} ions from the H_{2}SO_{4} electrolyte are co-inserted into W_{3}O_{8}; this is usually explained by the double charge injection model [56]. The cathodic peak is due to the reverse process. Importantly, in the case of W_{3}O_{8}, a greater oxygen deficiency increases the number of W^{5+} or W^{6+} states and thereby leads to the enhanced redox process [45]. More importantly, the CV results reveal the high-power characteristics of the U-WO electrode, suggesting fast charge transfer and ion diffusion. This can be supported by the relationship that the current density is quasi-linearly proportional to the scan rate, up to 200 mV s\(^{-1}\), in which the linear relativity (R) is as high as 0.992 (Figure S3, ESM).

Figure 4b presents the time dependence of the galvanostatic discharge profiles of the U-WO electrodes for a series of applied current densities. The variation in the slopes, with one broad plateau that is due to charge transfer, demonstrates the representative pseudocapacitive behavior of the U-WO electrode, which correlates with the results of the CV curves that show one pair of redox peaks (Figure S4, ESM). The discharge profiles also show a low voltage (IR) drop, indicating that the U-WO is a good electrode material for SCs. Especially, the U-WO electrode indicated very low values of IR drops (ca. 0.01 V below) at the relatively low current density of 0.5, 1, 2, and 5 A g\(^{-1}\), whereas they increased slightly when the higher current densities (i.e., 10 and 20 A g\(^{-1}\)) were applied, showing the IR drops of approximately 0.03 and 0.05 V, respectively. However, although these IR drops cause the C\(_{sp}\) loss, we believe that the U-WO electrode can lead to a good capacitive performance with a superior rate capability. Furthermore, the calculated Coulombic efficiency (\(\eta\)), which can be evaluated from the full galvanostatic profiles of U-WO electrode (Figure S4, ESM) along with a following equation: \(\eta\) (%)) = \((t/t_0) \times 100\) [57], also indicated to be more than 99% in all current densities. This means that the almost complete charge/ion transfer during the charge-discharge reaction can be occurred in U-WO electrodes. C\(_{sp}\) was calculated from the discharge profiles (see equation (1), Experimental details), and plotted as a function of the discharge current densities (Figure 4c). Impressively, the U-WO electrode delivered high C\(_{sp}\) values of 324, 315, 309, 296, 271, and 235 F g\(^{-1}\) at current densities of 0.5, 1, 2, 5, 10, and 20 A g\(^{-1}\), respectively. These values are much higher than previously reported values for WO_{3-x}-based materials, which are typically < 200 F g\(^{-1}\) at a current density of 2 A g\(^{-1}\) [19, 38]. In particular, it should be noted that ca. 73% of the C\(_{sp}\) was retained even at a high current density of 20 A g\(^{-1}\) as compared to that at 0.5 A g\(^{-1}\), which indicates the supercapacitive performance of the U-WO electrode (i.e., high rate-capability and high-power). This result can be further confirmed by the Ragone plot (energy density vs. power density; for details of the calculation, see equation (2) and (3) in Experimental details), as shown in Figure 4d. When the current density was increased from 0.5 to 20 A g\(^{-1}\), the U-WO electrode achieved specific energy and power density values ranging from 158 to 106 Wh kg\(^{-1}\) and 250 to 9500 W kg\(^{-1}\), respectively. These were located in the upper right corner of the Ragone plot compared to other reported cases based on WO_{3-x} (Figure S5, ESM). It is particularly impressive to achieve such enhanced power and energy densities at high current densities, such as 10 and 20 A g\(^{-1}\). In addition, to confirm the capacitive contribution of graphite sheets in U-WO electrodes, we also evaluated the CV of a bare graphite sheet under the
same measurement conditions and compared to that of the U-WO electrode (Figure S6, ESM). Especially, in the case of bare graphite sheet, the CV area, which is related to the capacitive values, is not only almost “zero” at all scan rates but also extremely much smaller than that of the U-WO electrode and thus, the capacitive effect of graphite sheets may be negligible.

More importantly, the U-WO electrode not only enhanced the $C_{sp}$, but also promoted sustainability at a high current density. Figure 4e demonstrates the cycling performance of the U-WO electrode determined with two different current densities. During the initial stages, it was demonstrated that the $C_{sp}$ increased steadily until the 100th cycle, demonstrating the surface activation of the U-WO electrode. In general, this increase in the capacitance can be demonstrated as the electro-activation process of the active materials along with the galvanostatic cycling, which is observed in both metal oxides and carbon-based materials. According to the previous reports [58-60], this phenomenon is likely related to a cycling-induced improvement in the surface wetting of the electrode, leading to more electroactive surface area and furthermore, the long-life cycling (i.e., long time charging and discharging) may also help the ions accessing fully the electrode materials to take full advantages of the surface area. Subsequently, the $C_{sp}$ stabilized without any capacitance loss and even slightly increased as the number of cycles increased, which was demonstrated by the $C_{sp}$ of ca. 235 F g$^{-1}$ for up to 1000 cycles at a current density of 20 A g$^{-1}$. The cycling performance and change in the current density were also continuously evaluated for up to 7000 cycles. When a higher current density of 40 A g$^{-1}$ was applied to the electrode, the $C_{sp}$ decreased to approximately half of that at 20 A g$^{-1}$ because of the sluggish redox reaction kinetics (i.e., the lower diffusion of charged ions) at rapid potential changes [61]. However, no obvious fading of the $C_{sp}$ was observed as the number of cycles increased, indicating the excellent long-life cycling stability of the U-WO electrode. At the (final) 7000th cycle, the $C_{sp}$ was ca. 176 F g$^{-1}$. Furthermore, the majority of the U-WO material maintained its original structure and morphology without significant collapse (Figure S7, ESM) which suggests that the high structural stability and long-life performance of the U-WO can be guaranteed. In addition, to further study the capacitive behavior and conductivity of U-WO electrode during the charge-discharge cycles, we also evaluated electrochemical impedance spectroscopy (EIS) analyses along with the increase of cycles (Figure S8, ESM). Importantly, the impedance spectra of U-WO electrode showed the very low charge-transfer resistances, which results from the electron transfer and can be calculated from the diameter of the semicircle, even though the charge-transfer resistances were slightly increased with the increase of cycles. Furthermore, it also revealed the low equivalent series resistance (ESR) related to a combination of the ionic resistance of the electrolyte, intrinsic resistance of the active materials, and contact resistance at the active material-current collector interface in the high-frequency region, where the impedance curve intercepts on the real axis. These results suggest a good conductivity as well as electrochemical stability of U-WO electrode; that is, a good capacitive behavior for the charge-discharge cycles and significant feasibility of redox reactions even after the long-life cycling.

In terms of the high rate-capability and long-life cycling stability, the supercapacitive performance of our material is fairly competitive, compared to the various reported electrodes based on tungsten oxides (see ESM, Table S1). The remarkably outstanding electrochemical performance of the U-WO as a SC electrode could mainly be attributed to the following effects owed to the unique morphological and structural features of the U-WO. First, the 3-D hierarchical structures generate large open spaces through the separation of adjacent U-WO and the development of a valley-like ‘V’ formation between the 1-D nanowires of individual U-WO. This facilitates the electrolyte penetration and shortens the diffusion path for both electrons and ions, resulting in an increased number of electroactive sites, reduced internal resistance, and high-power performance. Moreover, each nanowire of the U-WO can effectively function as a fast electron pathway.
Second, the presence of oxygen vacancies within the nonstoichiometric form of the W\textsubscript{18}O\textsubscript{49} structure results in an enhanced electronic conductivity, thus improving the electrochemical performance. Therefore, we believe that the combination of these factors in the U-WO electrodes resulted in the excellent supercapacitive performance.

3. Conclusions

In summary, U-WO were successfully synthesized using a simple solvothermal reaction, in which the U-WO exhibited a hierarchical formation consisting of numerous single-crystalline W\textsubscript{18}O\textsubscript{49} nanowires. The U-WO have a large BET\textsubscript{SSA} (ca. 123 m\textsuperscript{2} g\textsuperscript{-1}) as well as mesoporous properties, which provides more contact between the electroactive sites on the U-WO electrodes and the electrolyte. As a result, the U-WO electrodes realized an excellent supercapacitive performance with a high \(C_p\) of \(\sim 235\) F g\textsuperscript{-1} at 20 A g\textsuperscript{-1} and even \(\sim 176\) F g\textsuperscript{-1} at 40 A g\textsuperscript{-1} for up to 7000 cycles. Both the outstanding high-power and long-life performance can be attributed to the combination of the unique morphological and structural features of the U-WO, including the oxygen defects within its nanostructures.

4. Experimental details

4.1. Materials

WCl\textsubscript{6} (99.9\%) and absolute ethanol were purchased from Sigma Aldrich and used directly as the W\textsuperscript{6+} precursor and reaction solvent, respectively, without further purification.

4.2. Synthesis of Hierarchical, 3-D Urchin-like W\textsubscript{18}O\textsubscript{49} Nanostructures (U-WO)

The U-WO were prepared via a simple solvothermal reaction similar to previously reported solution-based methods [40]. Using a typical synthetic procedure, WCl\textsubscript{6} (0.405 g) was dissolved in absolute ethanol (70 ml), and the solution was sonicated for 10 min at room temperature, resulting in a transparent yellow solution. Subsequently, the solution was transferred to a Teflon-lined autoclave, which was sealed and heated at 200 °C for 10 h, and then naturally cooled to room temperature. A deep-blue precipitate was subsequently collected by centrifugation, and repeatedly rinsed with ethanol and distilled water to remove ions and possible remnants, followed by vacuum drying at 50 °C.

4.3. Materials characterization

The crystal structure and phase impurities of the product were identified by powder X-ray diffraction (XRD) analysis using a Bruker D8-Advance (Cu Kα radiation) diffractometer operated at 40 kV and 40 mA in the range of 20° to 60°; SEM observations were performed using a JEOL JSM-6330F field-emission scanning electron microscope (FE-SEM; JEOL Ltd., Japan). The morphology and microstructure of the U-WO were further investigated by a transmission electron microscope (TEM; model JEM-2100F, JEOL Ltd., Japan) equipped with an energy dispersive X-ray analysis system and a high-resolution TEM (HR-TEM) with an accelerating voltage of 200 keV. In addition, the nitrogen adsorption–desorption isotherms recorded at 77 K were examined to determine the BET specific surface area (BET\textsubscript{SSA}) and the Barret–Joyner–Halenda (BJH) pore size-distribution (model BELSORP-max, BEL Inc., Japan).

4.4. Electrochemical evaluation

All the electrochemical measurements were performed at room temperature using an Ivium-n-Stat electrochemical workstation (Ivium Technologies B. V., Netherlands) with a simple, homemade, beaker-type three-electrode cell system. A typical working electrode was prepared by thoroughly mixing the U-WO powder as the active material (80 wt\%) together with 10 wt\% conducting additives (Super-P\textsuperscript{TM} carbon black, MMM Carbon, Belgium) in an agate mortar until a homogenous black powder was obtained. The active material (U-WO powder) was typically used 1-2 mg and mixed with commercially available Super-P\textsuperscript{TM} carbon black. Then, as-dissolved KYNAR 2801 binder (10 wt\%, PVDF-HFP) in N-methyl-2-pyrrolidinone
(NMP, Sigma-Aldrich) solvent was added to form a slurry with the mixture composed of active material and conductive carbon. To achieve uniform mixing of all components, the slurry was mixed using a homo-mixer (model Dispenser T 10 basic ULTRA-TURRAX®, IKA, Germany) and was also carried out by ultrasonic treatment to give enough dispersion in several times. After the solvent was briefly allowed to evaporate, the resulting paste was coated onto a piece of graphite sheet (thickness: 0.09 mm) as current collector and was maintained at 110 °C in a vacuum oven for 6 h. The sheet was subsequently pressed under 10 MPa. As a result, the working electrode was fabricated, which contained the mass loading of typically 3–5 mg of the active material and had a geometric surface area of approximately 1 cm² on the current collector. A platinum gauze and a KCl-saturated Ag/AgCl electrode were used as the counter and reference electrode, respectively, and 1 M H₂SO₄ aqueous solution was utilized as the electrolyte. In addition, when the electrochemical measurements are carried out in the three-electrode system, the distance between the working electrode and the counter electrode (Pt gauze) was less than 1 cm.

Cyclic voltammetry (CV) was initially conducted to confirm the pseudocapacitive behavior of the U-WO electrode in a fixed voltage window of -0.6–0.4 V (vs. Ag/AgCl) at various scan rates (10 to 500 mV s⁻¹). Galvanostatic CD profiles were also obtained with current densities of 0.5, 1, 2, 5, 10, and 20 A g⁻¹ in a working potential range of -0.55 to 0.4 V (vs. Ag/AgCl) to provide more accurate capacitance values for the SCs. The long-term cycling stability was also evaluated using CD measurements at a current density of 20 A g⁻¹ for 1000 cycles, and subsequently at a current density of 40 A g⁻¹ for up to 7000 cycles.

4.5. Calculation of specific capacitance, energy density, and power density

The \( C_{sp} \), energy density (E), and power density (P) of the U-WO electrode were calculated from the constant current discharge profiles using the following equations [62]:

\[
C_{sp} \left( F g^{-1} \right) = \frac{1}{2} \frac{\Delta t}{M \Delta V} \tag{1}
\]

\[
E \left( Wh kg^{-1} \right) = \frac{1}{2} C_{sp} \Delta V^2 \tag{2}
\]

\[
P \left( kW kg^{-1} \right) = \frac{E}{\Delta t} \tag{3}
\]

where \( \Delta V \) (in V) is the working potential window, \( I \) (in mA) is the amount of current applied to the electrode during discharging, \( \Delta t \) (in sec) is the period of time elapsed during the discharge, and \( M \) (in mg) is the mass loading of the active materials.

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Electronic Supplementary Material: Supplementary material further N₂ adsorption-desorption isotherm, Plot of scan rate dependence of peak current, Ragone plot, XRD, FE-SEM analysis, and Table S1 is available in the online version of this article at [http://dx.doi.org/10.1007/s12274-***.****.*](http://dx.doi.org/10.1007/s12274-***.****.*).

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Electronic Structure of the Monoclinic and Hexagonal Trioxides of Tungsten and


Silver Nanowires with Semiconducting Ligands for Low Temperature Transparent Conductors

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Abstract

Metal nanowire networks represent a promising candidate for the rapid fabrication of transparent electrodes with high transmission and low sheet resistance values at very low deposition temperatures. A commonly encountered obstacle in the formation of conductive nanowire electrodes is establishing high quality electronic contact between nanowires in order to facilitate long range current transport through the network. A new system of nanowire ligand removal and replacement with a semiconducting sol-gel tin oxide matrix has enabled the fabrication of high performance transparent electrodes at dramatically reduced temperatures with minimal need for post-deposition treatments of any kind.

Keywords: Silver Nanowires, Sol-Gel, Transparent Electrodes, Nanocomposites
1. Introduction.

Silver nanowires (AgNWs) are long, thin, and possess conductivity values on the same order of magnitude as bulk silver (Ag) [1]. Networks of overlapping nanowires allow light to easily pass through the many gaps and spaces between nanowires, while transporting current through the metallic conduction pathways offered by the wires themselves. The high aspect ratios achievable for solution-grown AgNWs has allowed for the fabrication of transparent conductors with very promising sheet resistance and transmission values, often approaching or even surpassing the performance of vacuum-processed materials such as indium tin oxide (ITO) [2-6].

Significant electrical resistance within the metallic nanowire network is encountered only when current is required to pass between nanowires, often forcing it to pass through layers of stabilizing ligands and insulating materials that are typically used to assist with the synthesis and suspension of the nanowires [7, 8]. The resistance introduced by the insulating junctions between nanowires can be reduced through various physical and chemical means, including burning off ligands and partially melting the wires via thermal annealing [9, 10], depositing additional materials on top of the nanowire network [11-14], applying mechanical forces to enhance network morphology [15-17], or using various other post-treatments to improve the contact between adjacent wires [18-21]. Any attempt to remove insulating materials the network must be weighed against the risk of damaging the wires or blocking transmitted light, and so many such treatments must be reined in from their full effectiveness to avoid endangering the performance of the completed electrode.

We report here a process for forming inks with dramatically enhanced electrical contact between AgNWs through the use of a semiconducting ligand system consisting of tin oxide (SnO$_2$) nanoparticles. The polyvinylpyrrolidone (PVP) ligands introduced during AgNW synthesis in order to encourage one-dimensional growth are stripped from the wire surface using ammonium ions, and are replaced with substantially more conductive SnO$_2$, which then fills the space between wires and enhances the contact geometry in the vicinity of wire/wire junctions. The resulting transparent electrodes are highly conductive immediately upon drying, and can be effectively processed in air at virtually any temperature below 300 °C. The capacity for producing high performance transparent electrodes at room temperature may be useful in the fabrication of devices that are damaged upon significant heating or upon the application of harsh chemical or mechanical post-treatments.

2. Results and Discussion

2.1. Ink Formulation and Characterization

Dispersed AgNWs synthesized using copper chloride seeds represent a particularly challenging material system for promoting wire/wire junction formation, and often require thermal annealing at temperatures near or above 200 °C to induce long range electrical conductivity within the deposited network [22, 23]. The difficulties that these wires present regarding junction formation is potentially due to their relatively large diameters compared to nanowires synthesized using other seeding materials, which has the capacity to enhance the thermal stability of individual wires according to the Gibbs-Thomson effect. We have chosen these wires as a demonstration of pre-deposition semiconducting ligand substitution in order to best illustrate the contrast between treated and untreated wires.

Completed nanocomposite inks are formed by mixing AgNWs with SnO$_2$ nanoparticles in the presence of a compound capable of stripping the ligands from the AgNW surface. In this work, we have found that ammonia or ammonium salts act as effective stripping agents that are able to remove the PVP layer from the AgNW surface and allow for a new stabilizing matrix to take its place. Figure 1 shows a schematic of the process, starting from the precursors used in nanowire and nanoparticle synthesis and ending with the deposition of a completed film. The SnO$_2$ nanoparticle solution naturally contains enough ammonium ions from its own synthesis to effectively peel the insulating ligands from the AgNWs and allow the nanoparticles to replace them as a stabilizing agent. If not enough SnO$_2$ nanoparticles are used in the mixture, then the wires will rapidly agglomerate and settle to the bottom as large clusters. Large amounts of SnO$_2$ in the mixture gradually begin to increase the sheet resistance of the nanowire network upon deposition, but greatly enhance the uniformity, durability, and wetting properties of the resulting films. We have found that AgNW:SnO$_2$ weight ratios ranging between 2:1 and 1:1 produce well dispersed inks that are still highly conductive when deposited as films.

The nanowires were synthesized using a polyol method that has been adapted from the recipe described by Lee et al. [22, 23] Silver nitrate dissolved in ethylene glycol via ultrasonication was used as a precursor in the presence of copper chloride and PVP to provide seeds and produce anisotropic morphologies in the reaction products. Synthetic details can be found in the experimental section. Distinct from previous recipes, we have found that repeating the synthesis two times without cooling down the reaction mixture generally produces significantly longer nanowires than a single reaction step. The lengths of nanowires produced using this method fall over a wide range from 15 to 65 microns, with diameters between 125 and 250 nm. This range of diameters is common for wires grown using copper chloride seeds, although the double reaction produces a number of wires with roughly twice their usual diameter. The morphology of the as-deposited AgNWs as determined via SEM is shown in Figure 2(a), higher magnification images are also provided in Figures 2(c) and 2(d).
The SnO$_2$ nanoparticles were synthesized using a sol-gel method typical for multivalent metal oxide gelation reactions. A large excess of deionized water was added to SnCl$_2$·5H$_2$O dissolved in ethylene glycol along with tetramethylammonium chloride and ammonium acetate to act as surfactants. The reaction was then allowed to progress for at least one hour at near reflux conditions, after which the resulting nanoparticle dispersion can be collected, washed, and dispersed in a polar solvent of choice. The material properties of SnO$_2$ nanoparticles formed using a similar synthesis method have been reported previously [24], although the present recipe uses excess water to ensure that the hydrolysis reaction proceeds nearly to completion.

After mixing with SnO$_2$ nanoparticles, films deposited from AgNW/SnO$_2$ composite inks show a largely continuous nanoparticle layer on the substrate surface with some nanowires partially buried and some sitting more or less on top of the film. Representative scanning electron microscopy (SEM) images of nanocomposite films are shown in Figure 2(b). Regardless of their position relative to the SnO$_2$ film, all nanowires show a distinct shell on their outer surface that gives them a soft and slightly rough appearance, as is visible in the higher magnification images shown in Figure 2(e) and 2(f). The SnO$_2$ nanoparticles do a particularly good job coating the regions near and around junctions between wires, and frequently appear in the SEM images as bulges wrapped around the wire/wire contact points.

The precise morphology of the SnO$_2$ shell that effectively surrounded each AgNW was analyzed in more detail using transmission electron microscopy (TEM) imaging. Figures 3(a) to 3(e) show individual nanowires in the presence of different ligand systems: as-synthesized PVP in Figure 3(a), inactive SnO$_2$ in Figure 3(b), and SnO$_2$ activated with trace amounts of ammonium ions in Figure 3(e). The as-synthesized nanowires show sharp edges, and few surface features. In the presence of inactive SnO$_2$, which is formed by repeatedly washing the SnO$_2$ nanoparticles in ethanol until all traces of ammonium ions are removed, the nanowires coexist with somewhat randomly distributed nanoparticles that deposit all over the surface of the TEM grid. When AgNWs are mixed with activated SnO$_2$, a thick and continuous SnO$_2$ shell is formed along the nanowire surface. In when sufficiently dilute SnO$_2$ solutions are used to form the nanocomposite ink, nearly all of the nanoparticles are consumed during shell formation and effectively no nanoparticles are left to randomly populate the rest of the image.

As the AgNWs acquire their metal oxide coatings in solution, the properties of the mixture change dramatically. Freshly synthesized AgNWs coated with residual PVP ligands slowly settle to the bottom of their vial or flask over a time period of several hours to one day, forming a dense layer at the bottom. The AgNWs with SnO$_2$ shells do not settle to the bottom, but remain partially suspended even after many weeks at concentrations that are dependent on the amount of SnO$_2$ present in the solution.

A comparison of the settling behavior of various AgNW and SnO$_2$ mixtures after 24 hours is shown in Figures 3(d) and 3(e). The ratios 8:4, 8:16, and 8:8 indicate the concentrations of AgNWs and SnO$_2$ (in mg/mL) present in each solution. The 8:8 uncoupled solution, in which the PVP is not removed from the AgNW surface with ammonia, produces a situation in which the nanowires and nanoparticles do not interact with one another, and instead the nanowires settle as in the isolated nanowire solution while the nanoparticles remain well-dispersed as in the solution of pure SnO$_2$. The mixtures of nanowires and nanoparticles in which trace amounts of ammonia are present do not settle to the bottom, but instead concentrate themselves until repulsion between the semiconducting SnO$_2$ clusters is able to prevent further settling.

Our current explanation for the settling behavior of the wire/particle mixtures is that the PVP coating on the surface of the as-synthesized wires is sufficient to prevent interaction with the nanoparticle solution. The addition of ammonia into the solution quickly strips off the PVP surface coating and allowing the nanoparticles to coordinate directly with the nanowire surface. This explanation is in agreement with the effects of ammonia has on a solution of pure AgNWs, which rapidly begin to agglomerate into clusters and sink to the bottom as soon as any significant quantity of ammonia is added to the ink.

We attribute the stripping ability of ammonia in these mixtures to the strong dative interactions that occur via the lone pair on the nitrogen atom interacting with the partially filled $d$-orbitals of the Ag atoms on the nanowire surface. These interactions are evidently strong enough to displace the existing coordination of the five-membered rings and carbonyl groups contained in the original PVP ligands and allow the ammonia to attach directly to the nanowire surface. Since ammonia is one of the original surfactants used to stabilize the surface of the SnO$_2$ nanoparticles, we consider it reasonable that ammonia coordination on the nanowire surface would provide an appropriate environment for the nanoparticles to adhere to the AgNWs.
Scanning Energy Dispersive X-ray (EDX) Spectroscopy was also conducted on nanoparticle-coated AgNWs in order to image the presence of Sn and Ag in the nanowire and shell layer. The line scan results are shown in Figure 3(f), having been normalized to better compare the widths of the two signals. The visible broadening of the Sn lineshape compared to that of Ag is indicative of a Sn layer along the outside of the wire. The increasing strength of the Sn signal toward the center of the AgNW is likely due to the enhanced interaction between the TEM’s electron beam and the dense AgNW, which then improves the signal originating from the SnO₂ shell as well. It is also possible that there is some intermixing between the Ag and Sn x-ray signals, but we consider this to be less likely as the distance between their characteristic peaks should be larger than the detection system’s energy resolution.

2.2. Network Deposition and Device Applications

For the deposition of transparent conducting films, a weight ratio of 2:1 of AgNWs to SnO₂ nanoparticles was chosen in order to obtain a balance between the dispersibility of the nanowires, the uniformity of coated films, and the sheet resistance of the resulting conductive networks. Nanocomposite films were deposited on glass by blade coating from an ethanol solution using a Scotch tape spacer, with deposited networks then being allowed to dry naturally in air over several minutes.

The as-dried nanocomposite films are highly conductive, and require only minimal thermal treatment to dry and harden the film. Without the use of activated SnO₂ ligands, deposited nanowire networks are highly insulating, and become conductive only after annealing at above 200 °C. The sheet resistance values of representative films are shown in Figure 4(a). The capability to form transparent conductive networks in a single deposition step that remain useful over a wide range of processing temperatures provides a high degree of versatility for designing thin film device fabrication procedures.

Figure 5(a) shows the sheet resistance and transmission of a number of nanocomposite films deposited from inks containing different nanowire concentrations. The deposited films show excellent conductivity at transmission values up to 85%, and then rapidly increase in sheet resistance as the network begins to reach its connectivity limit. The optimum performance of these networks at low to moderate transmission values is a consequence of the relatively large nanowire diameters, which scatter a noticeable amount of light even when the conditions required for current percolation are just barely met. Nonetheless, the sheet resistance and transmission of the completed nanocomposite networks place them within an acceptable range for applications in a variety of optoelectronic devices. Figure 5(b) shows the wavelength dependent transmission spectra of several nanowire networks, which transmit light well out into the infrared region. The presence of high transmission values out to wavelengths well above 1300 nm, where ITO or other conductive oxide layers would typically begin to show parasitic absorption, is due to the use of semiconducting SnO₂ ligands, which is complimentary to the broad spectrum transmission of the silver nanowire network itself.

Avoiding the use of highly doped nanoparticles has the potential to provide optical advantages, but can create difficulties when attempting to make electrical contact to neighboring device layers. In order to investigate their functionality in thin film devices, we have incorporated AgNW/SnO₂ nanocomposite films as electrodes in amorphous silicon (a-Si) solar cells. Two contact structures were used during fabrication: one with the nanocomposite film directly in contact with the p-i-n absorber structure and one with a 10 nm Al/ZnO (AZO) layer present to assist in forming Ohmic contact with the device. The I-V characteristics of the resulting devices are shown in Figure 6(a).

The thin AZO contact layers typically show sheet resistance values greater than 2.5 kΩ/□, and so cannot be responsible for long range lateral current transport within the electrode structure. However, their presence is clearly beneficial in improving contact between the nanocomposite electrode and the absorber material, as the SnO₂ matrix material is evidently not conductive enough to form a high quality contact with the p-type side of the a-Si stack. We hope that future modifications to the AgNW/SnO₂ composite, or perhaps the use of islands of high conductivity material such as a discontinuous layer of doped nanoparticles will allow for the deposition of completed electrode stacks that provide both rapid fabrication and good performance.

Figure 6(b) contains the top view image of a completed device. The enhanced viscosity of the nanowire/sol-gel composite inks allows for films to be blade coated onto substrates with a variety of surface properties without reductions in network uniformity. In contrast with traditional back electrodes deposited in vacuum environments, the nanocomposite can be blade coated into place in a single pass under atmospheric conditions and dried within moments. We anticipate that the use of sol-gel mixtures to enhance wetting and dispersibility may prove useful in the formulation of other varieties of semiconducting and metallic inks for deposition onto a variety of substrate structures.

3. Conclusions

In summary, we have successfully exchanged the insulating ligands that normally surround as-synthesized AgNWs with shells of substantially more conductive SnO₂ nanoparticles. The exchange of one set of ligands for the other is mediated by
the presence of ammonia during the mixing process, which appears to be necessary for the effective removal of the PVP ligands that initially cover the nanowire surface. The resulting nanowire/nanoparticle mixtures allow for the deposition of nanocomposite films that require no annealing or other post-treatments to function as high quality transparent conductors with transmission and sheet resistance values of 85% and 10 Ω/□, respectively. Networks formed in this manner can be deposited quickly and easily in open air, and have been demonstrated as an effective n-type electrode in a-Si solar cells when a thin interfacial layer is deposited first to ensure good electronic contact with the rest of the device. The ligand management strategy described here could potentially be useful in any number of material systems that presently suffer from highly insulating materials that reside on the surface of otherwise high performance nano and microstructures.

4. Experimental Details

**Tin oxide nanoparticle synthesis.** Tin chloride pentahydrate was dissolved in ethylene glycol by stirring for several hours at a concentration of 10 grams per 80 mL to serve as a stock solution. In a typical synthesis reaction, 10 mL of the SnCl₄·5H₂O stock solution is added to a 100 mL flask and stirred at room temperature. Still at room temperature, 250 mg ammonium acetate and 500 mg ammonium acetate were added in powder form to regulate the solution pH and to serve as coordinating agents for the growing oxide nanoparticles. 30 ml of water was then added, and the flask was heated to 90 °C for 1 to 2 hours in an oil bath, during which the solution took on a cloudy white color. The gelled nanoparticles were then washed twice in ethanol in order to keep trace amounts of ammonia present in the solution. Additional washing cycles would deactivate the SnO₂, and then require the addition of ammonia to coordinate with as-synthesized AgNWs.

**Silver nanowire synthesis.** Copper(ii) chloride dihydrate was first dissolved in ethylene glycol at 1 mg/ml to serve as a stock solution for nanowire seed formation. 20 ml of ethylene glycol was then added into a 100 ml flask, along with 200 µL of copper chloride solution. the mixture was then heated to 150 °C while stirring at 325 rpm, and .35g of PVP (MW 55,000) was added. In a small separate flask, .25 grams of silver nitrate was dissolved in 10 ml ethylene glycol by sonicating for approximately 2 minutes, similar to the method described here. The silver nitrate solution was then injected into the larger flask over approximately 15 minutes, and the reaction was allowed to progress for 2 hours. After the reaction had reached completion, the various steps were repeated without cooling down. 200 µL of copper chloride solution and .35g PVP were added in a similar manner to the first reaction cycle, and another .25g silver nitrate were dissolved via ultrasonics and injected over 15 minutes. The second reaction cycle was allowed to progress for another 2 hours, before the flask was cooled and the reaction products were collected and washed three times in ethanol.

**Nanocomposite ink formation.** After the synthesis of the two types of nanostructures is complete,
the double washed SnO\textsubscript{2} nanoparticles and triple-washed nanowires can be combined at a variety of weight ratios to form the completed nanocomposite ink. The dispersibility of the mixture is improved when more SnO\textsubscript{2} is used, although the sheet resistance of the final networks will begin to increase if they contain excessive SnO\textsubscript{2}. AgNW agglomeration during mixing is most easily avoided if the SnO\textsubscript{2} and AgNW solutions are first diluted to the range of 10 to 20 mg/ml in ethanol, with the SnO\textsubscript{2} solution being added first to an empty vial and the AgNW solution added afterwards. The dilute mixture was then be allowed to settle overnight, and the excess solvent removed to concentrate the wires to a concentration that is appropriate for blade coating.

**Film and electrode deposition.** The completed nanocomposite ink was deposited onto any desired substrates using a razor blade and scotch tape spacer. The majority of the substrates used in this study were Corning soda lime glass, but the combined inks also deposited well on silicon, SiO\textsubscript{2}, and any other substrates tested. Electrode deposition onto a-Si substrates was accomplished by masking off the desired cell area with tape, and then depositing over the entire region. The p-i-n a-Si stacks and 10 nm AZO contact layers were deposited using PECVD and sputtering, respectively.

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Figure 1. Process flow diagram showing the synthesis of AgNWs and SnO$_2$ nanoparticles followed by stirring in the presence of ammonium salts to create the final nanocomposite ink. Transparent conducting films were produced by blade coating the completed inks onto the desired substrate.
Figure 2. (a,c,d) SEM images of as-synthesized AgNWs at various magnifications. (b,e,f) SEM images of nanocomposite films, showing the tendency of the SnO₂ nanoparticles to coat the entire outer surface of the AgNWs, increasing their apparent diameter and giving them a soft appearance.
Figure 3. Schematic diagrams and TEM images of (a) a single untreated AgNW, (b) an AgNW in the presence of uncoupled SnO₂ (all ammonium ions removed), and (c) an AgNW with a coordinating SnO₂ shell. Scale bars in images (a), (b), and (c) are 300 nm, 400 nm, and 600 nm, respectively. (d,e) Optical images of AgNW and SnO₂ nanoparticle dispersions mixed in varying amounts (d) before and (e) after settling for 24 hours. The numbers associated with each solution represent the AgNW:SnO₂ concentrations in mg/ml. The uncoupled solution contains AgNWs and non-coordinating SnO₂ nanoparticles, and shows settling behavior similar to the pure AgNW and pure SnO₂ solutions. (f) Normalized Ag and Sn EDX signal mapped across the diameter of a single nanowire, with the inset showing the scanning path across an isolated wire.
Figure 4. Sheet resistance versus temperature for films deposited using (red) AgNWs that have been washed three times in ethanol and (blue) mixtures of AgNW and SnO$_2$ with weight ratio of 2:1. The annealing time at each temperature value was approximately 10 minutes. The large sheet resistance values of the bare AgNWs when annealed below 200 °C is typical for nanowires fabricated using copper chloride seeds, which clearly illustrate the impact of SnO$_2$ coordination at low treatment temperatures.
Figure 5. (a) Sheet resistance and transmission data for samples deposited from solutions of varying nanostructure concentration. Each of these samples were fabricated starting from the same nanocomposite ink, which was then diluted to a range of concentrations while maintaining the same AgNW to SnO$_2$ weight ratio. (b) Transmission spectra of several transparent conducting networks chosen from the plot in plot (a).
**Figure 6.** (a) I-V characteristics of devices made with AgNW/SnO$_2$ rear electrodes with (blue) and without (red) a 10 nm AZO contact layer. The dramatic double diode effect is likely a result of a significant barrier to charge injection at the electrode/a-Si interface. (b) Top view SEM image of the AgNW/SnO$_2$ composite films on top of the textured a-Si absorber. (c) Schematic cross section of the a-Si device architecture used in solar cell fabrication. The thickness of the thin AZO contact layer is exaggerated for clarity.