Metal Nanowire-Based Hybrid Electrodes Exhibiting High Charge/Discharge Rates and Long-Lived Electrocatalysis

Rakesh K. Pandey,§†‡ Yuto Kawabata,§† Satoshi Teraji,† Tomohisa Norisuye,† Qui Tran-Cong-Miyata,† Siowling Soh,*†‡ and Hideyuki Nakanishi*†§

†Department of Macromolecular Science and Engineering, Graduate School of Science and Technology, Kyoto Institute of Technology, Matsugasaki, Kyoto 606-8585, Japan
‡Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117585, Singapore

Supporting Information

ABSTRACT: Nanostructured electrodes are at the forefront of advanced materials research, and have been studied extensively in the context of their potential applications in energy storage and conversion. Here, we report on the properties of core−shell (gold-polypyrrole) hybrid nanowires and their suitability as electrodes in electrochemical capacitors and as electrocatalysts. In general, the specific capacitance of electrochemical capacitors can be increased by faradaic reactions, but their charge transfer resistance impedes charge transport, decreasing the capacitance with increasing charge/discharge rate. The specific capacitance of the hybrid electrodes is enhanced due to the pseudocapacitance of the polypyrrole shells; moreover, the electrodes operate as an ideal capacitive element and maintain their specific capacitance even at fast charge/discharge rates of 4690 mA/cm² and 10 V/s. These rates far exceed those of other types of pseudocapacitors, and are even superior to electric double layer-based supercapacitors. The mechanisms behind these fast charge/discharge rates are elucidated by electrochemical impedance spectroscopy, and are ascribed to the reduced internal resistance associated with the fast charge transport ability of the gold nanowire cores, low ionic resistance of the polypyrrole shells, and enhanced electron transport across the nanowire’s junctions. Furthermore, the hybrid electrodes show great catalytic activity for ethanol electro-oxidation, comparable to bare gold nanowires, and the surface activity of gold cores is not affected by the polypyrrole coating. The electrodes exhibit improved stability for electrocatalysis during potential cycling. This study demonstrates that the gold-polypyrrole hybrid electrodes can store and deliver charge at fast rates, and that the polypyrrole shells of the nanowires extend the catalytic lifetime of the gold cores.

KEYWORDS: electrochemical energy storage, capacitance, rate performance, ethanol electrooxidation, conducting polymer, catalytic activity

INTRODUCTION

Nanowires (NWs) have been of great interest for use as electrodes for electrochemical capacitors (ECs)¹–³ and photo-electrochemical cells,⁴,⁵ since their one-dimensional (1D) nanostructures create short diffusion pathways for ions and excitons, leading to an increase in charge storage capacity and photoelectric conversion efficiency. Metal oxides have been extensively studied as electrode materials for these devices, and formed into complex NW structures, giving rise to intriguing functionality and properties (e.g., core−shell p−n junction allowing efficient charge separation, and radially grown NWs on fibrils for wearable energy devices).⁵,⁶ On the other hand, metal NWs, and hybrid electrodes using metal NWs and conducting polymers, have not been investigated nearly as extensively, even though metals exhibit high electrical conductivity, preventing energy dissipation,⁶ and have the ability to catalyze electrochemical reactions.⁴,⁵ Here, we demonstrate that gold (Au) NWs hybridized with polypyrrole (Ppy) exhibit enhanced...
electrochemical energy storage and electrocatalysis. Ppy is a promising pseudocapacitive material with high electrical conductivity that is environmentally friendly. Our electrodes are based on arrays of AuNWs covered with a thin layer of Ppy, forming a core–shell (Au–Ppy) NW structure. When characterized for use in ECs, these hybrid NW electrodes exhibit a dramatic increase in capacitance, due to the pseudocapacitance of Ppy, while their electrical resistance is remarkably low, allowing for ECs with simultaneously high energy and power densities. When used for the electro-oxidation of ethanol, the outer Ppy layer imparts a longer-lived catalytic activity to the Au cores, over repeated cycles of potential sweep. Achieving a balanced combination of high energy and power densities in ECs, and extending the lifetime of catalytic activity in noble metals, have been major challenges in developing high-performance ECs and electrocatalysts. In this work, we demonstrate the unique characteristics of hybrid Au-PpyNW electrodes, which represent significant progress toward meeting these challenges.

RESULTS AND DISCUSSION

We prepared arrays of AuNWs by electrodepositing Au through the cylindrical pores of anodic aluminum oxides, AAOs, on a preformed underlyng Au film. After removing the AAOs, pyrrole was electropolymerized on the AuNWs to form the outer layer of Ppy. This procedure produced arrays of hybrid NWs, with a core–shell nanostructure, with an Au core and a Ppy shell. The length and diameter of the inner AuNWs were modified by varying the time for the electodeposition and the pore diameter of AAO, respectively. The thickness of the outer Ppy was tuned by monitoring the time for the electro-polymerization.

To demonstrate the level of control in tailoring the nanoscale structure of the hybrid Au-PpyNW electrodes, we present scanning electron microscopy (SEM) images, and energy dispersive spectroscopy (EDS) element maps, for a typical hybrid NW array fabricated for use in an EC (Figure 1). The height of the array (~20 μm) was uniform over the entire electrode, and the AuNW cores were grown directly from, and aligned perpendicularly to the underlying film (Figure 1a,b). Unlike granular electrodes, the hybrid NW electrodes are a flexible, free-standing, and monolithic film, fabricated without the use of binders and additives. A close-up SEM image reveals a thin (~10 nm), uniform coating of Ppy over the AuNWs (Figure 1c), and EDS elemental mapping of a single hybrid NW confirms the formation of the core–shell NW structure (Figure 1d-f).

An EC was assembled, by placing an ion-permeable separator (8 μm thick porous membrane, Whatman) between two identical electrodes, using a 50 μm thick Teflon spacer, and filling the space between the electrodes with 2 M KCl electrolyte solution. To determine the effects of hybridization through control, we also tested electrodes fabricated with pristine AuNWs (Supporting Information (SI) Figure S1), and planar Au electrodes with an electropolymerized Ppy film on their surface prepared at the same charge consumption used in fabricating the hybrid Au-PpyNW electrodes (the thickness of the Ppy film is approximately 1–2 μm, as determined by the cross-sectional SEM image and EDS elemental mapping shown in SI Figure S2).

An ideal EC can be characterized by the relation, \( I = C \times dV/dt \), where \( I \), \( C \), and \( dV/dt \), are current (alternatively, current density), capacitance (specific capacitance), and time rate of change in voltage, respectively. In reality, most ECs deviate from this ideal capacitive behavior, due to irreversible reactions, self-discharging, and the equivalent series resistance of the electrodes. Among these undesirable contributions, the equivalent series resistance (internal resistance) is one of the most important factors dominating the actual performance of ECs, and it causes adverse effects, such as energy dissipation (ie. Joule heating) and the slowing of charge transport (related to changes in the equivalent RC time constant). In order to improve the performance of ECs, much effort has been devoted to reducing their internal resistance, through the modification of electrode materials and structures.

With this in mind, we characterized our electrodes by galvanostatic charge/discharge (CC) measurement. Figure 2a shows CC curves obtained at a slow charge/discharge rate of \( I = 1 \pm 390 \) mA/cm². The Au-PpyNW electrode exhibits a symmetric triangular CC curve, with a linear voltage variation \( (|dV/dt| = \text{const.}) \), indicating that the EC operates as an ideal capacitive element. On the other hand, the voltage suddenly rises and drops when the Au/Ppy film begins charging and discharging (at 0 and 12.2 s), respectively. Such sudden changes in voltage are caused by a large internal resistance, and become more visible at a faster charge/discharge rate of \( I = 1 \pm 4690 \) mA/cm² (Figure 2b). Compared with the Au/Ppy film electrode, the Au-PpyNW electrode retains its ideal capacitive behavior, even at the faster rate, demonstrating its reduced internal resistance. Figure 2c shows the rate dependence of \( C \), determined from the CC curves. At slow rates, the Au-PpyNW and Au/Ppy film electrodes show similar values for \( C \) (7.4 F/cm² and 6.5 F/cm² at 160 mA/cm², respectively), and both of the electrodes exhibit their maximum charge storage capacity (the specific capacitance at slow rates is most likely determined by the amount of Ppy; when the thickness of the Ppy for the Au/Ppy film is decreased from 1–2 μm to 10–20 nm, the specific capacitance is decreased accordingly with the Ppy thickness, as shown in SI Figure S3). The value of \( C \) for the Au/Ppy film electrode, however, declines with increasing rate. This apparent decrease in \( C \) is possibly due to a process that limits charge transport, which manifests itself as a large internal resistance.

Figure 1. (a,b) SEM images of the arrays of the hybrid NWs. (c) A close-up of the NWs shows the thin layer of Ppy formed on the AuNWs. The average diameter of the hybrid NWs is 200 nm. (d–f) EDS elemental mapping of a single hybrid NW with corresponding SEM image.
Analogous trends have also been reported for systems of agglomerated, granular electrodes, such as activated carbon using binders. Similarly, metal oxide NW-based ECs suffer from poor rate performance (reduction of \( C \) in response to increasing charge/discharge rate) due to their low electrical conductivity, although they achieve substantial specific capacitance at slow charge/discharge rates (e.g., 7 mF/cm\(^2\) at 0.2 mA/cm\(^2\) for \( \text{Fe}_3\text{O}_4@\text{SnO}_2 \) core–shell nanorods\(^{18} \) and 27 mF/cm\(^2\) at 0.2 mA/cm\(^2\) for \( \text{ZnO}@\text{MnO}_2 \) core–shell NWs\(^{19} \), and more data available in the literature\(^{20} \)). Similar trends have been also observed in asymmetric supercapacitors when the charge/discharge rates are increased.\(^{21,22} \) The Au-PpyNW electrode is distinguished by its excellent rate performance, which is even superior to leading-edge electric double layer (EDL) capacitance-based graphene electrodes (Figure 2c).\(^{17} \) The Au-PpyNW electrodes exhibit a value for \( C \) (7.0 F/cm\(^3\) at 4690 mA/cm\(^3\), or 37 mF/cm\(^2\) at 25 mA/cm\(^2\)) that is 8.4 times higher than that for the pristine AuNW electrodes at the identical rate.

To verify the properties of the hybrid Au-PpyNW electrodes, we performed cyclic voltammetry, and recorded current under various scan rates, \( \frac{dV}{dt} \). An ideal capacitive element is supposed to present a rectangular cyclic voltammogram (CV), and a linear variation between current and scan rate, according to the relation, \( I = C \times \frac{dV}{dt} \). Figure 2d. This scan rate is more than 2 orders of magnitude faster than most EDL-based, and metal oxide NW-based ECs, for which maximal rates are usually limited to 1 V/s, due to charge transport and/or charge transfer resistance. Beyond this limit, CVs deform into tilted ellipsoids, due to the influence of internal resistance. Rectangular CVs at such fast rates indicate rapid EDL formation, and fast charge transport within the AuNW array. Due to the superior transport properties of the
AuNW array at the core of the hybrid Au-PpyNW electrode, it maintains rectangular CVs up to 10 V/s (Figure 2e). In contrast, the Au/Ppy film does not function as an EC, and it is incapable of storing charge, as indicated by its completely collapsed CVs (Figure 2f). Furthermore, the charge current for the Au-PpyNW electrode linearly increases with the scan rate, showing no noticeable resistive contributions up to 10 V/s (100 V/s for the pristine AuNW electrode), whereas the current for the Au/Ppy film electrode deviates from a linear relation at much slower scan rates (Figure 2g).

The specific capacitance, charge/discharge rate, and rate performance observed for the mesh films are far below those for the Au-PpyNW, whose specific capacitance decreases by only ∼7% (from 40 to 37 μF/cm², or from 7.4 to 6.9 F/cm³) with a thirty-fold increase in rate (from 0.84 mA/cm² to 25 mA/cm², or from 160 to 4690 mA/cm³), as shown in Figure 2c. The electrical conductivities of individual metal-based NWs should be high, and differences in performance should arise from other factors, such as ion transport and charge collection from individual NWs. We attribute the reduced internal resistance of the Au-PpyNW to its unique structural features, which effectively eliminate possible rate-limiting processes. First, the vertical alignment of the NW decreases resistance by creating a short path length for ion and electron transport to the electrode’s surfaces. Second, the monolithic and seamless structure of the electrode is effective at circumventing the electrode’s interfacial resistance and thus enhances charge collection. Charge collection has been a problem with agglomerated electrodes composed of granular, or anisotropic materials, such as activated carbon, carbon nanotubes, graphene, or nanowires, which are often mixed with...
Figure 4. (a,b) CVs of the (a) pristine AuNW and (b) Au-PpyNW in 0.5 M NaOH. The annotation shows the concentration of ethanol in the solution. Scan rate is 10 mV/s. Thickness of Ppy is ~50 nm. (c) CVs in 0.5 M NaOH. Scan rate is 50 mV/s. Thickness of Ppy is ~100 nm. (d) Retention of the anodic current observed for the electrodes shown in (c), at 0.1 and 0.5 V under potential cycling between −0.8 and 1.0 V in 0.5 M NaOH with 1.0 M ethanol. Scan rate is 50 mV/s. For (a)–(b), current was divided by the electroactive surface area of the electrodes, determined from the CVs shown in SI Figure S7. The same method was used to transform current into current density for (c).

Figure 3. Impedance spectroscopy (EIS) of: (a) AuNW, (b) Au-PpyNW, and (c) Au-PpyNW electrolyzed with 1.0 M ethanol. Scan rate is 50 mV/s. Thickness of Ppy is ~10 nm. (c) Capacitance of electrolyzed Au-PpyNW and Au/PpyNW, and Pt/PpyNW. Scan rate is 50 mV/s. Thickness of Ppy is ~10 nm. (d) Capacitance of pristine AuNW, Au-PpyNW, and Pt/PpyNW. Scan rate is 50 mV/s. Thickness of Ppy is ~10 nm. (e) Full-range CVs of the pristine AuNW electrode, the Au-PpyNW electrode, and the Pt/PpyNW electrode. Scan rate is 50 mV/s. Thickness of Ppy is ~10 nm. (f) Full-range CVs showing the AuNW and Au-PpyNW electrodes are electrochemically active at low, intermediate, and high frequencies. (g) Retention of the anodic current observed for the electrodes shown in (f), at 0.1 and 0.5 V under potential cycling between −0.8 and 1.0 V in 0.5 M NaOH with 1.0 M ethanol. Scan rate is 50 mV/s. Current was divided by the electroactive surface area of the electrodes, determined from the CVs shown in SI Figure S7. The same method was used to transform current into current density for (f).

The ionic resistance of Ppy is significantly reduced from 70.4 Ω (Au/PpyNW electrode) to 0.2 Ω (Au-PpyNW electrode) by forming it into the thin, uniform layer on the AuNWs. The most insightful feature of the plots for the Au-PpyNW electrode is that the intersection with the real axis shifts closer to the original point (Z_re = 0.33 Ω) than for the pristine AuNW electrode (Z_re = 0.44 Ω). Since the distance between the two NW arrays is kept constant by the Teflon spacer, the difference in the impedence would be due to the electrical resistance across the interface between the NWs and the underlying electrode, rather than the ionic resistance of bulk electrolyte layer. Resistance across the interface between active materials and the underlying electrode has often been an issue, and may limit overall electron flow in ECs. To verify this hypothesis, we examined the structure of the junctions between the Au-PpyNWs and the underlying electrodes using SEM (Figure 3c,d). The core AuNWs become narrow and are partially disconnected at their junction with the electrode. These junction defects (bottlenecks and partial disconnects) can arise from pore defects in the AAO. The Ppy forms in a way that wraps and thickens the bottlenecks, and fills in these partial disconnects, strengthening the electrical connection of the AuNWs to the underlying film, resulting in a reduction of the internal resistance of the electrode. As a consequence of the reduced internal resistance and increased capacitance that result from the optimal Ppy deposition (~10 nm-thick Ppy; for detail, see the SI), the power density for the Au-PpyNW is enhanced by more than 1 order of magnitude, and the energy density is maintained at a very high level, compared to the Au/Ppy electrode (Figure 3e). The Au-PpyNW electrode is durable against the structural breakdown of the Ppy layer, and withstands thousands of charge/discharge cycles (Figure 3f). Additionally, the core AuNWs can be replaced with more affordable metals, such as nickel (Ni), which is often used as a current collector in ECs. NiNWs have been previously prepared using a similar electrodeposition technique, and show excellent electrochemical properties that are comparable to AuNWs. Pyrrole has been electropolymerized to form Ppy on a wide variety of common metals, such as nickel, copper and brass, and zinc–lead-silver alloys. We believe that similar hybrid NW structures are feasible in combination with inexpensive metals and Ppy, and analogous properties to the Au-PpyNW may be obtained.

Nanosopic Au, such as Au nanoparticles and nanoporous Au, have attracted great interest as high efficiency electrocatalysts for alcohol oxidation, in the context of their potential applications in direct fuel cells. We have tested small- diameter AuNWs (35 nm in diameter and 6 μm in length) for use in ethanol electro-oxidation, as shown in Figure 4a, where CVs...
establish the electrocatalytic activity of the AuNWs, and that the peak current in the anodic sweep monotonically increases with the concentration of ethanol in solution. Interestingly, the oxidation current does not change significantly with the addition of the Ppy coating on the AuNWs (Figure 4b). To verify that catalytically active sites on the AuNWs are preserved, we investigated the surface activity (electroactive surface), in the absence of ethanol, by means of cyclic voltammetry (Figure 4c). For the Au-PpyNW electrode, a large anodic current appears at ~0.06 V, indicating the formation of gold surface oxides, the precursors of which (chemisorbed OH− anions) play a crucial role in promoting catalysis in alkaline solutions.42,43 Gold surface oxides are subsequently removed during the cathodic sweep, as represented by the reduction peak at 0.05 V. The CV of the Au-PpyNW electrode overlaps with that of the pristine AuNW electrode, where the onset potential and peak potential, corresponding to the gold surface oxide formation, and its removal, respectively, are the same for both electrodes. These results emphasize that the surface activity of Au cores in the Au-PpyNW electrode is not affected by the Ppy coating, and is maintained at a nearly equivalent level to the pristine AuNW. The catalytic lifetime of the Au-PpyNW electrode for ethanol electro-oxidation was characterized by cyclic voltammetry. A potential was cycled between −0.8 and 1.0 V. The anodic current at 0.1 and 0.5 V was recorded and normalized with the initial current (Figure 4d). The Au-PpyNW electrode demonstrates a longer catalytic lifetime than the pristine AuNW electrode, as the Ppy coating imparts a longer catalytic lifetime to the core AuNW catalyst. It has been reported that nanoporous Au undergoes a degradation of catalytic activity, associated with a change in the surface structure of the Au. The extent of the degradation becomes more prominent with decreasing pore size, although catalytic activity increases accordingly, possibly due to metastable surface states at nanoscale.42 With this in mind, we have examined the structures of the electrodes using SEM, EDS, TEM, and HRTEM to gain insight into the longer catalytic lifetime observed for the Au-PpyNW. Figure 5a shows a SEM image of the pristine AuNWs, before conducting the potential cycling test demonstrated in Figure 4d. The Au-PpyNW electrode demonstrates a longer catalytic lifetime than the pristine AuNW electrode, as the Ppy coating imparts a longer catalytic lifetime to the core AuNW catalyst. It has been reported that nanoporous Au undergoes a degradation of catalytic activity, associated with a change in the surface structure of the Au. The extent of the degradation becomes more prominent with decreasing pore size, although catalytic activity increases accordingly, possibly due to metastable surface states at nanoscale.42 With this in mind, we have examined the structures of the electrodes using SEM, EDS, TEM, and HRTEM to gain insight into the longer catalytic lifetime observed for the Au-PpyNW. Figure 5a shows a SEM image of the pristine AuNWs, before conducting the potential cycling test demonstrated in Figure 4d. The SEM image confirms the well-defined AuNW structures, with an average diameter of 35 nm. However, the AuNWs coalesce into large structures after cycling potential over 50 times (Figure 5b), and the changes in the surface structure of Au could be responsible for the degradation of the electrocatalyst (cf. Figure 4d). In sharp contrast, the AuNW structures in the Au-PpyNW electrodes with 100 nm thick Ppy shell are maintained after potential cycling 50-times, and no noticeable structural changes in the core AuNWs and the encapsulating Ppy are observed, as shown in the SEM, TEM, and HRTEM images (Figure 5c−e), and in EDS elemental mapping (SI Figure S5,6). It should be noted that the Ppy shell has been adjusted to an optimal thickness of 100 nm, beyond which the individual NWs overlap, and pathways for mass transport within their arrays are lost. Based on these observations, we expect that the Ppy inhibits the degradation of the AuNW surface structure. Additionally, the Ppy coating on the AuNWs may protect the AuNWs against electrode poisoning caused by chemisorbed intermediates.44

**CONCLUSION**

We have designed hybrid NW electrodes composed of AuNW cores with Ppy shells, and have demonstrated their unique properties, and their suitability for use in ECs, and in the electrocatalysis of ethanol oxidation. Galvanostatic CC measurements and cyclic voltammetry reveal that an EC assembled with these hybrid electrodes functions as an ideal capacitive element, and is capable of charging and discharging at fast rates, with simultaneously high energy and power densities. The rate performance achieved is remarkable, and superior to metal- and metal oxide-NW based electrodes. The high charge/discharge rates possible with these hybrid electrodes is the result of a reduced internal resistance, as confirmed by EIS measurements, and these high rates are essential for surge-power delivery applications. The present work suggests that the ion transport in the active layers, and the charge collection from the active materials, are important rate-limiting processes that need to be addressed to maximize the performance of metal NW-based hybrid electrodes. It is demonstrated that the device performance is significantly enhanced by designing overall electrode structures that address the rate-limiting processes. Additionally, the outer Ppy layer of the hybrid electrodes does not impede the electrocatalytic activity of the core AuNWs, and serves to protect the active sites of the AuNW surface from degradation, thus prolonging the catalytic lifetime of the AuNW electrocatalyst for ethanol oxidation.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b07794.

Methods for electrode preparation and characterization (PDF)

AUTHOR INFORMATION

Corresponding Authors
*(S.S.) E-mail: chessl@nus.edu.sg.
*(H.N.) E-mail: hnakanis@kit.ac.jp.

ORCID

Siowling Soh: 0000-0002-4294-6772
Hideyuki Nakanishi: 0000-0001-8065-6373

Author Contributions

R. K. P. and Y. K. contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Education, Singapore, under grant R-279-000-048-112 and R-279-000-496-114 (to S.S.), and JSPS KAKENHI Grant Numbers JP15H05410 and JP16K13627 (to H.N.), the Ogawasawa Foundation (to H.N.), and the Project for Enhancing Research and Education in Polymer and Fiber Science at KIT (to S.S. & H.N.).

REFERENCES

19. Sun, X.; Li, Q.; Lü, Y.; Mao, Y. Three-Dimensional ZnO@MnO2 Core@Shell Nanostructures for Electrochemical Energy Storage. Chem. Commun. 2013, 49, 4456–4458.

DOI: 10.1021/acsami.7b07794
ACS Appl. Mater. Interfaces 2017, 9, 36350–36357