Synthesis of Diphenylalanine/Cobalt Oxide Hybrid Nanowires and Their Application to Energy Storage

Jungki Ryu, Sung-Wook Kim, Kisuk Kang,* and Chan Beum Park*

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), 335 Gwahangno, Yuseong-gu, Daejeon 305-701, Republic of Korea

ABSTRACT We report the synthesis of novel diphenylalanine/cobalt(II,III) oxide (Co_3O_4) composite nanowires by peptide self-assembly. Peptide nanowires were prepared by treating amorphous diphenylalanine film with aniline vapor at an elevated temperature. They were hybridized with Co_3O_4 nanocrystals through the reduction of cobalt ions in an aqueous solution using sodium borohydride ($NaBH_4$) without any complex processes such as heat treatment. The formation of peptide/Co_3O_4 composite nanowires was characterized using multiple tools, such as electron microscopies and elemental analysis, and their potential application as a negative electrode for Li-ion batteries was explored by constructing Swagelok-type cells with hybrid nanowires as a working electrode and examining their charge/discharge behavior. The present study provides a useful approach for the synthesis of functional metal oxide nanomaterials by demonstrating the feasibility of peptide/Co_3O_4 hybrid nanowires as an energy storage material.

KEYWORDS: peptide self-assembly · diphenylalanine · hybrid nanostructures · cobalt oxide · energy storage · nanowires

The synthesis of nanomaterials using biological templates is a promising alternative route to the development of functional materials because of their structural diversity and molecular recognition capability.[1] In particular, peptide-based materials have recently attracted considerable interests due to their functional flexibility and self-assembling capability.[2,3] For example, peptide-based nanotubes have been successfully used as a removable mold for synthesizing metallic nanowires.[4−6] Meanwhile, the use of genetically engineered viruses enabled the synthesis of organic/inorganic hybrid materials *via* peptide display on their surface.[7−9] Herein we report the synthesis of diphenylalanine/Co_3O_4 hybrid nanowires through peptide self-assembly. Co_3O_4 is a representative transition metal oxide that finds various applications because of its unique physical and chemical properties, such as in gas sensing,[10,11] catalysis,[12] magnetic resonance imaging,[13−15] drug delivery,[15,16] and energy storage.[8,17]

We have introduced self-assembled peptide nanowires as an adsorption site for cobalt ions to form Co_3O_4 nanoparticles. Peptide/Co_3O_4 hybrid nanowires were synthesized by the solid-phase self-assembly of diphenylalanine, one of the best-known self-assembling peptides,[5,18−20] in the presence of aniline vapor, as schematically illustrated in Figure 1a. An amorphous thin film of diphenylalanine was prepared by either simply drying or spin-coating a drop of peptide solution in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) under strictly anhydrous conditions. The amorphous peptide film was then treated with aniline vapor at 100 °C for 12 h to induce the growth of vertically aligned peptide nanowires.[19] The evaporation of the volatile solvent, HFIP, left a flat amorphous peptide thin film on the solid substrate while generating a gradient of chemical potential along the direction perpendicular to the underlying substrate, which is responsible for the vertical growth of peptide nanowires.[19,21] After cooling to room temperature, peptide nanowires were preincubated in an aqueous solution of 1 mM cobalt chloride ($CoCl_2$,10 mM Tris, pH 7.0), which resulted in the electrostatic adsorption of Co^{2+} ions onto peptide nanowires having an isoelectric point of 5.8.[22] After the reduction of Co^{2+} ions with $NaBH_4$ and the spontaneous oxidation of Co metallic nanoparticles in an aqueous solution, peptide/Co_3O_4 hybrid nanowires were produced.

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM) analysis revealed that there was an appreciable change in the morphology of peptide nanowires before and after the integration of Co_3O_4 layer (Figure 1b−d). While pure peptide nanowires exhibited a smooth

*Address correspondence to matlgen1@kaist.ac.kr, parkcb@kaist.ac.kr.

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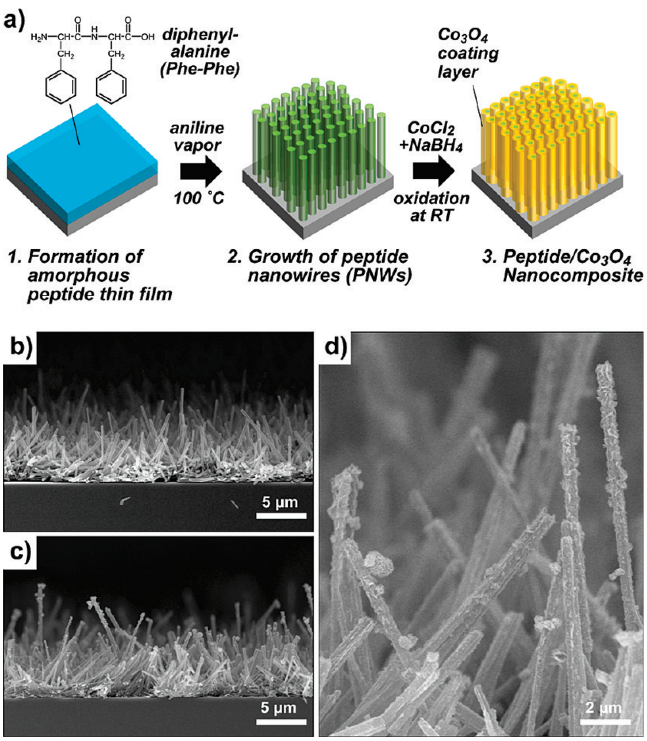

Figure 1. (a) Illustrative scheme for the synthesis of peptide/Co_3O_4 hybrid nanowires. Peptide nanowires, prepared by solid-phase self-assembly of diphenylalanine, were readily hybridized with Co_3O_4 by simple reduction of Co^{2+} ions with $NaBH_4$ into Co and further oxidation in an aqueous solution. The morphology of peptide nanowires was analyzed by SEM (b) before and (c,d) after Co_3O_4 coating.

surface with an average diameter of 200 nm (Figure 1b), peptide/Co_3O_4 hybrid nanowires had high surface roughness with a slightly increased diameter (Figure 1c,d). According to our observations using scanning transmission electron microscopy (STEM), the increased roughness was due to the formation of nanocrystalline inorganic materials on the surface of the peptide nanowires. Hybridized nanocrystallites appeared darker in the bright-field image (Figure 2a) and brighter in the high-angle angular dark-field image (Figure 2b) than the peptide nanowire template, implying that nanocrystallites were composed of heavy atoms (*i.e.*, Co). Elemental analysis by energy-dispersive X-ray spectroscopy confirmed that Co and O are main components of the inorganic nanocrystals (Figure 2c,d).

Transmission electron microscopy (TEM) analysis confirmed that nanoparticles formed along the surface of peptide nanowires are Co_3O_4 rather than pure Co or other oxides (Figure 3). The measured lattice spacing values of 4.59 ± 0.27 and 2.76 ± 0.13 Å were well-fitted to those of (111) and (220) planes of Co_3O_4, respectively (Figure 3a−c and Table S1 in the Supporting Information). A selected area electron diffraction (XRD) pattern (SAED, Figure 3d) also confirmed the formation of Co_3O_4 on diphenylalanine nanowires. While a pristine peptide nanowire exhibited diffraction spots (Figure S1), Co_3O_4 nanoparticles exhibited a set of diffuse rings, indicating that they are nanocrystalline (Figure 3d).

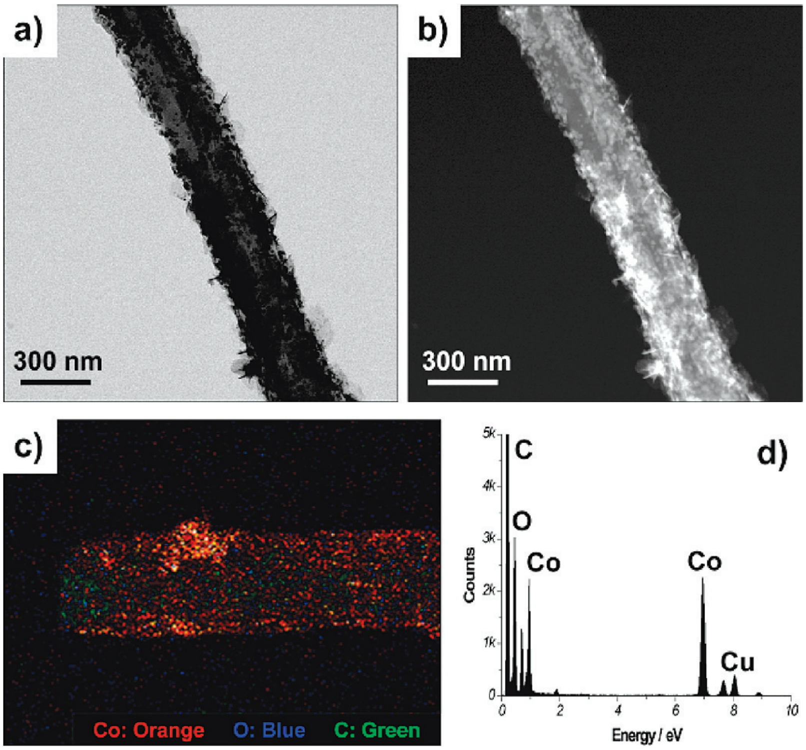

Figure 2. STEM and elemental analysis of peptide-based hybrid nanowires. Hybridization of peptide nanowires with inorganic components was observed by STEM in (a) a bright-field mode and (b) a high-angle angular dark-field mode. Energy-dispersive X-ray (c) mapping analysis (Co, orange; O, blue; C, green) and (d) spectroscopy revealed that Co and O are the main components of the outer coating layers.

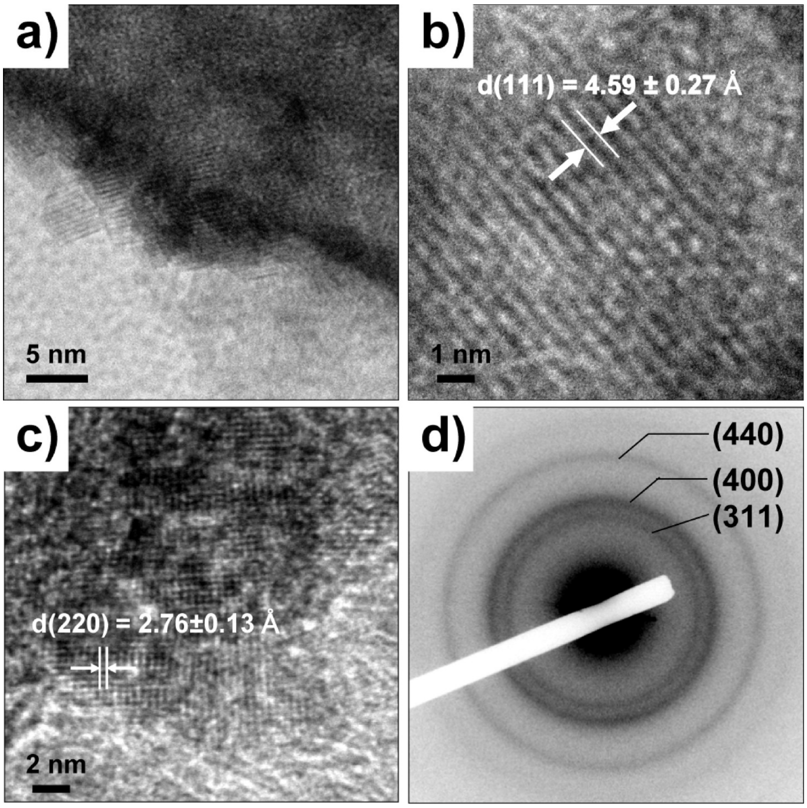

Figure 3. TEM micrographs and the electron diffraction pattern of peptide-based nanocomposites. (a−c) High-resolution TEM and (d) SAED analysis confirm that the outer coating layer is nanocrystalline Co_3O_4.

Note that the measured Co/O ratio (0.65) was slightly lower than the theoretical value for Co_3O_4 (Co/O = 0.75) because of oxygen-rich peptide molecules. We could prepare a free-standing film with peptide/Co_3O_4 nanowires by treating the film formed on a Si substrate in 1 M sodium hydroxide (NaOH) solution in the absence of mechanical agitation, which could be readily transferred to any type of substrate. The morphology of peptide nanowires is unchanged even after the treatment with highly basic solution (pH ~ 14). Previously, we reported that diphenylalanine nanowires are also highly stable under extremely acidic conditions[23,24] (pH < 1) and at high temperatures[19,24] ($T < 200$ °C). The high stability of peptide nanowires makes them suitable as a robust template for the synthesis of functional nanomaterials that often require harsh processing conditions.

In order to study the underlying mechanism for the growth of Co_3O_4 nanoparticles on the surface of diphenylalanine nanowires, we collected X-ray diffraction (XRD) patterns of peptide nanowires before and after the mineralization of Co_3O_4 and compared them with those of cobalt and cobalt oxides (Figure 4). Our results of XRD analysis suggest that not only electrostatic interaction between peptides and Co^{2+} ions but also epitaxial growth is also responsible for the growth of nanocrystalline Co, which can further oxidize into Co_3O_4 in an aqueous solution. In addition, a recent work by Heinz and colleagues on molecular interactions of peptides with noble metal surface would lead one to speculate that aromatic moieties abundant in diphenylalanine nanowires as well as polar moieties (*e.g.*, NH_3^+, COO^-, and −CONH−) may play an important role in the growth of Co nanoparticles.[25] Further studies are needed to unveil the detailed molecular mechanism.

As a possible application of peptide/Co_3O_4 hybrid nanowires, we tested their potential as a negative electrode for Li-ion batteries by constructing Swagelok-type cells using the hybrid nanowires as a working electrode and examining charge/discharge behavior. Figure 5a shows a schematic diagram for the basic operation of a Li-ion battery cell. The cell was composed of a Li metal counter electrode, an electrolyte, a separator, and a working electrode (*i.e.*, the hybrid nanowires). Figure 5b shows the discharge−charge characteristics of the hybrid nanowire electrode. During the discharge (or charge) process, Li ions are removed from the Li metal and are then electrochemically stored in the hybrid nanowires through the electrolyte (or *vice versa* for charging). As a result of discharge (or charge), voltage *vs* Li^+/Li decreases (or increases) because the electrochemical potential of the working electrode is strongly affected by the amount of Li ion present in the peptide/Co_3O_4 hybrid nanowires. Before investigating the Li-uptake phenomenon in the hybrid nanowires, we tested the discharge−charge characteristics of pure peptide nanowires. Interestingly, pure peptide nanowires exhibited electrochemical activity with Li. The spe-

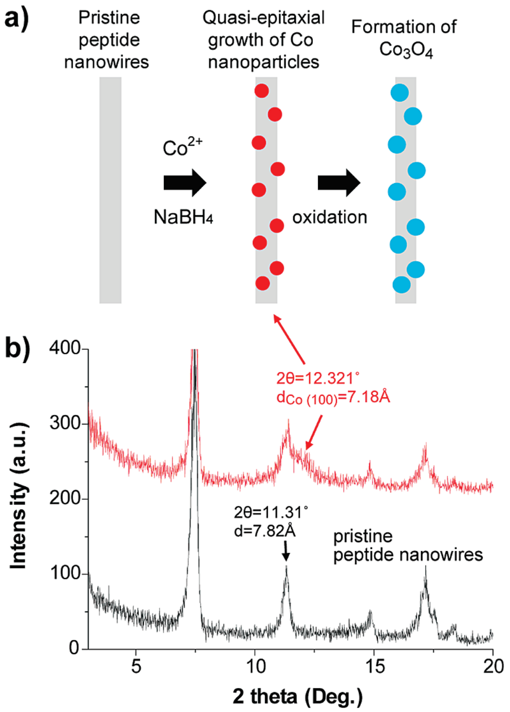

Figure 4. (a) Suggested mechanism for the growth of Co_3O_4 nanoparticles on diphenylalanine peptide nanowires and (b) thin film XRD patterns supporting the proposed mechanism. When we collected the XRD pattern of peptide nanowires treated with aqueous solution containing 1 mM $CoCl_2$ and 5 mM $NaBH_4$ for only a few hours, which is not enough for complete oxidation of Co into Co_3O_4, we could observe a broad peak corresponding to the (100) plane of nanocrystalline Co near the specific peptide nanowire peak at 11.31°. This suggests that cobalt nanoparticles were initially formed quasi-epitaxially on the peptide nanowires and then oxidized into Co_3O_4.

cific capacity of the pure peptide nanowire was approximately 80 mAh/g at the first discharge cycle, and it was saturated to 25 mAh/g. In order to check the origin of the electrochemical activity of the pure peptide nanowires, the crystallinity of the pure peptide nanowires before and after the discharge was investigated and compared (Figure 5c). Significant peak changes were not observed after the discharge, indicating that Li uptake is mainly from the surface adsorption/desorption on the large surface area of peptide nanowires. However, a slight broadening of peaks after discharge was observed. This implies that some Li ions may have been incorporated in the peptide, which warrants further detailed studies.

The peptide/Co_3O_4 hybrid nanowires exhibited a much higher specific capacity of approximately 280 mAh/g at the first discharge cycle, and then it was saturated to 80 mAh/g (Figure 5b). This indicates that the electrochemical activity of Co_3O_4 was utilized in the hybrid nanowires, effectively enhancing the specific capacity as an electrode for the Li-ion battery. The reaction mechanism of Co_3O_4 with Li, so-called "conversion reaction", is as follows.[17,26]

$$Co_3O_4 + 2Li \leftrightarrow 3CoO + Li_2O \qquad (1)$$

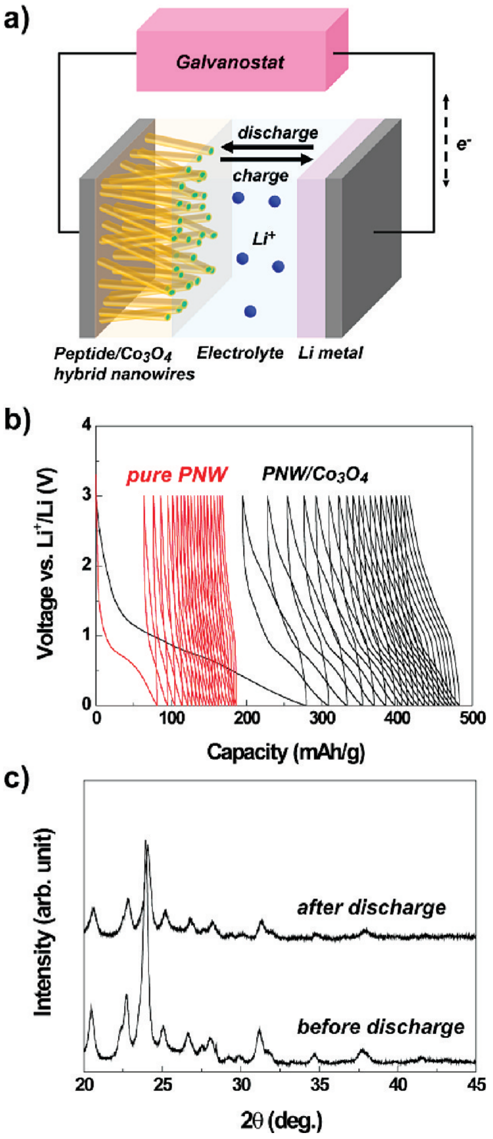

Figure 5. Li storage capability of pure peptide nanowires and peptide/Co_3O_4 hybrid nanowires. (a) Test cell was configured using the nanowires as an anode to examine charge−discharge characteristics of (b) pure peptide nanowires (red) and peptide/Co_3O_4 composite nanowires (black). (c) XRD analysis of peptide before and after the discharge.

$$3CoO + 6Li \leftrightarrow 3Co + 3Li_2O \qquad (2)$$

In general, the voltage plateaus of crystalline Co_3O_4 are observed at near 1.3 and 1.0 V, which correspond to electrochemical reactions 1 and 2, respectively.[27,28] In the case of peptide/Co_3O_4 nanowires, there was no clear voltage plateau related to the conversion reaction of Co_3O_4; nevertheless, a gentle slope region was observed (Figure 5b). The sloped voltage plateau is attributed to very small crystallites of Co_3O_4 synthesized at room temperature.

CONCLUSION

In summary, we synthesized peptide/Co_3O_4 hybrid nanowires through peptide self-assembly. Through the reduction of cobalt ions in an aqueous solution with $NaBH_4$, diphenylalanine nanowires were readily coated with Co_3O_4 nanostructures. The aqueous-phase synthesis of diphenylalanine/Co_3O_4 hybrid nanowires at room temperature allowed a versatile and facile fabrication of functional materials without any complex processes such as heat treatment. The present study has also demonstrated the feasibility of self-assembled peptide nanowires as an energy storage material. We believe that a similar strategy with self-assembled peptide nanowires containing metal oxides such as Co_3O_4 can find further application in areas such as gas sensing and catalysis.

METHODS

Materials: Lyophilized powder of diphenylalanine peptide was obtained from Bachem AG (Bubendorf, Switzerland). HFIP, $CoCl_2$, and $NaBH_4$ were purchased from Sigma-Aldrich (St. Louis, MO).

Synthesis of Diphenylalanine/Co_3O_4 Hybrid Nanowires: Fresh solution of diphenylalanine peptide was prepared by dissolving lyophilized peptide in HFIP at 100 mg mL^{-1}. Peptide solution was always prepared immediately prior to use in order to avoid the formation of any aggregates. A transparent and amorphous diphenylalanine film was obtained by either spin-coating or drying a drop of peptide solution on a solid substrate under anhydrous condition at room temperature. Amorphous peptide thin film was then treated with aniline vapor at 100 °C for 12 h in a sealed Petri dish to induce the growth of vertically well-aligned peptide nanowires. The grown peptide nanowire film was then used as a template for the synthesis of Co_3O_4 nanostructures. Diphenylalanine/Co_3O_4 composite nanowires were synthesized by treating the peptide nanowire film with 1 mM $CoCl_2$ solution in 10 mM Tris (pH 7.0) overnight and reducing adsorbed Co^{2+} ions with 5 mM $NaBH_4$. Note that, during the preincubation step, Co^{2+} ions are initially adsorbed onto the surface of peptide nanowires through electrostatic interactions between negatively charged peptide and positively charged Co^{2+} ions. After reducing Co^{2+} ions into metallic Co, the peptide nanowire film was further incubated for 12 h in aqueous solution to oxidize Co into Co_3O_4. The prepared peptide/Co_3O_4 hybrid nanowires were thoroughly washed with deionized water and dried by nitrogen gas for further analysis.

Characterization: Pure peptide nanowires and peptide/Co_3O_4 hybrid nanowires were analyzed with an S-4800 field emission SEM instrument and an HD-2300A STEM instrument (Hitachi High-Technologies Co., Japan). For SEM imaging, samples were coated with a thin film of Pt using SCD005 Pt-coater (Bal-Tec AG, Liechtenstein). For STEM analysis, peptide/Co_3O_4 hybrid nanowire film grown on Si substrate was treated with 1 M NaOH solution. With mechanical agitation, peptide/Co_3O_4 nanowire film was disintegrated into individual nanowires by the selective etching of native oxide with NaOH solution. Dispersed nanowires were then transferred onto carbon/Formvar-coated Cu grids for further analysis. Note that, when no agitation was applied, free-standing nanowire film was obtained and could be transferred to virtually any type of substrate. The diffraction patterns of peptide nanowire before and after discharge were measured with a D/MAX-RC thin film X-ray diffractometer (Rigaku Co., Japan) under the following conditions: scan speed, 1°/min; Cu K radiation, $\lambda = 1.5418$ Å; scan range, 20−45°.

Electrochemical Test: For an electrochemical characterization, an electrode was prepared with Co_3O_4-coated peptide nanowires (62 wt %), carbon black (super P) (22 wt %), and polytetrafluoroethylene (PTFE) binder (16 wt %). Test cells were assembled into two-electrode Swagelok-type cells with a Li metal counter electrode, a separator (Celgard 2400), and an electrolyte of 1 M lithium hexafluorophosphate in a 1:1 mixture of ethylene carbonate and dimethyl carbonate (Techno Semichem). Discharge/charge tests were performed in the voltage range of 0.001 to 3 V at current rates of the 8.90 mA/g using a multichannel potentiogalvanostat (WonA Tech, WBCS3000).

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Supporting Information Available: Table of *d* spacing values of cobalt and various cobalt oxides to determine the phase of nanocrystallites in Figure 3 and TEM micrograph and SAED pattern of the pure peptide nanowire. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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