

UNIQUE EXTRA-LONG CHEMICALLY-DERIVED GRAPHITIC PYRAMIDAL RIBBONS

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ABSTRACT

In this letter, unique extra-long chemically derived pyramidal graphitic ribbons (PGR) were individualized and deposited onto a SiO₂ substrate via simple spin-coating. The length of the individualized PGRs was found to exceed the average length of graphene nanoribbons (GNRs) by hundreds of microns. The physicochemical individualization method resulted in the creation of a novel “graphene nanoribbon intercalation compound” (GNRIC), following a strict stoichiometric relation between the GNR powder and alkali metals. Our experiments were conducted with the use of Na and K as intercalants at NaC₈, KC₈, and KC₂₄ concentrations. Furthermore, we exposed them to THF and discovered that the nanoribbon bundles obtained from CVD bottom-up bulk synthesis of GNRs can be exfoliated. The exfoliated nanoribbons (ex-GNRs) were analyzed using SEM, Raman spectroscopy, optical microscopy, and AFM, revealing the existence of ribbon-like pyramidal nanostructures that are larger than 100 μm. The morphology of these graphitic ribbons, brings a new starting point and immense potential to the development of graphene-based devices for optoelectronics and solar cells.

Keywords: Pyramidal graphitic ribbons, Individualization, Intercalation compounds, Raman spectroscopy, Atomic force microscopy

Cintas Piramidales Grafiticas Únicas y Extralargas Derivadas Químicamente

RESUMEN

En esta carta, se individualizaron y depositaron cintas de grafito piramidal (CGP) extralargas únicas derivadas químicamente sobre un sustrato de SiO₂ mediante el método simple de “spin coating”. Se descubrió que la longitud de los CGP individualizados excedía la longitud promedio de las nanocintas de grafito (GNR) en cientos de micrones. El método de individualización fisicoquímica dió como resultado la creación de un nuevo “compuesto de intercalación de nanocintas de grafito” (GNRIC), siguiendo una estricta relación estequiométrica entre el polvo de GNR y los metales alcalinos. Nuestros experimentos se realizaron empleando Na y K como intercalantes en concentraciones de NaC₈, KC₈ y KC₂₄. Adicionalmente, los GNRIC fueron expuestos a THF y descubrimos que las cintas de grafito obtenidas de la síntesis en masa por CVD se pueden exfoliar fácilmente. Las nanocintas exfoliadas (ex-GNR) se analizaron mediante SEM, espectroscopía Raman, microscopía óptica y AFM, revelando la existencia de nanoestructuras piramidales en forma de cinta que miden más de 100 μm. La morfología de estas cintas de grafito, aporta un nuevo punto de partida y un inmenso potencial para el desarrollo de dispositivos basados en grafito para optoelectrónica y celdas solares.

Palabras claves: Cintas de grafito piramidal, Individualización, Compuestos de intercalación, Espectroscopía Raman, Microscopía de fuerza atómica

INTRODUCTION

Graphene nanoribbons (GNRs) are narrow strips of graphene with interesting electronic and magnetic

properties based on their quantum confinement effects.[1], [2].

The bottom-up synthesis approach for obtaining GNRs involves polymerizing monomer molecules from highly concentrated carbon precursor sources like ethanol. These

molecules rise to atomically precise carbon nanostructures, which are the fundamental platform for future molecular electronics device applications.[3] In addition, GNRs are predicted to be an excellent building block along the development of a new generation of nanoscale integrated circuits based on their ability to transport charge and spin under high mobility ranges due to their lateral confinement of charge carriers.[4], [5] In particular, when graphene is deposited on a flat Si wafer it develops a Schottky contact and induces a built-in electric field at the interface, which serves as heterojunctions for the development of solar cells.[6] However, the challenge for the development of GNRs devices lies in their ease of mass production, and industrial processes are limited by the existing bottom-up production methods such as lithography, catalytic cutting, chemical assembly, and epitaxial growth.[3], [7] On the other hand, GNRs are being produced from a top-down approach by means of: i) chemical vapor deposition (CVD) methods,[3], [8] and/or ii) by the unzipping of multi-walled carbon nanotubes (MWCNTs).[9], [10] However, in this last approach either the structure or the morphology of the ribbons are compromised or they remain in large bundles that do not serve for their integration into electronic devices.

We have recently demonstrated the feasibility of producing stable “graphene nanoribbon intercalation compounds” (GNRICs) from bulk synthesized CVD graphene nanoribbons [8] as described in reference [11]. It is well known that exposing bundles of carbon nanotubes or graphitic nanoplatelets to alkali-metals in a highly polar solvent environment or aggressive reagents derives into a rapid Coulomb chain explosion reaction that breaks the Van der Waals interaction inducing an individualization of the carbon nanostructures.[12], [13], [14] However, and to the best of our knowledge, this method of chemically-derived exfoliation to obtain graphitic pyramidal ribbon heterojunctions with hundreds of microns in length on SiO₂ has not been reported yet. We introduce a chemically-based intercalation/exfoliation method that

utilizes alkali metals (K and Na) for individualizing CVD-grown GNRs in tetrahydrofuran (THF). We obtained nanostructures that resemble pyramidal ribbons that are hundreds of microns in length on SiO₂, which could be used as a platform for electronic devices.

EXPERIMENTAL

The GNRs were produced by chemical vapor deposition based on reference.[8] The synthesis conditions were: a) Precursor solution with 280 mL of ethanol, 0.266 mL of thiophene, and 2.8 g of ferrocene. b) Argon flux of 0.8 L/min in a quartz tube. c) Growth temperature 950 °C during 30 min. growth time.

The intercalation compounds were prepared in an argon-filled glovebox (<0.1 ppm of H₂O and O₂). Na or K were mixed in a glass vial with GNRs powder in three proportions: a) 11.38 mg of GNRs per 2.73 mg of sodium (~NaC₈), b) 3.2 mg of GNRs per 1.3 mg of potassium (~KC₈) and c) 13.4 mg of GNRs per 1.87 mg of potassium (~KC₂₄). The mixtures were placed in a heating plate where the temperature was slowly increased up to 200 °C. The samples were then stirred carefully every 20 minutes during the first hour and were then kept at 200 °C on the heating plate for 48h to receive a homogeneous intercalation compound.[15]

Graphene nanoribbons intercalation compounds (GNRICs) of NaC₈, KC₈, and KC₂₄ were formed. The stoichiometry of our intercalated compounds was confirmed by Raman spectroscopy based on standard methods.[15] GNRICs and THF were added into a glass vial in a proportion of 0.1 mg per ml. The THF solution was previously pump-freeze in order to remove the oxygen, dried reaching 3.3 ppm of H₂O, sealed, and stored in a glove box. The solutions of NaC₈ and KC₂₄ GNRICs were sonicated for 90 seconds with two pulses per second with a tip sonicator with 0.465 J. The solutions of KC₈ GNRICs were sonicated for 2 min to 5 min with the same tip. Complete precipitation of the sample was observed after 6 days, and the exfoliated solutions of ex-GNR

(NaC₈), and (KC₂₄) were characterized and re-dispersed by shaking and characterized again. Finally, the supernatant was separated from the precipitate. The precipitate from each sample was placed into a new glass vial with 5 ml of THF. We fished the floated GNRs by dipping a SiO₂/Si wafer into the solution. The wafers had a 300 nm layer of SiO₂ and were pre-cleaned with acetone and isopropanol using a spin coater. The samples were characterized using: I) Horiba LabRAM Aramis and a HR evolution Raman spectrometer with a 532nm laser. II) AFM was carried out in tapping and non-contact modes using a Veeco Dimension 3100 AFM equipment. III) SEM was conducted by placing the GNRs on a carbon tape and analyzed with 5 kV at a Helios NanoLab DualBeam scanning electron microscope.

RESULTS AND DISCUSSION

In our previous communication[11] we demonstrated the possibility of synthesizing GNRICs at the KC₈ stage of intercalation and its importance. Thus, we prepared a fresh KC₈ GNRIC from bulk CVD-grown GNRs (see Figure 1 a). From our SEM micrographs, we can notice the presence of extremely long (>20 μm) bundles of corrugated GNR (inset Figure 1 a). The intercalation compound was stable inside the glove box (Figure 1 b). As it can be seen in Figure 1 c)-top the three main features of the GNRs are clearly depicted: I) D-line at ~1340 cm⁻¹, II) G-line at ~1570 cm⁻¹, III) a 2D-line at ~2680 cm⁻¹, and IV) D+G feature at ~2900 cm⁻¹ as reported previously for this

kind of GNRs.[16] On the other hand, the Raman spectra of the GNRIC depicted a characteristic Fano line shape of the G-line as expected for KC₈. [15]

We further induced a strong Coulombic reaction between the GNRIC and THF by mixing the material *via* tip sonication in the glove box. Several steps of dilution were conducted as explained in the experimental section. A drop of the solution was deposited on a SiO₂ wafer as it can be seen in Figure 2 a-b). As marked in red circles, small (<100 μm) stripes can be obtained. Characterizing them by AFM enabled us to confirm their ribbon-like morphology. However, as it can be observed in Figure 2 (c-d) these ex-GNR from KC₈ are full of residues attached to the surface, and their size was rather short (~10 μm). To contrast the previous observation, we made a close-up AFM measurement of a single ex-GNR (KC₈) in Figure 2 e) showing a width of about 400 nm and a height of 300 nm. The Raman spectrum of this individual ex-GNR revealed the presence of the D, G and 2D bands, located at 1350, 1600, and 2705 cm⁻¹, respectively (Figure 2 f). In general, these values are in the range of the ones reported for this kind of CVD-grown GNRs.[8], [16] Important to notice is: i) the D band exhibited the highest intensity derived from the high proportion of edges and within the ribbons, and ii) the disorder-induced combination mode (D + G) at about 2940 cm⁻¹ is at the same order of magnitude when compared to the 2D line.

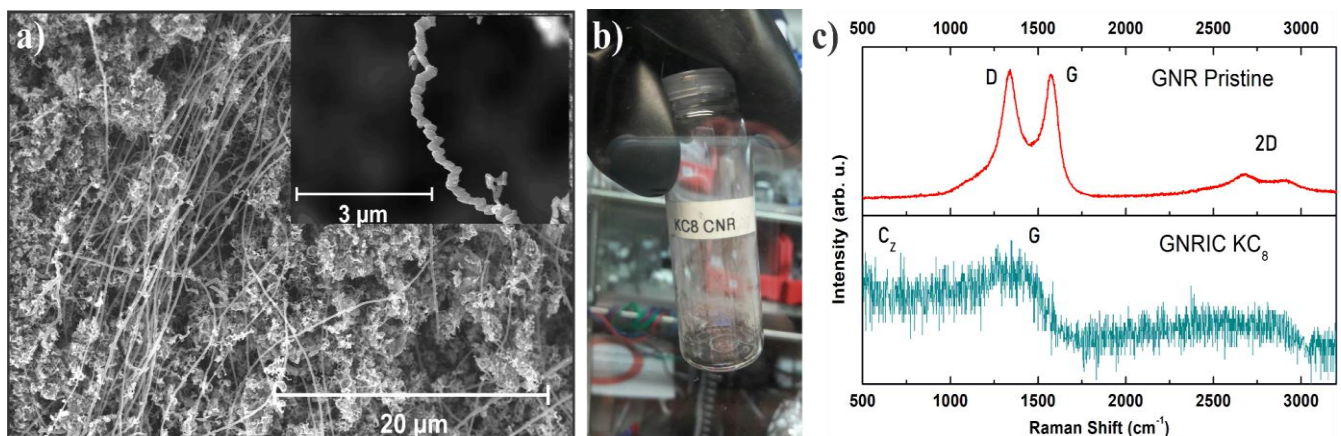


Fig. 1. Pristine and intercalated GNRs. a) SEM micrograph of pristine CVD-grown GNRs in bundles. A single GNR is shown in the inset revealing a wavy morphology with several microns in length. b) GNR intercalation compound prepared in a glass vial under inert Ar conditions. c) Raman spectra of pristine graphene nanoribbons (top) compared to the ones after intercalation on a KC_8 stage (bottom).

We aimed to obtain longer and cleaner ex-GNRs. Therefore, we made GNRICs in a KC_{24} , and NaC_8 fashion to disclose the effect of the alkali-metal during the exfoliation process. In Figure 3 (a, c, e) we can observe the resulting ex-GNRs from the NaC_8 GNRIC, while in Figure 3 (b, d, f) the as obtained KC_{24} ex-GNRs are shown. In both cases, stripes are notorious and present on the wafers (red arrows in Figure 3). However, it was clear that reducing the concentration of potassium enhances the production of the ex-GNRs without improving their length. On the other hand, by using sodium we obtained a cleaner set of ex-GNRs with hundreds of microns in length.

When looking closer at the samples obtained from NaC_8 , and KC_{24} (Figure 4 a and b respectively) we confirm that the ex-GNRs obtained from the sodium GNRIC are more than four times longer than the ones obtained from potassium KC_{24} . When looking at the tips of these ex-GNRs (inset Figure 4 a and b) we can observe two main differences in the morphology: I) the ex-GNR from KC_{24} have a tip pyramidal shape with about $0.17 \mu\text{m}$ of height and a width of $\sim 300 \text{ nm}$ (Figure 4 e). II) the ex-GNR obtained from Na have a fine multi-layer stacked flat structure along its length with a width and height of $\sim 300 \text{ nm}$ (Figure 4 b).

We then focused on a second ex-GNR from both samples to confirm the homogeneity of the resulting material and conducted a Raman analysis plus a line profile analysis of their tips. The Raman spectra in both cases confirmed the GNR-line Raman response with the difference that the full-width at half maximum from the D-line of the KC_{24} sample was wider as compared to the one from Na, which means that the sample is more defective and it may contain a larger concentration of defective sites within the structure for the ex-GNR obtained from KC_{24} (see Figure 4 c-i and f-i respectively). These observations are clearly

confirmed when one looks at the line-profile analysis of these tips (see Figure 4 c-ii and f-ii respectively). We can see that the ex-GNR obtained from Na (Figure 4 c-ii) has a flat step-like multi-layer structure with a height of $\sim 300 \text{ nm}$ and a width of $\sim 600 \text{ nm}$; whereas the KC_{24} ex-GNR has a nonregular pyramidal shape of $\sim 200 \text{ nm}$ in height, and $\sim 300 \text{ nm}$ in width.

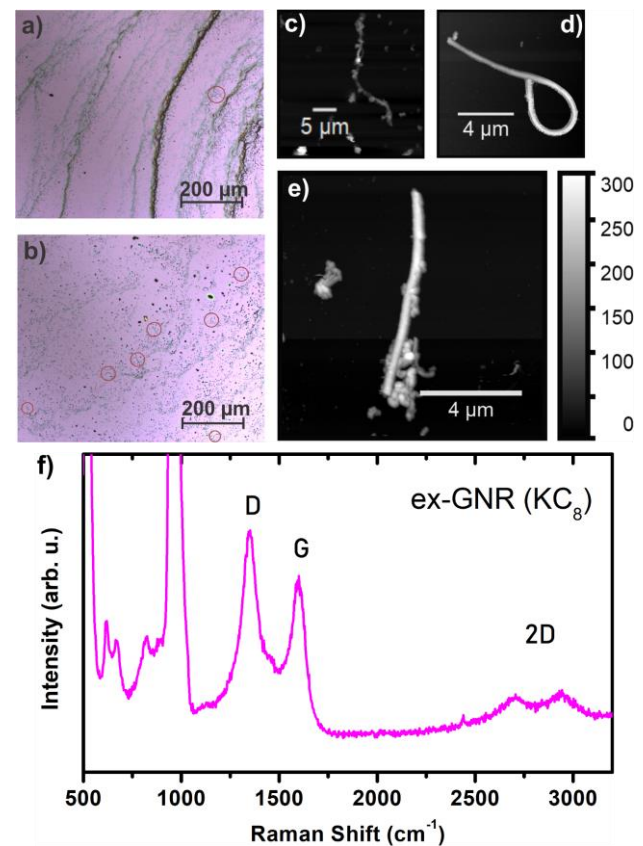


Fig. 2. Ex-GNR prepared with a KC_8 . a-b) ex-GNR deposited on a SiO_2 , c) AFM image of an ex-GNR coated with residues along the ribbon, d) AFM image from a rolled individual ex-GNR with no apparent surface defects and a length of $\sim 10 \mu\text{m}$, e) AFM image of an individual ex-GNR with residues, effects and a height of 300 nm . f) Raman spectra of the ex-GNR e) measured centered in the ribbon.

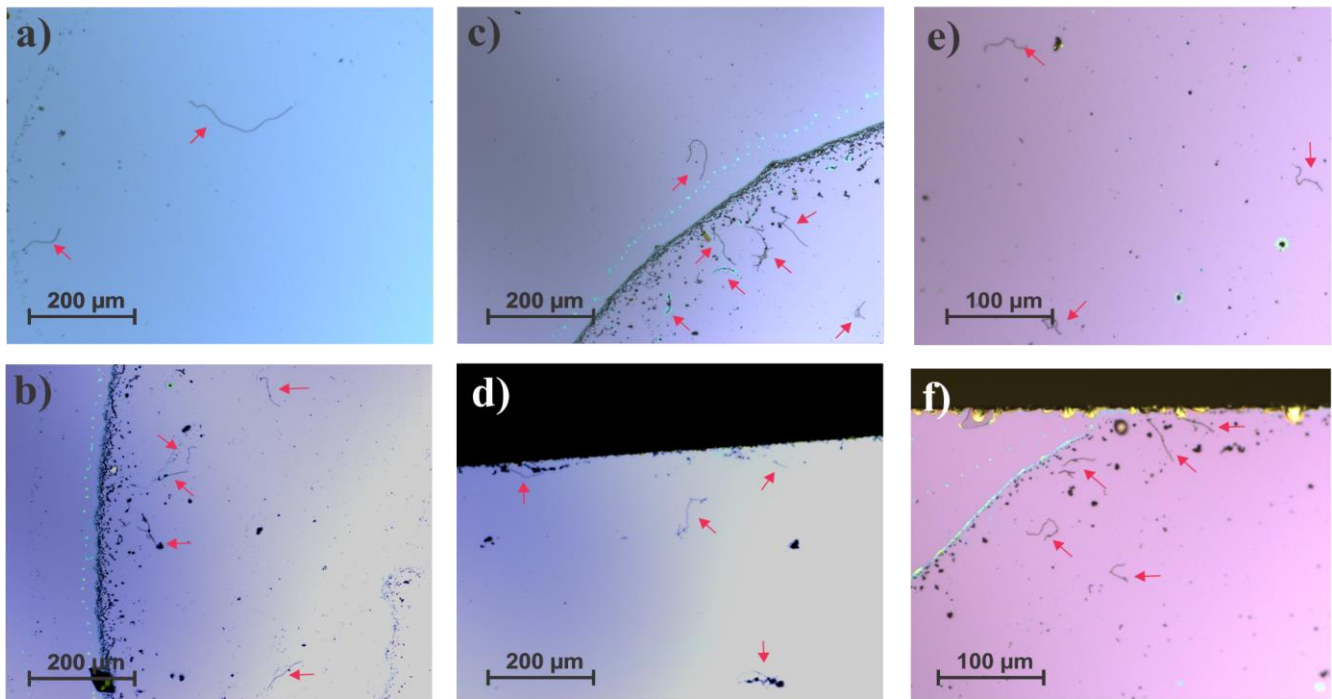


Fig. 3. Optical microscope images of a) ex-GNR (NaC_8) and b) ex-GNR (KC_{24}). c) ex-GNR (NaC_8) after being shook and d) ex-GNR (KC_{24}) after being shook. e) ex-GNR (NaC_8) re-dissolved in 5ml of THF and f) ex-GNR (KC_{24}) re-dissolved in 5ml of THF. Both experiments were made in parallel. Details of the preparation can be found in the experimental section.

Finally, we deposited a drop of the ex-GNR with Na on a Cu TEM grid to confirm the morphology of the ribbon (Figure 5). When looking at the Cu grid, we observed a couple of individualized ex-GNRs shown with precisely the same wavy shape with a length of around $20\ \mu\text{m}$ and a width of $\sim 300\ \text{nm}$. However, when compared to the ones deposited on SiO_2 we can see corrugations on the ribbons set on Cu. This effect is explained by the strong

electrostatic interaction between the oxide layer of silicon and the graphitic ribbon surface. This strong interaction is not existing within the Cu grid. We could then summarize two main important results at this point: i) the spin-coating procedure applied in ex-GNRs provides a facile platform to individualize graphene ribbons, and ii) The strong oxide surface of SiO_2 allows for flat extended ribbon heterojunctions, while Cu keep their corrugation.

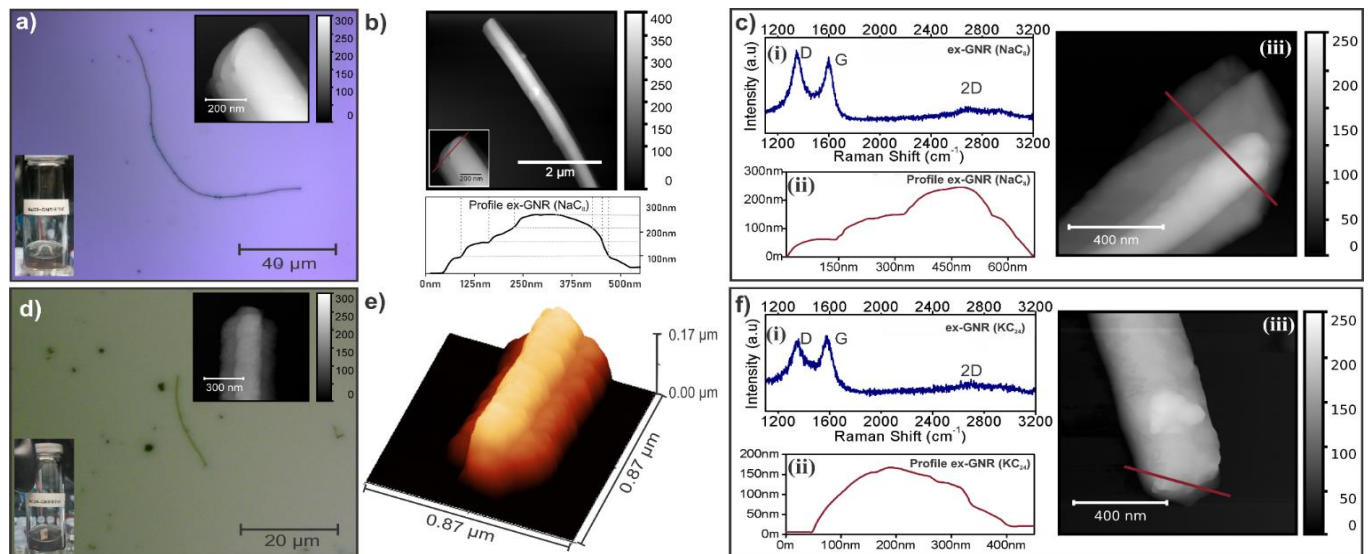


Fig. 4. NaC₈ and KC₂₄ atomic force analysis of individual ex-GNR. Optical microscope image at 100x magnification of a) ex-GNR (NaC₈), and d) ex-GNR (KC₂₄). b) Profile AFM analysis for an individual ex-GNR (NaC₈). c) Raman spectrum of ex-GNR@NaC₈ and AFM profile analysis of an individualized tip ex-GNR [scale in nm]. f) Raman spectrum of ex-GNR@NaC₂₄ and AFM profile analysis of an individualized tip ex-GNR [scale in nm].

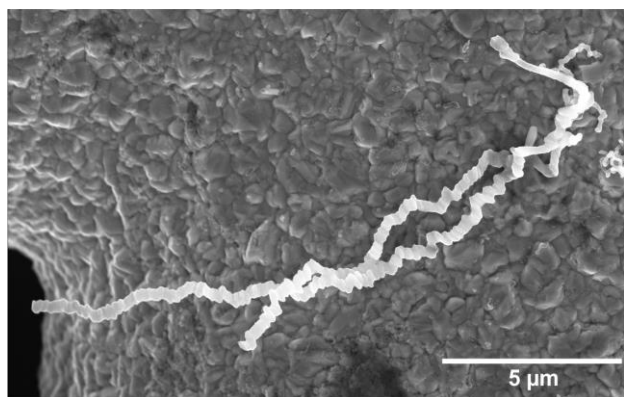


Fig. 5. SEM image of drop deposited ex-GNR (NaC₈) on a Cu TEM grid.

CONCLUSIONS

The Coulombic repulsion generated by the exothermic reaction between GNRICs and THF effectively separates and individualizes the CVD grown GNRs. Individualization of GNRs using Na leaves less carbon residues and produces ribbons that are longer. The ex-GNRs in Cu retain their original wavy shape unless they are deposited on a SiO₂ where they get completely extended. Scaling up the production of these long and extended pyramidal ribbons on SiO₂ can lead to the development of electronic devices like contacts and photovoltaic PGR/SiO₂ heterojunctions for solar cells.

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