

Synthesis of vertical nanographene network as platform for electrochemical applications

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ABSTRACT

Carbon nanowalls (CNWs) are few-layer graphenes with open boundaries, standing vertically on a substrate forming three-dimensional structure. The maze-like architecture of CNWs with large-surface-area graphene planes would be useful as electrodes for energy storage devices, electrochemical and biosensors. CNWs can be fabricated using plasma-enhanced chemical vapor deposition technique. From a practical point of view, structures of CNWs including spacing between adjacent nanowalls and crystallinity should be controlled according to the applications. We report the current status of the control of the CNW structures during the growth processes, together with an example of application using CNWs as a platform in the area of electrochemistry. Nanoplatfrom based on vertical nanographene offers great promise for providing a new class of nanostructured electrodes for electrochemical sensing, biosensing and energy conversion applications.

1. INTRODUCTION

It is well known that sp^2 carbon can lead to various kinds of layered structures. Among these structures, graphene (monolayer and few layers) is an actual two-dimensional material with the large anisotropy between in-plane and out-of-plane directions. Graphene is a promising material for future electronic applications due to its outstanding properties. Planar graphene films have been fabricated by mechanical exfoliation from highly oriented pyrolytic graphite, thermal decomposition of carbon-terminated silicon carbide, and chemical vapor deposition (CVD) on metals such as

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nickel and copper substrates. On the other hand, plasma-enhanced CVD (PCVD) is among the early methods to synthesize vertically standing carbon sheet structures (Wu 2002, Hiramatsu 2004, Wang 2004). These structures are called as carbon nanowalls (CNWs), carbon nanoflakes, and carbon nanosheets. CNWs are few-layer graphenes standing vertically on a substrate to form a self-supported network of wall structures. Figures 1(a) and 1(b) show a schematic illustration of CNWs and plan view SEM image of CNWs grown using PCVD, respectively. The maze-like architecture of CNWs with large-surface-area graphene planes would be useful as a platform for electrochemical sensing and biosensing, and energy conversion, due to the large surface area of conductive carbon and the wide capability of surface modification with nanoparticles and biomolecules.

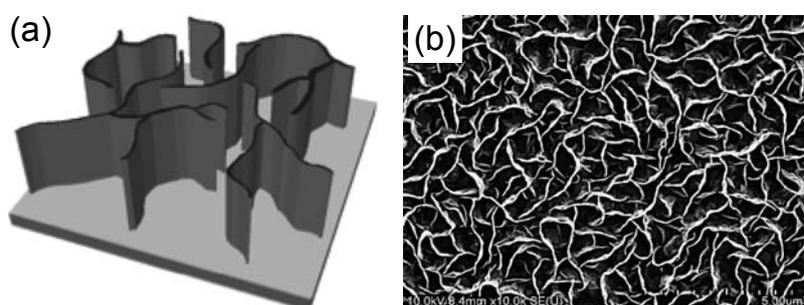


Fig. 1 (a) Schematic illustration of CNWs, (b) SEM image of CNWs

CNWs can be fabricated using PCVD technique. From a practical point of view, structures of CNWs including spacing between adjacent nanowalls and crystallinity should be controlled according to the applications. Moreover, post processes such as integration techniques including etching and surface functionalization should also be established. Most important factor affecting morphology, crystallinity and growth rate of CNWs is the balance between carbon precursors and etching radicals. Composition of gas mixture, pressure and power determine the balance between carbon precursors and etching radicals such as H atoms. For example, as the H atoms in the plasma increased, interspaces increased and crystallinity of CNWs was improved, while the growth rate decreased (Cho 2014). Alternatively, the increase of ion flux incident on the substrate surface would enhance the nucleation of vertical nanographene, resulting in the formation of dense (small interspaces) CNW films. Moreover, metal nanoparticles such as Ti on Si and SiO₂ enhance the nucleation of nanographene (Hiramatsu 2013). We report the current status of the control of the CNW structures during the growth processes, together with an example of application using CNWs as a platform in the area of electrochemistry.

2. EXPERIMENTS

CNWs were grown using inductively coupled plasma-enhanced chemical vapor deposition (ICP-CVD) (Hiramatsu 2013). Substrates used for growth experiments were

Si and SiO₂-coated Si with the thickness of the thermally grown oxide layer of 50 nm (which is called as “SiO₂” hereafter). On one hand, carbon fiber paper (CFP) was used as a substrate for the electrode in the electrochemical applications. Figure 2 shows a schematic of the ICP reactor used for the growth of CNWs. The ICP reactor was 16 cm in diameter and 30 cm in height. A one turn coil antenna with a diameter of 10 cm was set on a quartz window at the top of the reactor. An RF (13.56 MHz) power was applied to the coil antenna and plasma was generated in the chamber. Si or SiO₂ substrates were set on the middle of the substrate holder at 10 cm below the quartz window. A mixture of CH₄ and Ar was introduced into the chamber, and the total gas pressure was maintained in the range from 15 to 20 mTorr. The temperature of the heater for sample heating was maintained at 700-750 °C during the CNW growth. To investigate the effect of ion bombardment on the change of morphology and crystallinity of CNWs, gas flow rate ratio of CH₄ and Ar was changed. On the other hand, Ti-decorated SiO₂ substrate was used to investigate the influence of Ti nanoparticles on the change of space between adjacent nanowalls. Ti nanoparticles were deposited on a SiO₂ substrate by using the pulsed arc discharge. The pulsed arc discharge with a Ti electrode yielded Ti nanoparticles approximately 1–2 nm in size. Moreover, SiO₂ substrates were set on the top and side surfaces of heated Mo block. To find another way to control the surface morphology of the CNW films, deposition was carried out on the substrate set perpendicular to the electrode stage.

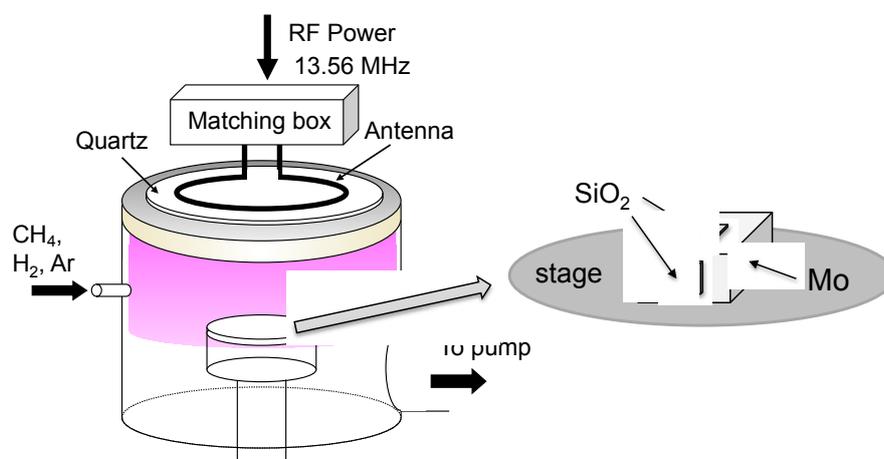


Fig. 2 Schematic of ICP setup, including the detail of stage with Mo block

As an example of application, CNWs were used as a platform for hydrogen peroxide (H₂O₂) sensing. This kind of application is based on the large surface area of conducting carbon and surface modifications including decoration with metal nanoparticles. It is known that H₂O₂ is a major messenger molecule in various redox-dependent cellular signaling transductions. Therefore, sensitive detection of H₂O₂ is greatly important in health inspection and environmental protections. For the H₂O₂ sensing, CNWs were grown on carbon fiber paper (CFP) to increase the surface area. Then, CNW surface was decorated with Pt nanoparticles to monitor H₂O₂ as

electrochemical technique. CNWs were grown on one side of CFP using ICP-CVD employing CH₄/Ar mixture for 90 min at 720 °C, RF power of 500 W, total gas pressure of 15–20 mTorr, and flow rates of CH₄ and Ar of 50 and 20 sccm, respectively. After the CNW growth on the CFP, surface hydrophilic treatment was carried out using Ar atmospheric pressure plasma. The CNWs with the hydrophilic surface were decorated with Pt-nanoparticles by the reduction of H₂PtCl₆ in solution. As a reduction agent, NaBH₄ was added in the water where H₂PtCl₆ was dispersed. Then, a CFP sheet with CNWs (CNW/CFP) was immersed into the mixed solution for 1.5 h.

Electrochemical measurements were carried out using a standard three-electrode setup with a Solartron SI 1287 potentiostat. Three electrodes: a working electrode, a counter electrode, and a reference electrode, were immersed in an electrolytic solution containing H₂O₂. In the electrochemical measurements, the detection efficiency of H₂O₂ and the catalyst activity of Pt nanoparticles are evaluated by cyclic voltammogram (CV) and amperometry. Cyclic voltammetry is one of major electrochemical measurement methods. The electrode potential is repeatedly scanned in the electrolytic solution containing the target substance. The amount of electrons exchanged between the target substance and the electrode is observed on a cyclic voltammogram as a pair of current peaks of oxidation and reduction reactions as a function of electrode potential. We conducted cyclic voltammetry using the counter electrode of a Pt coil, the reference electrode of Ag/AgCl, and the electrolytic solution of 0.1 M phosphate-buffered saline (PBS). For the working electrode, we prepared two types of electrodes, CNW/CFP without Pt nanoparticles and Pt-decorated CNW/CFP. The starting potential was set to –0.4 V and the return potential was set to 0.8 V. The scanning range was from –0.4 to 0.8 V. The number of measurement cycles was 20. The measurements were carried out at a potential scanning speed of 50 mV/s. Amperometry is the other method of electrochemical measurement for the analysis of temporal changes of electrical current. Only slight changes in the CV measurements of low-concentration substances such as H₂O₂ can be measured. The potential of the working electrode is fixed at the target potential, so that no reaction occurs and no current flows. By adding the target substance, the reaction current flows with the redox potential of the surface of the working electrode fixed at the value obtained by cyclic voltammetry. From this current, the concentration of the target H₂O₂ can be analyzed. An electrode sample was set on the working electrode. After 200 s elapsed for the initial measurement applying the potential, H₂O₂ was added dropwise into the electrolyte solution. The dropped H₂O₂ diffused spontaneously in the solution to reach the Pt nanoparticle surface and the electrical current immediately reached the stationary state. 100 μL of H₂O₂ was added dropwise every 100 s until the total concentration of 1500 μM was reached.

2. GROWTH CONTROL OF CARBON NANOWALLS

Most important factor affecting morphology, crystallinity and growth rate of CNWs is the balance between carbon precursors and etching radicals. Previously (Cho 2014) carried out plasma diagnosis using optical emission spectroscopy in the case of CNW growth using VHF plasma with H radical injection. By introducing small amount of Ar into plasma region, the actinometric measurements were carried out, where the emission intensity ratios ([CH]/[Ar] and [Hα]/[Ar]) were monitored by detecting the

spectral lines associated with H α 656.1 nm, CH 431.2 nm, and Ar 751.4 nm for determining the relative densities of H atoms and CH radicals. As the total pressure increased, the wall density decreased or interspaces between adjacent nanowalls increased, while [CH]/[Ar] decreased and [H]/[Ar] increased. On one hand, as the VHF power increased, the wall density increased or interspaces between adjacent nanowalls decreased, while [CH]/[Ar] increased and [H]/[Ar] decreased. It was found that the wall density could be controlled using the total pressure and the VHF power, and that H and CH radicals are the important chemical species and the density ratio [CH]/[H] can be useful and simple index for controlling the wall density.

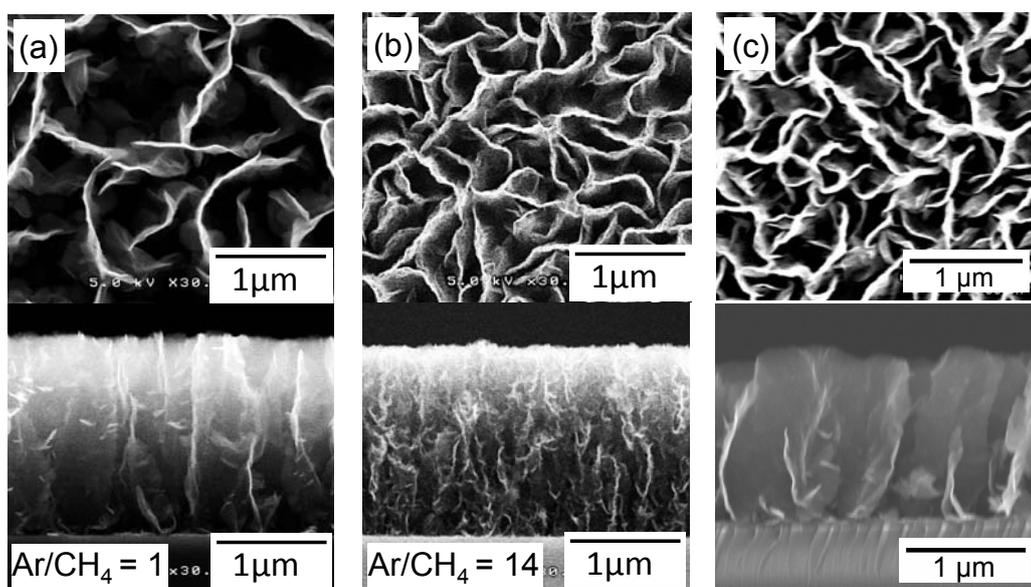


Fig. 3 Top view and cross-sectional SEM images of CNWs grown at (a) typical condition of Ar/CH₄ mixture, (b) high Ar flow rate, and (c) grown on Ti-nanoparticle decorated SiO₂ at low Ar flow rate

Ion bombardment on the substrate would play an important role in the nucleation by creating active sites for neutral radical bonding. Previously, (Kondo 2010) reported that the fluxes and energies of incident Ar ions would influence the nucleation of vertical nanographenes using multibeam CVD. Owing to the low-pressure operation in the case of ICP-CVD, the ion bombardment would be more effective for the nucleation of CNWs. Moreover, Ion bombardment on the growing surface would influence on the crystallinity of CNWs in the steady state growth. Growth experiments were carried out at different gas flow rate ratios of Ar/CH₄ using ICP-CVD. Typical top view and cross-sectional SEM images of CNWs grown at Ar/CH₄=1 are shown in Fig. 3(a). As the content of Ar in the mixture increased, space between walls decreased (top of Fig. 3(b)), probably due to the nucleation enhancement by the increase of the flux of incident Ar ions on the substrate. Due to secondary nucleation induced by the excess ion flux on

the growing surface, however, sheets were bent and branched, resulting in the poor crystallinity (bottom of Fig. 3(b)).

Recently, (Hiramatsu 2013) reported that some metals would enhance the nucleation of vertical nanographene. In the present study, Ti nanoparticles were deposited on a SiO₂ substrate by using the pulsed arc discharge, and Ti-decorated SiO₂ substrate was used to investigate the influence of Ti nanoparticles on the change of space between adjacent nanowalls. Figure 3(c) shows top view and cross-sectional SEM images of CNWs grown on Ti-nanoparticle decorated SiO₂ substrate at low Ar flow rate. In spite of low flow rate ratio of Ar/CH₄, dense CNW film was obtained (top of Fig. 3(c)), while keeping the smooth surfaces as shown in the bottom of Fig. 3(c). These results indicate that the interaction between metal nanoparticles and radicals can be also used to control the CNW structures.

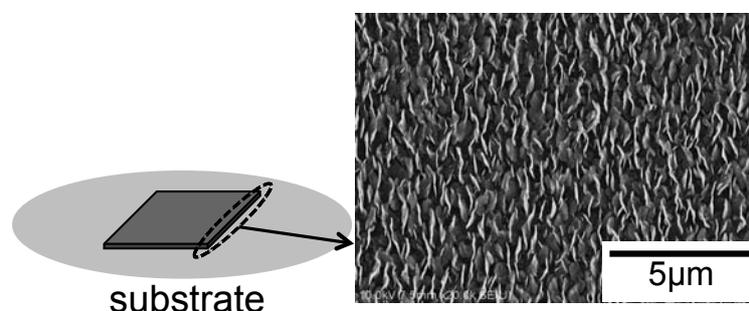


Fig. 4 SEM image of CNWs grown on the side surface of Si substrate under typical growth condition employing Ar/CH₄ mixture

It is noted that CNWs were grown on the side surface of the Si substrate set horizontally on the grounded electrode, and the morphology of the CNWs on the side surface of the substrate was very different from that of typical CNWs (Hiramatsu 2006). Figure 4 shows SEM image of CNWs grown on the side surface of Si substrate under typical growth condition employing Ar/CH₄ mixture. CNWs grown on the top surface of substrate had a typical maze-like structure, while aligned CNWs were grown on the side surface of the substrate as shown in Fig. 4. In this work, deposition was carried out on the substrate set perpendicular to the electrode stage using the Mo block. Figures 5(a) and 5(b) show SEM images of CNWs grown on SiO₂ substrates set horizontal and perpendicular to the electrode stage, respectively. Growth experiment was carried out for 2 h. In the case of deposition on the substrate set perpendicular to the electrode stage, straight and aligned CNWs were obtained as shown in Fig. 5(b). By the SEM observation of CNWs grown for different periods, it was found that the surface morphology in the early growth stage exhibited a typical maze-like structure even on the substrate set perpendicular to the electrode, then changed to an aligned structure after approximately 25 min. On the other hand, typical CNW film was prepared on the SiO₂ substrate for 1 h, and then successive growth was carried out for another 1 h on the same CNW film set perpendicular to the electrode stage. Consequently the surface

morphology was changed from a maze-like structure to an aligned one. The alignment mechanism of CNWs is currently under consideration. The findings in the present work would expand the range of applications using CNWs.

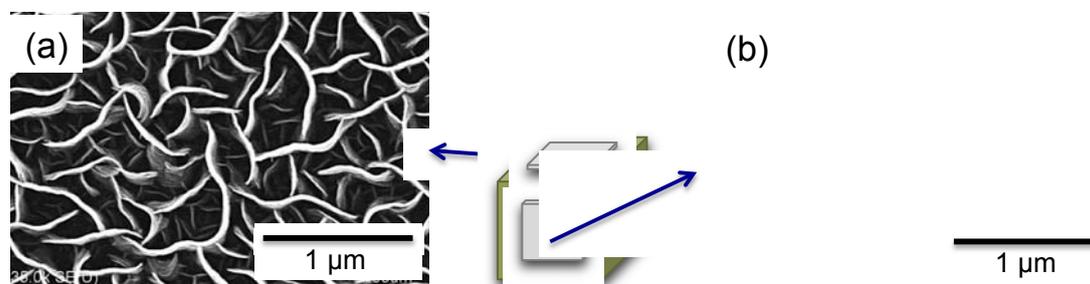


Fig. 5 SEM images of CNWs grown on SiO₂ substrates set on (a) top surface and (b) side surface of heated Mo block

3. APPLICATION OF NANOPATFORM BASED ON VERTICAL NANOGRAFENE

CNW film has many graphene edges and CNW sheet itself is composed of nanographite domains of a few tens of nanometers in size (Kobayashi 2007). These graphene edges and domain boundaries are chemically reactive, and are modified or decorated easily with several types of surface termination including metal nanoparticles and biomolecules. Therefore, the maze-like architecture of CNWs with large-surface-area graphene planes and a high density of graphene edges and domain boundaries can be suitable for the platform of electrochemical and biosensing applications. The electrochemical property of Pt-decorated CNW/CFP as the electrode of H₂O₂ sensor was explored.

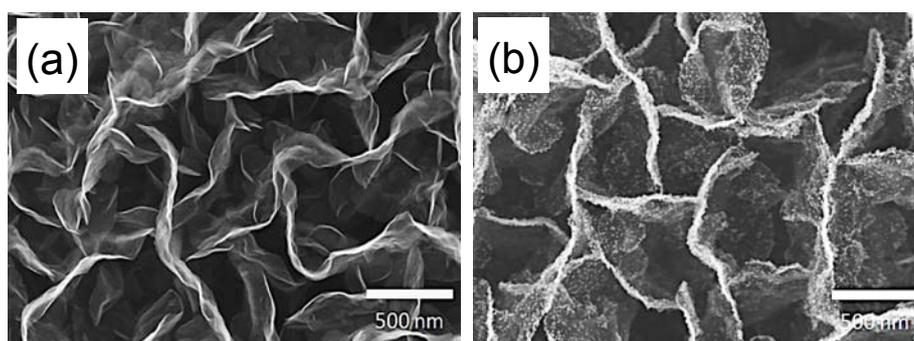


Fig. 6 SEM images of CNWs (a) before and (b) after Pt-nanoparticle decoration

Figures 6(a) and 6(b) show SEM images of CNWs grown on carbon fiber before and after Pt decoration, respectively. Pt nanoparticles were observed on the surface of

the CNWs after the Pt decoration, as shown in Fig. 6(b). The sizes of the Pt nanoparticles on the surface of the CNWs ranged from 5 to 7 nm. It is noted that Pt nanoparticles were formed even at the root region of the CNWs on the carbon fiber surface. X-ray photoelectron spectroscopy analysis indicated that only pure non-oxidized Pt existed on the surfaces of the CNWs. Therefore, it was confirmed that whole surfaces of CNWs were decorated with non-oxidized, catalytically active Pt nanoparticles uniformly by loading with liquid-phase reduction.

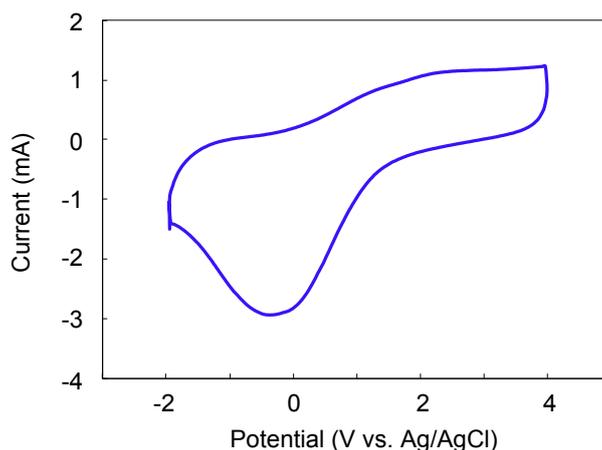


Fig. 7 Cyclic voltammogram response using Pt-decorated CNW/CFP electrode

Electrochemical property of Pt-decorated CNWs was evaluated by the cyclic voltammetry (CV) measurement in a standard three-electrode setup. Electrochemical performances of Pt-decorated CNWs towards H_2O_2 were investigated in 0.1 M PBS containing H_2O_2 with various concentrations. Figure 7 shows CV response of 240 μM H_2O_2 in 0.1 M PBS (pH=7.4) detected using Pt-decorated CNW/CFP as the working electrode. With a reaction between the working electrode and the substance during potential sweeping, a peak current is obtained in a potential range in which a reaction occurs as shown in the CV response. At zero potential, a positive peak current indicates that an oxidation reaction occurs, while a negative peak current indicates that a reduction reaction occurs. In the case of using Pt-decorated CNW/CFP as the working electrode, a reduction peak was observed at a potential in the range of -0.2 to -0.1 V. In the case of using CNW/CFP without Pt-nanoparticles as the working electrode, no peak current was observed in a range from -0.4 to 0.8 V. There is no doubt that the reduction peak appeared only when the CNWs were decorated with Pt nanoparticles.

The amperometric response of the Pt-decorated CNW/CFP electrode was measured at various H_2O_2 concentrations obtained by periodic addition of small amounts of H_2O_2 solution. Amperometry was performed at -0.1 V in PBS, since the redox potential of H_2O_2 with respect to Pt nanoparticles was approximately -0.1 V, as shown in Fig. 7. After setting the potential at -0.1 V, the current was traced

continuously. After the addition of a drop of H_2O_2 , the current abruptly overshoot, then plateaued gradually. The current generated at this plateau is proportional to the concentration of the H_2O_2 in the PBS. Figure 8(a) shows response current values as a function of H_2O_2 concentration. It was found that response current values increased linearly with H_2O_2 concentrations, indicating that the Pt-decorated CNW/CFP electrode displays a good linear relationship between response current and H_2O_2 concentration in PBS. Figure 8(b) shows a plot of response current against H_2O_2 concentration at mid concentrations of H_2O_2 obtained using the same Pt-decorated CNW/CFP electrode. It was found that the calibration plot was linear over a wide concentration range from 10 μM to 1.5 mM.

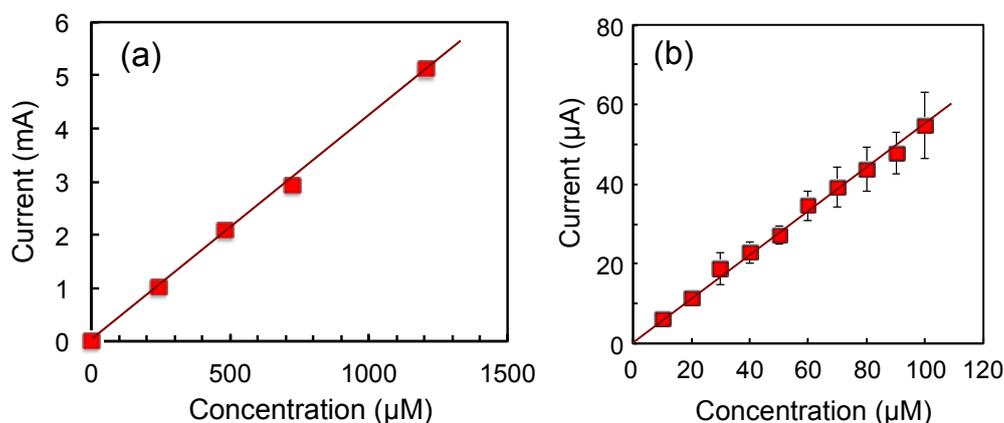


Fig. 8 Response current values as a function of H_2O_2 concentration at (a) high and (b) mid concentrations

At present, the detection limit for H_2O_2 in this work is lower than 1 μM . The Pt-decorated CNW/CFP electrode exhibits excellent electrocatalytic capability towards H_2O_2 due to a large amount of Pt nanoparticles present on conductive carbon providing a large specific surface area. The CNWs act as a good support for achieving a high dispersion of Pt nanoparticles, preventing them from aggregation after more than 10 repeated measurements and thus preserving the high catalytic performance of Pt nanoparticles. By increasing the height of CNWs to increase the specific surface area, together with the optimization of the size and quantity of supported Pt nanoparticles, the electrode performance including detection sensitivity and linear range of the calibration plot could be improved further.

Pt-decorated CNWs were successfully used as an electrode for H_2O_2 sensing. Electrochemical experiments indicate that nanoplatform based on vertical nanographene with large surface area and high electrocatalytic activity offers great promise for providing a new class of nanostructured electrodes for electrochemical sensing and biosensing applications.

4. CONCLUSIONS

We focused on the control of density and crystallinity of CNWs. As the content of Ar in the mixture increased, space between walls decreased. Due to secondary nucleation induced by the excess ion flux, however, sheets were bent and branched, resulting in the poor crystallinity. On the other hand, in the case of CNW growth on the Ti-nanoparticle decorated SiO₂ at low Ar low rate, dense CNW film with smooth surfaces was obtained. In addition, deposition was carried out on the substrate set perpendicular to the electrode stage. As a result, straight and aligned CNWs were obtained.

As an application, CNWs were used as a platform for H₂O₂ sensing, which is based on the large surface area of conducting carbon and surface decoration with Pt nanoparticles. Amperometric response results indicated that the Pt-decorated CNWs grown on CFP exhibited a wide linear range of 10-1500 μM. Electrochemical experiments demonstrate that nanostructures based on vertical nanographenes offer great promise for providing a new class of nanostructured electrodes for electrochemical sensing and biosensing applications.

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