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Application-Specific Catalyst Layers: Pt-Containing Carbon Nanofibers for Hydrogen Peroxide Detection

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Supporting Information

ABSTRACT: Complete removal of metal catalyst particles from carbon nanofibers (CNFs) and other carbon nanostructures is extremely difficult, and the envisioned applications may be compromised by the left-over impurities. To circumvent these problems, one should use, wherever possible, such catalyst materials that are meant to remain in the structure and have some application-specific role, making any removal steps unnecessary. Thus, as a proof-of-concept, we present here a nanocarbon-based material platform for electrochemical hydrogen peroxide measurement utilizing a Pt catalyst layer to grow CNFs with intact Pt particles at the tips of the CNFs. Backed by careful scanning transmission electron microscopy analysis, we show that this material can be readily realized with the Pt catalyst layer thickness impacting the resulting structure and also present a growth model to explain the evolution of the different types of structures. In addition, we show by electrochemical analysis that the material exhibits characteristic features of Pt in cyclic voltammetry and it can detect very small amounts of hydrogen peroxide with very fast response times. Thus, the present sensor platform provides an interesting electrode material with potential for biomolecule detection and in fuel cells and batteries. In the wider range, we propose a new approach where the selection of catalytic particles used for carbon nanostructure growth is made so that (i) they do not need to be removed and (ii) they will have essential role in the final application.

INTRODUCTION

Despite its simple structure, hydrogen peroxide (H₂O₂) has a widespread usage ranging all the way from industrial to alimentary and clinical applications. It can be either electrochemically oxidized to O₂ (E⁰ = 0.695 V) or reduced to water (E⁰ = 1.763 V) in diffusion-controlled two-electron processes.¹ Hydrogen peroxide and its redox reactions are closely linked to fuel cell technology as it is formed as a reaction intermediate in the oxygen reduction reaction.¹–³ Furthermore, H₂O₂ is formed as a byproduct in various enzymatic reactions such as those catalyzed by glucose oxidase,⁴ glutamate oxidase,⁵ and cholesterol oxidase.⁶ Enzymatic production makes H₂O₂ feasible for biosensor applications as it can be indirectly detected at lower potentials compared to the enzyme substrate molecules. However, H₂O₂ is typically detected indirectly in sensor applications by its chemical interaction with metallic electrode surfaces, which then produce the current, as is the case, for example, with Pt.

Pt-based electrodes have been frequently used to detect hydrogen peroxide.⁸–¹⁰ Likewise, carbon-based nanostructures in the form of nanotubes and nanofibers have been extensively used in the detection of different biomolecules via and without enzymatic detection.¹¹–¹⁷ The structure of oriented carbon nanofibers (CNFs) is especially ideal for enzyme linking without any additional polymer layers. For example, glutamate detection via enzymatic reaction that produces hydrogen peroxide with various metal-particle-containing carbon nanotubes (CNTs) and CNFs has been demonstrated.¹⁸,¹⁹ These metal particles typically remain in the catalyst layers used to grow the carbon nanostructures that stay on the tubes or fibers despite the cleaning procedures. Consequently, unwanted electrochemical features are often introduced and the interpretation and control of the reactions taking place in the systems become complicated. On the basis of the available information, it appears that carbon alone is not as active toward the hydrogen peroxide as the carbon hybrids containing...
metallic nanoparticles. Hence, we introduce the concept of utilizing application-specific catalyst layers in this article to realize carbon nanostructures where metallic nanoparticles on the tips of the nanostructures are present not because they are optimum for the growth process but because they have a specific electrochemical role in the final structure. This approach requires no removal procedures as the remaining metallic catalyst is actually needed for the intended application. Thus, as a proof-of-concept, we combine here the structural features of CNFs with the known electrocatalytic properties of Pt to demonstrate the growth of Pt-containing CNFs and show that they can be used for hydrogen peroxide detection with high sensitivity. The objective is to fabricate a structure with a high amount of small catalytic particles that do not experience coarsening during continuous use and that are directly electrically connected to the electrode surface. Detailed high-resolution transmission electron microscopy (HRTEM) analysis combined with the electrochemical characterization is utilized to support our arguments and rationalize the growth of these novel materials.

**RESULTS**

**Structure.** Figure 1 shows the resulting structures from the growth process for two different Pt layer thicknesses. The 2 nm thick Pt catalyst layer did not produce proper fibers; instead, formation of cone-like structures with a large number of small Ti particles randomly scattered throughout the structure is seen.

The height of these cone-like features is on the order of a few tens of nanometers. One can also clearly observe that the Ti layer has reacted with Si to form Ti-silicide (most likely TiSi$_2$); consequently, there are many characteristic trenches for the silicide formation reaction at the Si interface. In addition, there is no continuous Ti layer on top of Si, but the Ti is either distributed inside the cone-like structures or incorporated in the Ti-silicide, as shown by energy-dispersive spectrometer (EDS) elemental map (Supporting Information). Pt is also similarly distributed within the whole reaction zone.

In contrast, the 10 nm thick Pt catalyst layer has produced CNFs. The length of the fibers is typically a few hundreds of nanometers, but some structures are up to the micrometer scale. Again, one can see a fairly large number of finely dispersed Ti particles along the body of the fiber. However, Pt particles are also seen at the tip of the fibers (Figure 2), which was not the case with the cone-like structures. In addition, the original Ti layer is still mostly preserved at the Si/Ti interface in contrast to the samples with the 2 nm thick Pt layer (see EDS elemental maps in Supporting information) despite the formation of Ti-silicide(s) at some locations. A notable feature is that the CNFs appear to adhere to the surface only from the locations where the Ti layer is still intact and not where Ti-silicide formation has taken place. Thus, this underlines the role of Ti as the adhesion layer in our structure. Despite the fact that the 10 nm thick Pt catalyst layer does produce CNFs, the
growth kinetics is rather slow when compared to that of the same process with Ni catalyst.\textsuperscript{20,21}

Higher-magnification imaging of the CNFs grown with the 10 nm Pt catalyst layer reveals several features: (i) in most cases, the Pt can be found exclusively at the tip of the CNF as a particle. At some locations, it appears that Pt particles are also distributed along the fiber body, but this represents a minority case. In addition, in many cases, this may be a result of fibers of different lengths crossing each other. (ii) Pt particles at the tip of the fibers do not seem to have any specific shape or size, but they are more or less of random orientation and size. This is likely to be a result of the mostly repulsive interaction between Pt and C as discussed later on. However, the structure seems to be single crystal. (iii) The number of finely dispersed Ti particles strongly decreases as one moves from the root of the fiber toward the tip. (iv) The ordering of graphene planes in the fibers and around the Pt particles is not so pronounced as with other catalyst materials such as Ni,\textsuperscript{20,21} which again most likely has its origin on the repulsive interaction between Pt and C.

**Electrochemistry.** Only the CNF/Pt samples with the 10 nm Pt catalyst layer produced clear Pt-type characteristics during cyclic voltammetry. This indicates that the amount of exposed Pt was not high enough with the samples grown from the 2 nm Pt catalyst layer. Therefore, only the results from the samples with the 10 nm Pt layer are presented here in Figure 3a, showing the cyclic voltammogram of the CNF/Pt hybrid material in 0.15 M H\textsubscript{2}SO\textsubscript{4}. A similar voltammogram for the polycrystalline thin-film Pt sample is shown in Figure 3b, and Pt-like features are evident from a comparison of Figure 3a,b. At the anodic end of Figure 3a, one can see the shoulder related to the formation of Pt-oxide although it is not possible to observe clearly all the three peaks corresponding to the gradual formation process of Pt-oxide on polycrystalline Pt in ultrahigh-purity H\textsubscript{2}SO\textsubscript{4}.\textsuperscript{22} Also, the reduction peak of Pt-oxide is clear with the CNF/Pt electrode. Likewise, at the cathodic end, the hydrogen adsorption and desorption peaks are evident although they are not as clearly exhibited as with the thin-film Pt sample. The slight attenuation of the Pt features in the case of CNF/Pt samples might be caused by impurities present in the system. However, as the current at the anodic end does not rise significantly at the Pt-oxide formation region, the amount of oxidizable impurities is not expected to be very high. In fact, the most likely origin of any oxidizable and other impurities in the case of CNF/Pt electrodes would be the samples themselves. Therefore, we believe that we can to a large extent ignore these minor additional features in the electrochemistry of these samples. Thus, we can state that the CNF/Pt electrode clearly shows the features of polycrystalline Pt, indicating that the Pt particles present in the structure are not predominantly of
certain orientation (e.g., only (111) or (200)) but more or less randomly oriented. The notable differences between the CNF/Pt and thin-film polycrystalline Pt samples include (i) the cathodic shift and less-well-defined shape of the Pt-oxide reduction peak and (ii) the narrower double-layer region and higher background current density in the case of the CNF/Pt electrode. These differences are likely to be a result of CNF/Pt having a higher active area than that of the geometrically same-sized thin-film Pt electrode and because Pt is in the form of nanoparticles instead of a film, as discussed later on. It is to be noted that there is no observable electrochemical effect from the Ti nanoparticles embedded within the CNF.

Figure 4a shows the results from the chronoamperometry measurements with different amounts of H$_2$O$_2$ in phosphate-buffered saline (PBS) with the CNF/Pt (10 nm) samples. The potential is stepped to $-0.1$ V versus Ag/AgCl reference, that is, to the double-layer region, and the solutions were not purged with argon. The reasons for these choices are that (i) we are detecting the reduction current originating from the reduction of the unstable Pt-oxide formed as a consequence of the chemical decomposition of H$_2$O$_2$ on the originally metallic Pt and that (ii) we need to assess if oxygen, which is inevitably present under the in vivo conditions, would disturb our measurements. Details of the mechanism related to (i) are described elsewhere.$^{7,9}$ As can be seen in Figure 4, the presence of hydrogen peroxide increases the cathodic current that starts to significantly deviate from the charging current already after 20 ms although the differences in the concentrations become more evident after about 60 ms. Thus, the response time is very fast as required by many applications such as enzymatic glutamate detection for example.$^{23}$ Figure 4b shows that the CNF/Pt (10 nm) electrode also has a fairly long linear range for H$_2$O$_2$, which together with the fast response time and high sensitivity makes this material a promising platform for hydrogen peroxide detection.

**DISCUSSION**

To gain more insight into the growth mechanism responsible for the observed structures, cross-sectional STEM investigations of the as-fabricated and preannealed Si/Ti/ta-C/Pt (2 or 10 nm) samples were carried out.

Figure 5 shows the two types of samples (2 or 10 nm Pt) after the deposition process. The 2 nm Pt catalyst layer shows an uneven rough structure and some discontinuities in the film (Figure 5a,b) whereas the 10 nm Pt layer appears to be uniform with a relatively flat surface (Figure 5c,d). The Ti adhesion layer and ta-C layer are of similar thicknesses and morphologies in both types of samples. The ta-C layer is slightly thinner in both cases than expected (e.g. 5 vs 7 nm). The interface between the Ti and ta-C layers is not particularly sharp in either sample type, indicating some degree of mixing, but there is no evidence of excessive interfacial reaction or interdiffusion after the deposition. There is an additional layer at the Si/Ti interface in both samples, which has been shown to be an oxygen-rich SiO$_x$ type of layer.$^{24,25}$ The above arguments are further confirmed by the dark-field images (Figure 5b,d).
To obtain further information about the structures of catalyst layers after fabrication, we carried out X-ray reflection (XRR) and grazing incidence angle X-ray diffraction (GIXRD) measurements for the two types of samples. While comparing the GIXRD spectra (Figure 6) for the 2 and 10 nm Pt films, it is evident that there are significant differences in the film structure already after fabrication. Whereas in the 10 nm Pt film all five Pt peaks are clearly present, in the 2 nm Pt film hardly any Pt features can be seen and peaks most likely originating from the underlying Ti and Si layers can also be observed (the peak around 50°, which has not been indexed in Figure 6 as the origin of it is not unambiguously known). This indicates that the 10 nm Pt film is clearly continuous and polycrystalline with no preferred orientation, whereas the 2 nm Pt film is likely to be relatively non-uniform with varying thickness, which is consistent with the STEM micrographs seen in Figure 5a–d. On the basis of the analysis of full width at half-maximum of the Pt peaks, the grain size could be estimated to be in the range of 5 nm in the 10 nm Pt catalyst film. The XRR measurements (Figure S3a,b) from the two types of samples further suggest that whereas the 10 nm Pt film appears to be fully continuous and uniform the 2 nm Pt film appears to be relatively discontinuous, and some mixing with the underlying ta-C film seems to have occurred already during deposition. Thus, on the basis of the information from the literature and from the results of this work, it is evident that Pt is not a particularly good catalyst for CNF or CNT growth.29,30 This is caused most likely by the repulsive interaction between Pt and C, which leads among other things to a very low solubility of graphite to fcc-Pt. In addition, there are no known Pt-carbides (stable or metastable), further highlighting the lack of any attractive interaction between Pt and C. The repulsive interaction between Pt and C by no means excludes the
mixing of the elements as the latter process is fundamentally driven by the increase in the configurational entropy of the system. Contributions from the entropy can be expected to overrun any enthalpy contributions (interaction term) quite easily at these relatively high temperatures. However, the lack of favorable interaction between Pt and C leads to a long incubation time at the start of the growth phase. This is the case of the 2 nm thick Pt layer, leading to the disintegration of the whole initial structure owing to the following reasons: (i) on the basis of the micrographs in Figures 5 and 7, as well as GIXRD and XRR results (Figures 6 and S3), the 2 nm Pt layer is highly discontinuous already after the deposition stage and becomes more and more irregular during the preannealing stage before the growth phase starts. (ii) Consequently, the ta-C layer is directly exposed (at least partly) to the acetylene (carbon plasma) in the chamber. When the acetylene decomposes on the surface, it produces mostly carbon and hydrogen.\(^3\) The hydrogen from the decomposition will etch and graphitize the ta-C thin films (see the Raman results in Figure S4), which then leads to the partial (or total) disappearance of the ta-C film. (iii) As a result, there is no fully protective ta-C film on top of the Ti layer and it will start to react with the incoming carbon, leading to the production of the mixed carbon and titanium cones. Pt is also distributed randomly along the cones as there is practically no “growth” phase in this case (Figure 8a,b).

Some of the Ti also reacts with the underlying Si substrate to produce Ti-silicide, which together with the cone formation results into the disappearance of the original Ti layer. In contrast, the 10 nm Pt film, owing to its uniform morphology after the preannealing stage, manages to protect the underlying ta-C (and consequently also Ti) films until the actual CNF growth phase kicks in. Thus, this results into the observed structure where Pt particles are at the tips of the resulting CNF. In contrast, the 10 nm Pt film, owing to its uniform morphology after the preannealing stage, manages to protect the underlying ta-C (and consequently also Ti) films until the actual CNF growth phase kicks in. Thus, this results into the observed structure where Pt particles are at the tips of the resulting CNF (Figure 7b,d). Also, the structure of the fibers in this case is somewhat less ordered than, for example, that with Ni catalysts, owing to the repulsive nature of the Pt interaction with the graphene sheets. The Pt particles observed at the CNF tips are mostly single crystals (Figure 9), but their size is too large in general that they could be directly traced back to the original Pt film with the grain size on the order of 5 nm. It is possible that during the initial CNF growth stage the Pt film partly disintegrates and recrystallizes to produce these larger grains that can be found at the tips of the CNF. However, this issue requires further studies. The ta-C layer is again decomposed after the exposure to the growth environment by hydrogen formed during the decomposition of acetylene and perhaps partly used for the CNF growth.

Hence, we can conclude that owing to the repulsive interaction between Pt and C and the resulting relatively poor catalytic properties of Pt for CNF growth, the incubation...
time at the start of the growth becomes long. This then leads to complete disintegration of the Si/Ti/ta-C/Pt (2 nm) structure before any actual growth can occur, subsequently leading to the observed cone-type structures where Ti and Pt particles are randomly scattered along the disordered structure. In contrast, the 10 nm Pt catalyst layer is able to protect the underlying structure from disintegration until the actual growth phase starts and therefore leads to the observed CNF structures where Pt particles sit on the top of the fibers and are not randomly scattered in the reaction zone.

The electrochemical features seen in Figure 3 and especially the cathodic shift in the Pt-oxide reduction potential and the shape of the peak can be understood on the basis of the above discussion. The reduction peak is shifted cathodically with respect to that of the thin-film Pt electrode, owing to the small size of the Pt particles at the tip of the CNF, which leads to a higher adsorption strength of OH on these particles in comparison to that on the Pt thin film, as shown in refs 32, 33. Thus, the reduction of the Pt-oxide becomes harder than that in a case of a uniform (“infinite”) Pt film. The electrode shown in Figure 3a has been cycled already ca. 50 cycles before recording the voltammogram in the figure. This exemplifies the stability of the CNF-anchored nanoparticles as the Pt-oxide reduction peak does not become narrower and shifts back to that of bulk Pt, which would indicate significant coarsening/agglomeration of the structure even with this prolonged cycling. Thus, the desired high active catalyst area is retained. This is a clear advantage over conventional Pt nanoparticle carbon hybrids where Pt is deposited on top of an existing carbon structure and can be expected to be beneficial not only in basic research of nanoparticle electrochemistry but also, for example, in fuel cell technology. In addition, as shown in Figure 8, there is a relatively large size distribution among the Pt particles. This is suggested to lead to the broadening of the Pt-oxide reduction peak as the OH adsorption strength will change as a function of the Pt particle size and lead to a gradual reduction (thus wide peak) reaction where largest particles are reduced first followed by the smaller ones. Finally, the various single Pt crystals at the CNF tips must possess different orientations as the voltammogram clearly shows features of polycrystalline Pt without any signs of electrochemical response arising from only certain orientations of Pt films, such as (111), (110), and (100). 35

The amperometric response of our structure toward H₂O₂ is shown in Figure 4. The current density (circular sample area, r = 1.5 mm) was averaged between 0.05 and 0.2 s from step 2 to evaluate the linear response. Between 10 and 1000 μM, the ta-C/CNF hybrid shows a linear behavior with a limit of detection of ∼0.2 nM (S/N = 3) and sensitivity of 0.1478 μA μM⁻¹ cm⁻² (Table 1). An earlier study with vertically aligned CNFs showed a detection limit of 66 μM and sensitivity of 0.0906 μA μM⁻¹ cm⁻² at anodic current (at 0.6 V vs Ag/AgCl). Here, we have gained significant improvement in sensitivity, over 300 000-fold, at the cathodic end (−0.1 V) when the calculated limit of detection is considered. Thus, incorporating Pt (and only Pt) intentionally to CNF tips has had a significant positive effect on the electrochemical performance of the CNF structure as desired.

Compared to that of other carbon nanomaterials, the improvement in sensitivity is also significant as can be seen from Table 1 and remains unmatched even by Pt nanoparticles on CNTs. 36 Also, if one compares the present material to mesoporous Pt and Pt nanowires, CNF + Pt electrodes outperform these structures significantly both in sensitivity and temporal resolution. The fact that we utilize a reductive potential of −0.1 V (vs Ag/AgCl) most likely reduces the interference from, for example, dopamine and ascorbic acid as these typically oxidize at higher (positive) potentials on carbon-based structures and Pt. 32−34 Moreover, the response time of our electrode material for H₂O₂ is clearly faster than for any
other structure shown in Table 1. This is a huge advantage in enzymatic sensing of different biomolecules such as an important neurotransmitter glutamate. In situ detection of glutamate is an extremely difficult task especially owing to the strict temporal and spatial requirements (response times must be few tens of microseconds and measurement probe size approximately 1−5 μm).23 On the basis of the values shown in Table 1, our structure is the only one that can meet the temporal requirement and has the potential to provide physically meaningful information from in situ measurements. The CNF structure also provides means to meet the spatial requirement as the individual CNF-Pt fibers have diameters less than 100 nm, thus making the present material platform extremely interesting from sensing point of view. This is an important advantage over various other Pt-incorporated carbon nanostructures obtained with electrospinning and subsequent carbonization,55−57 as it would be very difficult to realize devices with micrometer or nanometer size dimensions from these ones. Finally, the crucial role of Pt particles at the CNF tips for reaching the present sensitivity and time resolution levels toward H₂O₂ can be appreciated when considering the results from the identical amperometric measurements made by utilizing Pt-free CNFs reported by us earlier in ref 19. In this study, we processed similar CNF structures by the same growth parameters as here but by utilizing nanodiamonds as a catalyst layer, thus achieving metal-free CNF structures. The response of these structures towards H₂O₂ was significantly weaker than that of the present structure,19 highlighting the necessity of having the Pt particles at the CNF tips to achieve superior performance. Likewise, in the same study,19 we also used Ni catalyst (and again the same processing parameters) to grow CNF structures with Ni particles at their tips,19 but again the performance was of markedly lower quality than that achieved with the CNF/Pt structures in the present study.

## CONCLUSIONS

We have introduced a novel concept of using application-specific catalyst material for CNF growth that is meant to stay in the structure. Thus, no metal particle removal steps are required. As a proof-of-concept, we have realized a hybrid structure in which Pt nanoparticles are integrated into CNFs. A growth model to explain the evolution of the different types of structures has been presented with the aid of a detailed TEM analysis. The electrochemical analysis shows that the material reveals characteristic features of Pt and that it can detect small amounts of hydrogen peroxide with very fast response times. The latter is very important in many applications, for example, in enzymatic detection of various biomolecules such as glutamate. Benchmarking the present results to those obtained by CNF or Pt alone highlights that the present hybrid material has performance significantly higher than that of its individual components. Thus, the present material platform provides an
extremely interesting basis for further applications in biomedical technology, fuel cells, battery technology, and related areas.

**EXPERIMENTAL WORK**

**Synthesis.** The CNFs were grown on n-type Si(100)/Ti(20 nm)/ta-C(7 nm)/Pt(2/10 nm). The synthesis can be briefly described as follows: n-type Si (100) wafer substrates (Ultrasil) were mounted by hanging in a rotating carousel (0.04 rpm) in a chamber with a base pressure of $10^{-3}$ Pa. The expected tetrahedral amorphous carbon (ta-C) film thickness was about 7 nm. Prior to deposition, the wafers were etched with a gridless argon ion source and coated with Ti using a continuous-current arc source equipped with 60° magnetic filtering. The role of Ti is to ensure excellent adhesion of the ta-C layer on the substrate. A 2 or 10 nm thick Pt catalyst layer was deposited on Ti using cathodic arc deposition. The catalyst-coated wafers were placed in a cold-wall plasma-enhanced chemical vapor deposition (PECVD) reactor (Aixtron, Black Magic, Germany) with the chamber pressure pumped down to <1 Pa, and the samples were annealed at 400 °C for 3 min before the growth process was started. The chamber was heated to 400 °C by a ramp speed of 250 °C/min. After the annealing step, the NH$_3$ buffer was used to fill the chamber (100 sccm) while the chamber pressure was maintained at 0.1 mbar. The temperature was increased to

![Figure 8](image_url)

Figure 8. (a, c) Bright-field as well as (b, d) dark-field STEM micrographs showing the resulting structures from the growth process with (a, b) Si/Ti/ta-C/Pt (2 nm) and (c, d) Si/Ti/ta-C/Pt (10 nm) samples. (e) Schematic presentation of the resulting structures.
750 °C with a ramp speed of 300 °C/min. After the temperature had reached 675 °C, 150 W DC plasma was ignited while injecting the carbon precursor, C2H2, to the chamber (30 sccm) and increasing the NH3 flow to 125 sccm. The growth phase lasted 10 min and produced vertically aligned fibers that were ∼0.2−1 μm tall, as shown in Figure 1a,b, depending on the Pt layer thickness. After the growth process, the pressure was maintained below 0.2 mbar until the temperature decreased to 300 °C.

**STEM Analysis.** Cross-sectional STEM samples were prepared by focused ion beam (FIB) using first 30 kV for thinning and subsequently 5 kV for final polishing. Polymer ink was used as the filler material with 70−80 nm of sputtered Pt and FIB-deposited Pt-C to protect the vertical CNF during thinning. HRTEM of the samples was performed using a double-aberration-corrected microscope, JEOL 2100 (JEOL, Japan), equipped with a X-ray EDS operating at 200 kV. A Gatan 4k × 4k UltraScan 4000 CCD camera was employed for digital recording of the HRTEM images.

**GIXRD and XRR Measurements.** GIXRD and XRR measurements were performed using Rigaku SmartLab diffractometer equipped with a 9 kW rotating Cu anode (1.54 nm wavelength) and HyPix-3000 2D single photon counting detector operated in a 1D mode. All measurements

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Table 1. Comparison of the Properties of Amperometric Carbon-Based H2O2 Sensors

<table>
<thead>
<tr>
<th>material</th>
<th>detection potential (V vs Ag/AgCl)</th>
<th>LOD (μM)</th>
<th>sensitivity (μA μM−1 cm2)</th>
<th>detection time (s)</th>
<th>linear range (μM)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtNPs/CNT on GC</td>
<td>0.55</td>
<td>0.025</td>
<td>3.57</td>
<td>N/A</td>
<td>0.025−10</td>
<td>36</td>
</tr>
<tr>
<td>AgNPs/Chit-GO/cysteamine on Au</td>
<td>−0.442</td>
<td>0.7</td>
<td>1.5</td>
<td>N/A</td>
<td>0.05−5</td>
<td>37</td>
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<tr>
<td>PB/graphene on GC</td>
<td>−0.2</td>
<td>0.02</td>
<td>1.6</td>
<td>N/A</td>
<td>50−500</td>
<td>38</td>
</tr>
<tr>
<td>GNPs/SGS on GC</td>
<td>−0.242</td>
<td>0.25</td>
<td>0.00321</td>
<td>3</td>
<td>2300−16 000</td>
<td>39</td>
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<tr>
<td>Chit-MWCNTs/Hb/AgNPs on GC</td>
<td>−0.3</td>
<td>0.347</td>
<td>N/A</td>
<td>5</td>
<td>6.25−93</td>
<td>40</td>
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<tr>
<td>ERGO-ATP-Pd on GC</td>
<td>−0.2</td>
<td>0.016</td>
<td>0.49209</td>
<td>10</td>
<td>0.1−10 000</td>
<td>41</td>
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<tr>
<td>CNT/PB</td>
<td>0</td>
<td>0.00474</td>
<td>31.4</td>
<td>5</td>
<td>0.05−5</td>
<td>42</td>
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<tr>
<td>nanoCoPc-graphene on GC</td>
<td>0.278</td>
<td>10.1</td>
<td>N/A</td>
<td>0.2</td>
<td>14−63</td>
<td>43</td>
</tr>
<tr>
<td>Pt/porous graphene on GC</td>
<td>−0.1</td>
<td>0.5</td>
<td>0.34114</td>
<td>3</td>
<td>1−1477</td>
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<tr>
<td>Au@Ag@C nanocomposite on GC</td>
<td>−0.55</td>
<td>0.14</td>
<td>0.07602</td>
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<td>5−75</td>
<td>45</td>
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<tr>
<td>Au@C@Pt nanocomposite on GC</td>
<td>0</td>
<td>0.13</td>
<td>0.1447</td>
<td>10</td>
<td>9−1860</td>
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<td>Pd core-PtNPs/PDDA-rGO on GC</td>
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<td>0.027</td>
<td>0.672753</td>
<td>5</td>
<td>5−500</td>
<td>47</td>
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<td>CNFs</td>
<td>0.6</td>
<td>66</td>
<td>0.0906</td>
<td>N/A</td>
<td>N/A</td>
<td>48</td>
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<td>MnO2/rGONRs on GC</td>
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<td>0.071</td>
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<td>several seconds</td>
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<td>49</td>
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<td>Mesoporous Pt</td>
<td>0.45</td>
<td>4.5</td>
<td>2.8</td>
<td>N/A</td>
<td>20−40 000</td>
<td>50</td>
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<tr>
<td>Pt nanowires</td>
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<td>0.05</td>
<td>0.54</td>
<td>N/A</td>
<td>0.1−6000</td>
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<tr>
<td>Pt-CNFs</td>
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<td>0.000195</td>
<td>0.1478</td>
<td>&lt;0.05</td>
<td>10−1000</td>
<td>this work</td>
</tr>
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</table>

*PtNP: Pt nanoparticle; AgNP: Ag nanoparticle; Chit: chitosan; GO: graphene oxide; PB: Prussian Blue; GNP: gold nanoparticle; SGS: sulfonated graphene; MWCNT: multiwalled carbon nanotubes; Hb: hemoglobin; ERGO: electrochemically reduced graphene oxide; ATP: aminothiophenol; CoPo: cobalt phthalocyanine; PtND: Pt nanodendrite; PDDA: poly (diallyldimethylammonium chloride); rGO: reduced graphene oxide; rGONR: reduced graphene oxide nanoribbons.*
were conducted in parallel beam mode on 10 \times 10 \text{mm}^2 samples with an incidence \alpha_1 monochromator, a 5 \text{ mm} horizontal slit, and 5\degree angular aperture Soller slits at both ends. Incidence vertical slit varied according to investigated GIXRD omega angles determined from XRR profiles. Thus, the grazing incidence angles varied from 0.25 to 0.40\degree with vertical slits of 0.043–0.069 mm for the 2\text{ Pt} sample and from 0.6 to 2.0\degree with vertical slits of 0.104–0.348 for the thicker 10 \text{ nm} Pt sample. GIXRD scans were performed in steps of 0.2\degree and 1\degree / min in the range of 25–93\degree.

**Electrochemical Measurements.** Cyclic voltammetry and amperometry were performed with a Gamry Reference 600 potentiostat and Gamry Framework software (Gamry Instruments). The reference electrode was a Ag/AgCl/KCl saturated electrode (+0.199 vs SHE, Radiometer Analytical) and the potentiostat and Gamry Framework software (Gamry Instruments). Cyclic voltammetry and amperometry were performed with a Gamry Reference 600 min in the range of 25–93\degree.

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