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Electrochemical processing of carbon nanostructures

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Carbon based electrodes have a long tradition in electrochemistry. Glassy carbon (which is now recognised as also predominantly sp^2 type) has been used for electrochemical analysis as well as mechanistic and kinetic studies of multitude of electrochemical reactions. Highly oriented pyrolitic graphite (HOPG) has been of interest because of the large difference in electrode kinetics between the graphene basal plane with slow kinetics compared to the edge planes with large electrodekinetics. As such, the edges can be decorated by nanoparticles by selective electrodeposition. With the recent advent of the graphene based nanostructures: one-dimensional nanotubes and nanofibres, vertically standing carbon nanosheets (CNS) and monolayer graphene itself, the electrochemical characterization and functionalization of these novel nanostructured materials has been explored. In this paper, the functionalization of CNT and CNS by electrodeposition will be discussed. Also some examples will be shown were the carbon is used as the functionalizing electroactive coatings.

Electrodeposition on CNT happens on defects as the CNT outer graphene sheet exhibits low electrode kinetics similar to the basal of HOPG. This can be used to decorate the defects (Ni-decorated CNT grown out of a contact hole, Fig. 1a). When the tubes are fiber-like, they can be completely coated with metal (Ni-coated CNT bundle grown out of contact hole, Fig. 1b). The selective deposition can be used for the fabrication of local contacts. Figure 1c shows as-grown CNT bundles from contact holes coated with Ni by electrodeposition, and contacted with nanoprobes for electrical characterization. Figure 1d shows CNT bundles with a plated nickel cap after encapsulation of the CNT bundles in oxide and planarization with CMP. The selectively plated Ni metal contact on top of the CNT via is used for electrical probing with a nanoprober.

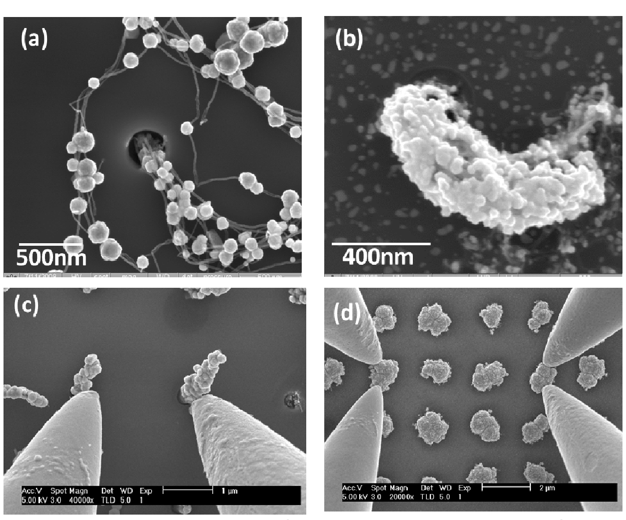

Fig.1 Electrodeposition of Ni on CNT:(a) low-defective and highly-defective (b) CNT grown in 300nm contact holes); contacting of metallized CNT bundles in nanoprober for (d) as-deposited CNT bundles, and (d) oxide encapsulated and CMP'ed bundles.

Carbon nanosheets (CNS) are 8-10 thin graphite sheets which are grown vertically (CNS on TiN substrate in Figure 2a). These sheets can be grown up to a few micron high and are all electrically connected, rendering this a suitable electrode material. The electrode kinetics at the sheet edges is extremely fast and exceeds that of CNT and platinum [1]. When coating these high surface area electrodes with a functional materials they can be used as highly conductive current collectors for e.g. energy storage (thin-film batteries) and conversion (fuel cells, electrolyzer) applications. Figure 3 shows CNS coated with anodic MnO_2 films which can be used as positive electrode for both alkaline and lithium ion batteries.

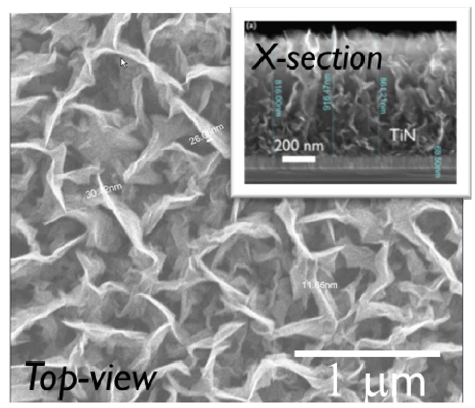

Fig.2 Top-view and X-scetional view of 1um high CNS layer grown on TiN substrate.

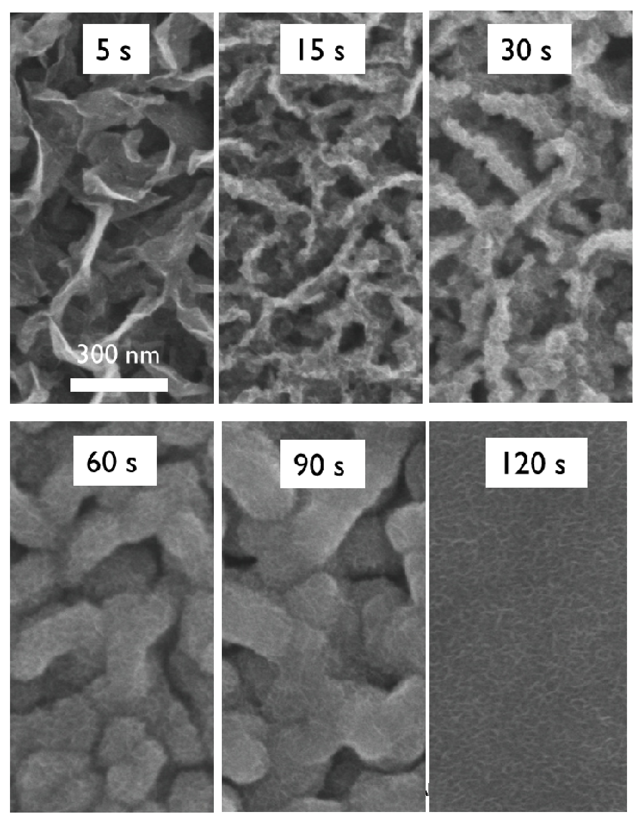

Fig.3 Top-view of CNS electrodes after anodic deposition of MnO_2 for different times .The CNS are fully coated after 2 min of deposition.