Atomic Layer Deposition of Tantalum Oxide for enhanced stability of CNTs during Photoelectrochemical Water Splitting

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To mitigate climate change the global energy landscape is shifting towards Hydrogen with demand reaching 100 Mt in 2024 [1]. Photoelectrochemical (PEC) water splitting has emerged as a vital pathway for sustainable green H_2 production. However, widespread implementation is hindered by thermodynamic bandgap mismatches, the sluggish kinetics of the four-electron oxygen evolution reaction (OER) and stability issues of photo-electrocatalyst.

Carbon nanotubes (CNTs) provide an ideal conductive scaffold due to their exceptional axial charge transport and high effective surface area. Despite these advantages, it has been observed that the high curvature of the graphene lattice renders CNTs susceptible to structural degradation in oxidative PEC environments [3]. In particular, bare CNT electrodes exhibit severe structural degradation after 1 h chronoamperometry (CA) stability testing under illumination in 1 M KOH, as illustrated in Fig. 1.

To preserve the structural integrity of CNTs, we used Atomic Layer Deposition (ALD) to deposit a protective Tantalum Oxide (Ta_2O_5) shell on CNT's (see Fig 2). ALD was chosen considering its sub-nanometric precision, which allows the deposition of conformal, pinhole-free films on high aspect ratio CNT's packed in a complicated forest, and the restricted carrier diffusion length in tantalum-based compounds (~50-100 nm), which demand a controlled thickness Fig 1. The ALD deposition process was carried out utilizing pentakis-(dimethyl-amino)-tantalum (PDMAT) and H_2O as co-reactant, yielding an optimized growth per cycle (GPC) of 0.5 Å/cycle, as monitored by in-situ spectroscopy ellipsometry.

X-ray diffraction (XRD), and X-ray reflectometry (XRR) confirmed the growth of dense (~6.4 g/cm^3), high-purity Ta_2O_5 amorphous films, while X-ray photoelectron spectroscopy (XPS) verified a Ta/O ratio of 2.8 with negligible carbon contamination. Transmission Electron Microscopy (TEM) and Energy Dispersive Spectroscopy (EDS) mapping demonstrated ultra-conformal coating of Ta_2O_5 along the entire CNT length, ensuring complete surface passivation (cf. Fig 2).

PEC performance was evaluated using cyclic voltammetry (CV), linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS), and chronoamperometry (CA). The Ta_2O_5 film significantly reduced charge-transfer resistance and effectively suppressed the morphological collapse observed in bare CNTs during stability tests (cf. Fig 1). Moreover, CA measurements under chopped illumination revealed a distinct photo-response associated with the Ta_2O_5 bandgap, confirming the shell's active role in the PEC process. While Ta_2O_5 successfully stabilizes the conductive core, its wide bandgap limits visible-light harvesting. Consequently, this work establishes a robust baseline for transitioning toward nitrogen-doped Tantalum Oxynitride (Ta-O-N) to optimize bandgap alignment (~2.1 eV) thereby targeting theoretical solar-to-hydrogen (STH) efficiencies of up to 15.25 % with photocurrent densities of 8.1 mA cm^{-2} [4].

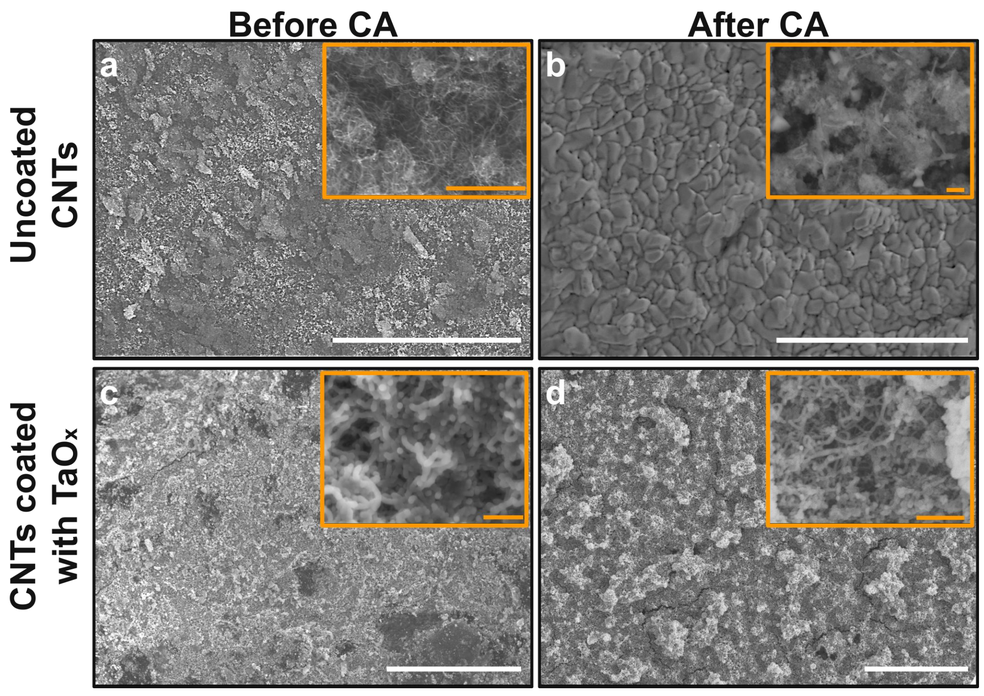

Fig 1. SEM images of CNT's uncoated and coated with TaO_x before and after CA. a) Uncoated CNTs before CA. b) uncoated CNTs after CA. (c) CNTs coated with TaO_x before CA. (d) CNTs coated with TaO_x after CA. All the scales represent 50 μm. All the scales in insets represent 1 μm.

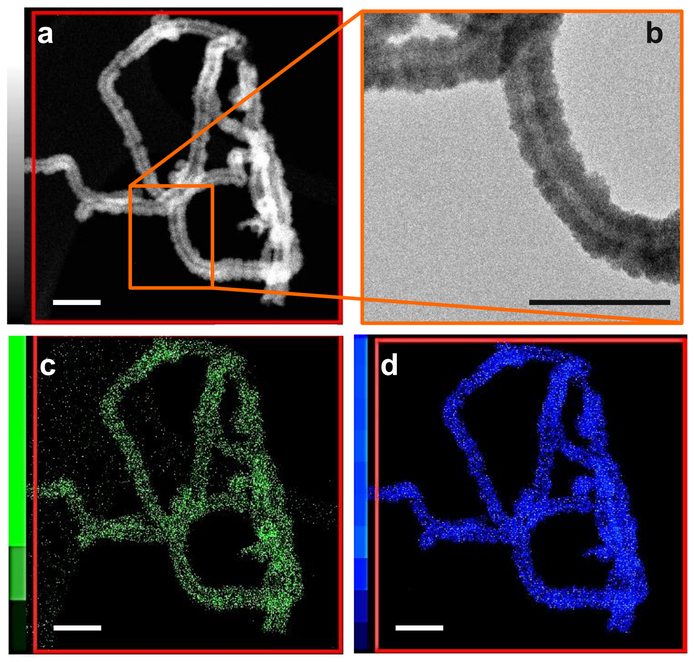

Fig 2. TEM images of coated CNT's (cf. Fig. 1a). a) lower magnification. b) higher magnification. c, d) O and Ta EDS elemental mappings of image (b). All the scales represent 100 nm.

References

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