

Purification of multilwalled CNTs

The CNTs were purified by refluxing in 3 M HNO₃ for 48 h, and then filtered with 2.5 μm pore size membrane with the aid of a pump and thoroughly washed with water to pH *ca.* 7, finally dried under vacuum at 60 °C overnight. The resulting CNTs were dispersed in dimethylformamide (DMF) at a concentration of 0.2 mg/ml with the aid of ultrasonic agitation. Before each deposition, the CNTs solution was further sonicated for 10 min.

Preparation procedure of the CNTs/thionine self-assembled multilayers

Quartz slide was cleaned with “piranha solution”, a 3:7 solution mixture of 30% hydrogen peroxide (H₂O₂) and concentrated sulfuric acid (H₂SO₄) at 80 °C for 1 h (Caution: Since piranha solution reacts violently with many organic compounds, extreme care must be taken when handling it), followed by rinsing with water, and drying with a high purity nitrogen stream. ITO-coated glass was sonicated in acetone for 5 min, followed by rinsing with water, ultrasonic agitation in concentrated NaOH in 1:1 V/V water/ethanol, rinsing further with water, immersion in CHCl₃ for 10 min, and drying with high purity nitrogen stream.

Before assembly, the cleaned ITO glass or quartz slide was immersed in 4% (v:v) (3-aminopropyl)trimethoxysilane (APTMS) methanol solution for 1 day. After exhaustive rinsing by methanol, the APTMS-derivatized substrate was then immersed in 0.2 mg/ml CNT + DMF for 30 min resulting in the first layer of CNTs on the amino pre-modified surface using a known process [see reference 7]. After thoroughly rinsing with DMF and drying with a nitrogen stream, the CNTs-terminated substrate was transferred to 1.5 mM thionine + DMF for 30 min resulting in one layer of thionine. By alternate treatment with thionine solution and CNTs suspension until the desired number of bilayers was achieved, three-dimensional nano-architectures could be formed. The thickness and amounts of the multilayers were readily adjusted by choosing different number of cycles in the whole preparative process.

The chemical structure of thionine molecule

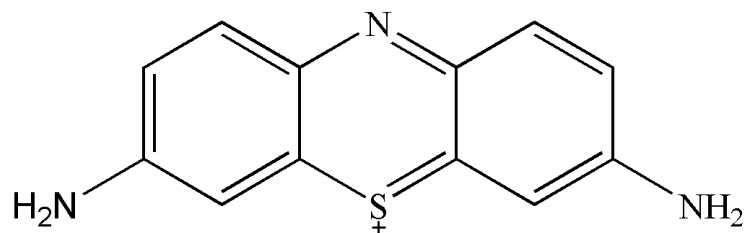


Fig. S1 The chemical structure of thionine molecule.

Raman Spectroscopy Characterization of the CNTs/thionine self-assembled multilayers

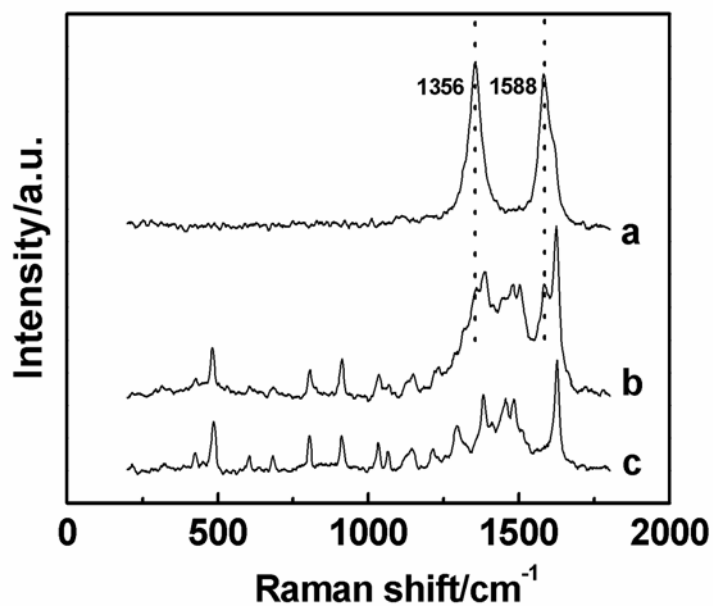


Fig. S2 Raman spectra of (a) the bulk CNTs sample, (b) the (CNTs/thionine)₁₄ multilayer (thionine as the outmost layer), and (c) the bulk thionine sample.

**Electrocatalytic NADH oxidation on one layer CNTs modified films and
(CNTs/thionine)₁ modified films**

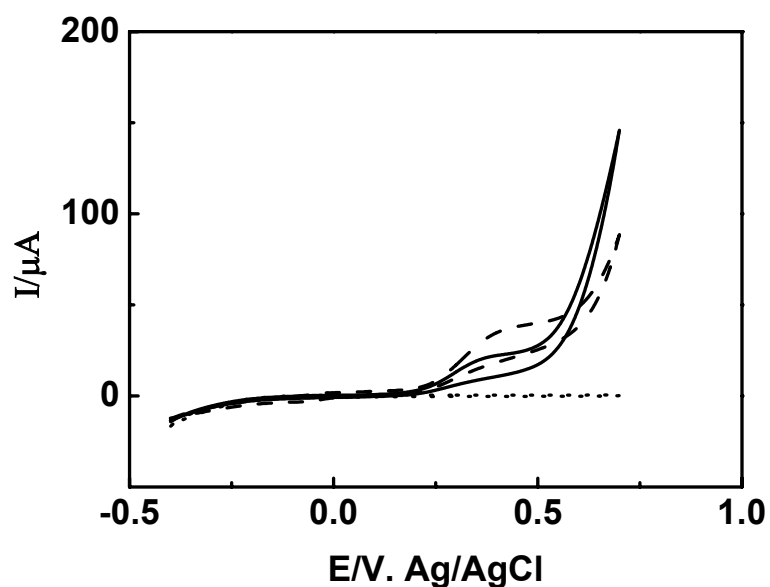


Fig. S3 CVs of one layer CNTs modified film in absence (dotted line) and presence (solid line) of 0.5 mM NADH. The dashed line shows CV of (CNTs/thionine)₁ modified film in presence of 0.5 mM NADH. It clearly indicates that both thionine and carbon nanotube catalyze the NADH oxidation.