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Studies on Electrochemical Properties of Functionalized Carbon Nanotube Bucky Paper Electrodes for Biosensor Applications

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ABSTRACT

This paper investigates the effect of different conditions for conventional acid functionalization of carbon nanotubes in order to fabricate most uniform buckypaper with enhanced electrochemical properties for biosensor applications. This study compares the electrochemical properties of those electrodes in regard to detection of a biomolecule, dopamine. Carbon nanotubes (CNT) due to its inherent structures are difficult to be dispersed in any solvent. This hinders its application in many different areas in spite of its unique electrical, mechanical and chemical resistant properties. However functionalization of CNTs with different chemical groups helps to form a homogeneous dispersion which show enhanced properties when applied in dispersion or as film. In this work multi-walled carbon nanotubes are modified with mixture of strong acids under different conditions to impart functionality in nanotubes. Further thin sheets, commonly known as buckypapers are fabricated and have been used as electrodes in electrochemical biosensors. Their electrochemical properties are compared in electrochemical sensing system for a biomolecule, dopamine, a neurotransmitter and a biomarker for Parkinson's disease. Thermal characterizations, structural characterizations and electrochemical activity of modified CNT buckypapers towards dopamine are presented in this article.

INTRODUCTION

Compared to many other carbon based materials carbon nanotubes (CNT) are excellent for electrochemical applications due to its surface characteristics. As described in the review by Mao et al., the presence sp^2 carbon in side walls and sp^3 carbon at the open end (the closed end opens up after functionalization) of carbon nanotube renders very special properties to it in terms of surface chemistry and electro catalytic activity^[1]. The surface electronic structure causes poor electron transfer whereas the presence of sp^3 carbon generated after covalent functionalization at the open end of each nanotube enhances electron transfer^[2]. Pristine carbon nanotubes also exist in long bundles with closed end which are thermodynamically stable due to strong pi-pi interaction amongst the sp^2 carbons at the surface^[3]. Thus pristine carbon nanotubes (CNTs) are insoluble in most liquids, such as water, most solvents and polymer resins and it is very difficult to achieve homogeneous dispersion. Surface modifications of pristine CNTs are done by various methods^[4-7]. After surface modification, electrochemically active moieties can be added to CNTs and these are used to accelerate the electron transfer kinetics of some kinds of biologically important species^[8-10].

In last few decades extensive effort has been made to use as such CNTs and surface modified CNTs in electrochemical applications^[8-10], mainly as coating or modifier of other electrodes, such as glassy carbon electrodes or gold electrodes. Based on our previous and on-going research experience and based on literatures^[11-13], CNT films (conventionally known as buckypapers) based on modified CNTs are excellent candidates as electrodes in electrochemical applications. This motivated us to study the effect of surface functionalization of carbon nanotubes and fabricate buckypaper with surface functionalized nanotubes. However in order to form a uniform film of CNTs, uniform dispersion of CNTs in an appropriate solvent is the key. By means of functionalization, carbon nanotubes are not only be dispersed in solvents, but can attach to molecules physically or chemically without significantly changing its inherent unique properties^[3,12,13]. In this paper, pristine multiwall carbon nanotubes are oxidized using a 3:1 mixture of concentrated sulphuric and nitric acid^[4,5,14,15] for varying lengths of time. These modified MWCNTs were dispersed in DI water by probe sonication without any conventional surfactants^[16]. Further buckypapers are formed with the above acid functionalized MWCNTs. Acid functionalized carbon nanotubes are characterized by thermal analysis, FTIR spectroscopy and by transmission electron microscopy and finally the electrode properties for buckypaper has been studied by conventional electrochemical methods.

The electronic conductivity of nanotubes is most important for its application in electrochemistry. Amongst SWCNT and MWCNT, the latter is regarded as metallic conductors, which is considered as a highly attractive property for electrodes. In this research only multi-walled CNTs are functionalized using acid mixture for different time periods, and further buckypaper has been fabricated using those modified CNTs. These buckypapers are used as working electrodes in three electrode system to detect dopamine. Thus the electrochemical properties of these buckypapers towards dopamine are determined and compared in terms of their sensitivity towards the detection of dopamine. Dopamine (DA) is one of the most important neurotransmitters belonging to the catecholamine family. It plays a significant role in the functioning of central nervous, renal, and hormonal systems^[17,18]. This is also a biomarker for Parkinson's disease^[19,20]. Due to its chemical structure it can be oxidized by any oxidizing functionality, such as by carboxyl group into dopaquinone. Thus it is electrochemically active molecule. Considering this structural aspect, in this research dopamine has been chosen as biomolecule to compare the electro catalytic activity for acid modified CNT buckypapers. Carboxyl functionality of CNT buckypapers oxidize dopamine molecule into dopaquinone depending on the extent of functionalization. Thus the electrochemical activities for each type of buckypaper are compared.

MATERIALS AND METHODS

Multiwall nanotubes (Multi-Wall: SWeNT SMW200) were purchased from SWeNT corporation (Ok, USA). All other chemicals were purchased from Sigma Aldrich Corporation. Methods

Acid modification of carbon nanotubes

200 mg of CNT is poured into a mixture of 3:1 sulphuric acid and Nitric acid (750 ml of sulphuric acid and 250 ml of nitric acid in a bottle and the mixture is heated at 70°C with continuous stirring at 400 rpm with magnetic stirrer for 2 hr. The same procedure just mentioned was followed to more times varying the stirring times to 8 hrs and 24 hrs. Immediately following the heating process, the acid solution is diluted with deionized water in 1000 mL batches (200 ml acid solution to 800 ml water) and then filtered using a drain disk and polycarbonate filter paper. The CNTs are repeatedly washed with DI water until the filtrate reaches pH 7. Carbon nanotubes are further dried in vacuum oven at 60°C and these samples are named throughout the paper as aMWCNT-2, aMWCNT-8 and aMWCNT-24.

Fabrication of buckypaper with acid modified CNTs

60 mg of acid modified MWCNT were dispersed in 150 ml of DI water by probe sonication for 30 minutes at amplitude of 75% with 30 seconds on and 10 seconds off cycles. Finally this dispersion was filtered using 40 mm polycarbonate filter paper and filtered under vacuum and finally washed with 500 ml of DI water. Buckypaper was removed from the polycarbonate filter paper and was press dried in absorbent material for 24 hours.

Thermogravimetric Analysis

As such and modified MWCNT samples are thermally analyzed in presence of air using a TA Instruments Q50 Thermogravimetric Analyzer using a heating ramp of 10°C/minute. Approximately 3 mg of samples are heated from 40°C to 800°C. The degradation temperatures are noted to determine the thermal and oxidative stability of modified CNTs.

Fourier Transform Infrared Analysis

About 2 mg of aMWCNT sample are mixed with 250 mgs of KBr(0.8% with respect to KBr) and made into a pellet and finally Attenuated Total Reflection Infrared spectra of samples are done from 400-4000 cm⁻¹ in order to qualitative analysis for the functional groups in a MWCNT samples.

Raman spectroscopy

Raman spectra were collected using a Renishaw inVia micro-Raman system with two excitation wavelengths a 785 nm (1.58 eV) diode laser and a 488 nm (2.54 eV) laser, respectively. Typical laser power was 0.5 mW and 1.25 mW, respectively, with a 50-

magnification objective lens. Electrical property measurement: The electrical conductivity as measured via a four-probe method using a probe station (Jandel, UK) attached to a Nano voltmeter and an alternating current (AC)/direct current (DC) current source (Keithley, Fotronic Corporation, MA, USA). Both types of modified BP exhibited an electrical conductivity in the range 30-45 s/cm

ELECTROCHEMICAL STUDIES

All electrochemical experiments were carried out in a regular, standard glass cell (part number, AKCELL1, Pine Instruments) with three electrode system using a Ag/AgCl reference electrode, platinum counter electrode (platinum mesh, 45 mesh woven from 0.198 mm dia pt. wire fitted with platinum wire, thickness, 0.404 mm) and the buckypaper as working electrode. A small piece of each buckypaper sample (4 mmx5 mm) was placed in a platinum mesh (same as the counter electrode) which acted as a working electrode. A Potentiostat (Versastat 3, Princeton Applied Research, NJ USA) equipped with Versa Studio software was used to carry out electrochemical experiments. Cyclic voltametry experiments are carried out at different voltage ranges -1V to +1V versus Ag/AgCl reference electrode, and a scan rate of 50 mV/sec. Transmission electron microscopy are done with dispersion of aMWCNT and the chain length of individual nanotubes has been measured.

RESULTS AND DISCUSSION

Table 1 shows the thickness of BP samples and their electrical conductivity values. aMWCNT_8_BP shows highest conductivity. MWCNT after 24 hrs of acid soaking, show lower conductivity. It might be due to the fact that the length of carbon nanotubes decreased upon acid treatment for longer hours and more defects are introduced on carbon nanotube resulting in loss of some of its intrinsic properties [21, 22]. Transmission electron micrographs (**Figure 3**) confirmed the decrease of length with longer acid exposure. From the TEM micrographs for each types of nanotubes, the length size distribution show very similar results for 2 hr and 8 hr acid modified samples (0.5-1.5 micron), whereas the size of CNTs are significantly reduced after 24 hrs. of acid functionalization. The Raman data (**Figure 1**) also confirms this fact. In Raman spectra, the D band (related to defect derived mode) and G band (graphite structure derived mode), are the characteristic bands for MWCNT. The peak intensity of D band (normally around 1350 cm^{-1}) increases to the defect introduction caused by the acid treatment, whereas the peak intensity of G band at $\sim 1570\text{ cm}^{-1}$ also changes with the quality of the nanotubes. The ratio of Intensity for D band to G band increases due to increase of defects [21]. The Id/Ig ratio for pristine MWCNT and 2 hr, 8 hr and 24 hr. acid treated MWCNTs are 0.87, 1.00 and 1.09 and 1.11 respectively. It is obvious from the Raman spectra data that the G band is strongly affected by acid treatment. These results for the peak intensities also show presence of defects but no disruption of graphitic structures on the surface of nanotubes.

Table 1. Electrical Conductivity for buckypaper samples (thickness~0.45micron).

Sample	Name	Electrical Conductivity(s/cm)
1	aMWCNT_2_BP	42.5
2	aMWCNT_8_BP	62
3	aMWCNT_24_BP	32

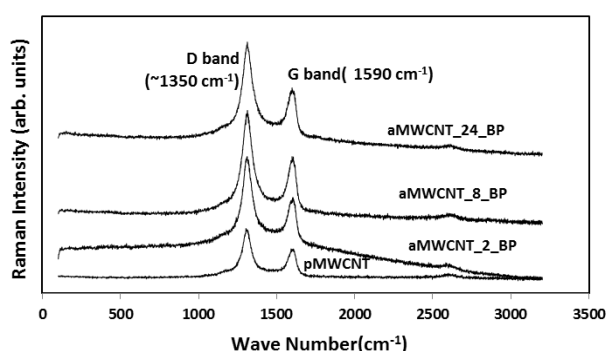


Figure 1. Raman spectra for acid modified MWCNT

In FTIR spectra (**Figure 2a**) the C=O stretching at 1710 cm^{-1} and O-H bending at 1410 cm^{-1} are clearly observed for all the acid modified CNT samples though the peak intensity is much lower for 2 hr acid modified samples. The pristine MWCNT does not show intensities (**Figure 2b**) specific to the C=O stretching or due to -O-H bending deformation. The transmission electron micrographs have captured the images of different acid modified CNT samples. From multiple images for each sample the size distribution can be obtained and the size ranges from 1-1.5 micron for 2 hr. and 8 hr. acid modified samples as shown in **Figures 3a and 3b** and about 0.5- 1 micron for 24 hr. acid modified samples (**Figure 3c**). Nanotubes are also appeared as more intact for 2 hr and 8 hr. acid modified samples compared to 24 hr. acid modified sample. Thermogravimetric data (**Figure 4**) has shown that the 24 hr acid modified samples have lower thermal stability compared to aMWCNT_2 and aMWCNT_8 samples. The electrochemical properties for the buckypaper samples have been studied in presence of $0.1\text{ M K}_3\text{ Fe(CN)}_6$ solution in 0.1 M KCl and PBS buffer presented in figure at a scan rate on 20 mV/sec are presented in **Figure 5**. The well-defined oxidation and

reduction peaks are observed due to $\text{Fe}^{+3}/\text{Fe}^{+2}$ redox couple. For both 2 hr. and 8 hr. acid modified samples peak current for both oxidation and reduction are same where that has been reduced for the aMWCNT_24 buckypaper. The higher oxidation peak currents for aMWCNT_2 and aMWCNT_8 samples indicate better electrode properties for these buckypaper samples compared to aMWCNT_24 buckypaper. The cyclic voltammetry plots 0.1M $\text{K}_3\text{Fe}(\text{CN})_6$ solution in at different scan rates from 10 mV/sec to 100 mV/sec using all buckypaper samples are shown in **Figures 6a-c**. The effect of different scan rates on the oxidation and reduction current response has been studied for all systems to demonstrate the electrodes' behavior and the mechanism of electron transfer. The plot of ipa vs $v^{1/2}$ gave straight line indicating the electron charge transfer was a diffusion controlled process [22-24] possibly scan rate of 100 mV/sec. The peak to peak separation in each CV plot also increases with increasing scan rate. A good linear relationship has been found for all the samples though the CV and hence the linear plot for aMWCNT24 BP samples are slightly different compared to the other two BP samples. Finally all these electrodes are used in electrochemical biosensor for dopamine and the results are shown in **Figure 7a-c**. Differential pulse voltammograms are obtained for 50 μM , 90 μM , 130 μM , 160 μM and 200 μM dopamine solutions in 0.1 PBS buffer using all three different types of buckypaper electrodes. Well defined voltammetric signals for dopamine are obtained and the inset illustrates the relation between different concentration and anodic peak current with a correlation coefficient varying from 0.94-0.99. This indicates that detection of very low concentration of DA is possible with this buckypaper samples. The LOD and the sensitivity values are calculated based on the calibration plot for each samples are stated in **Table 2**. The limit of detection is comparable with available data [24-28]. All the buckypaper electrodes have shown electrochemical sensitivity towards detection of dopamine. The limit of detection for aMWCNT_8 BP has been found to be the lowest which means that aMWCNT_8 BP has better electrode performance in a biosensor for dopamine.

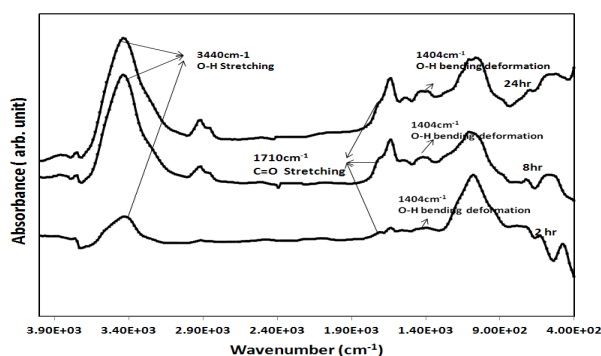


Figure 2a. FTIR spectra for acid modified.

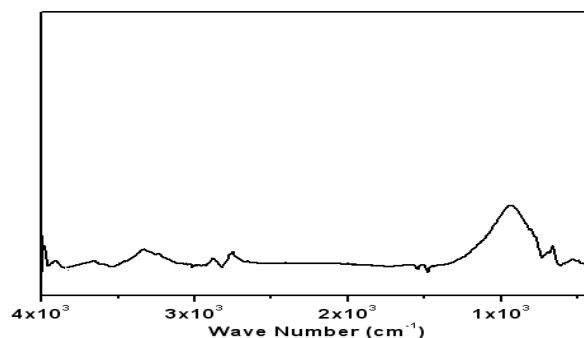


Figure 2b. FTIR spectra for pristine.

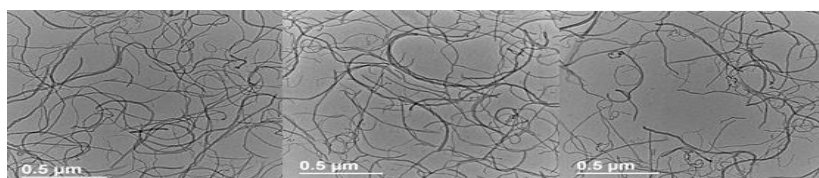


Figure 3a. Transmission electron micrographs for 1MWCNT_2_BP

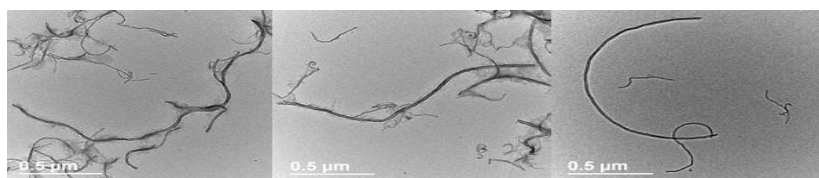


Figure 3b. Transmission electron micrographs for 1MWCNT_8_BP.

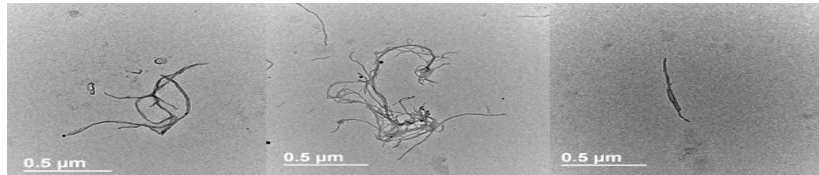


Figure 3c. Transmission electron micrographs for 1MWCNT_28_BP.

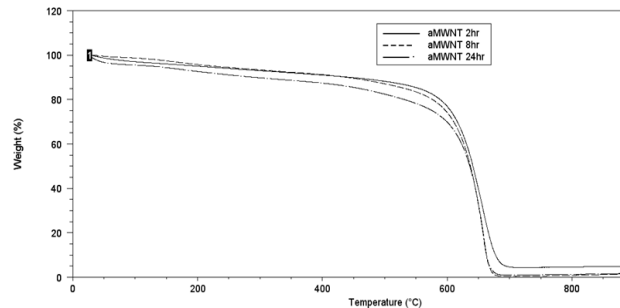


Figure 4. Thermogravimetric analysis data for all acid modified MWCNT samples.

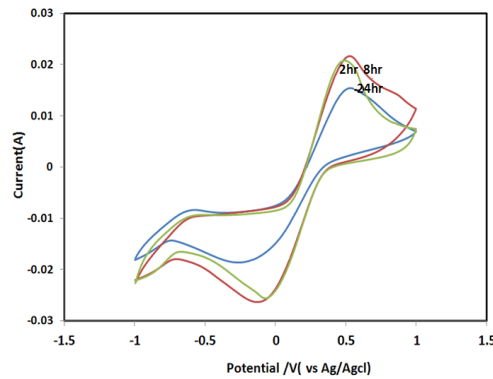


Figure 5. Cyclic voltammogram of the aMWNT_BP electrodes ensemble. The curves were taken in a solution 0.1M K₃ Fe (CN)₆ solution in 0.1M KCl and PBS buffer at a scan rate of 20mV/sec.

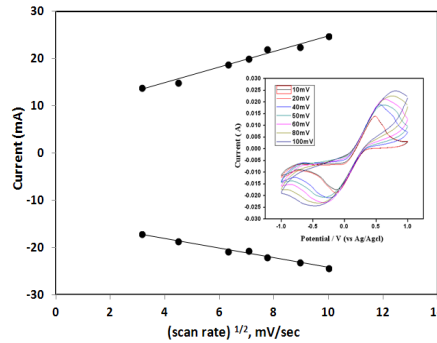


Figure 6a. Current vs. Scan rate data (derived from cyclic voltammogram of aMWNT_2_BP electrodes ensemble). The curves were taken in a solution 0.1M K₃ Fe (CN)₆ solution in 0.1M KCl and PBS buffer at 10mV/Sec-100mV/Sec scan rates.

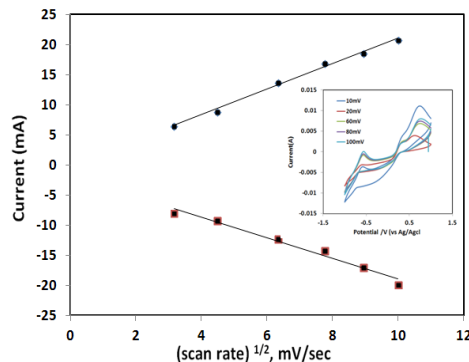


Figure 6b. Current vs. Scan rate data (derived from cyclic voltammogram of aMWNT_8_BP electrodes ensemble). The curves were taken in a solution 0.1M K₃ Fe (CN)₆ solution in 0.1M KCl and PBS buffer at 10mV/Sec-100mV/Sec scan rates.

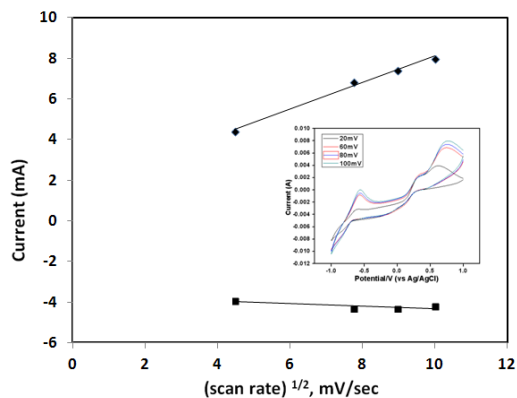


Figure 6c. Current vs. Scan rate data (derived from cyclic voltammogram of aMWCNT_24_BP electrodes ensemble. The curves were taken in a solution 0.1M $K_3 Fe(CN)_6$ solution in 0.1M KCl and PBS buffer at 10mV/Sec-100mV/Sec scan rates.

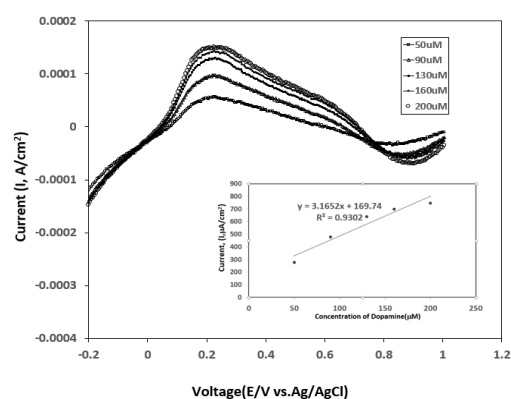


Figure 7a. Differential pulse voltammograms for different concentration of dopamine using aMWCNT_2_BP electrodes.

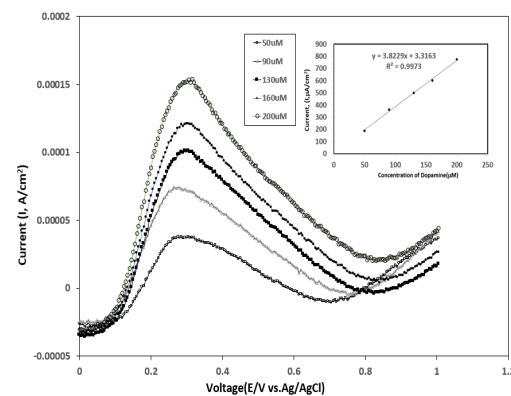


Figure 7b. Differential pulse voltammograms for different concentration of dopamine using aMWCNT_8_BP electrodes.

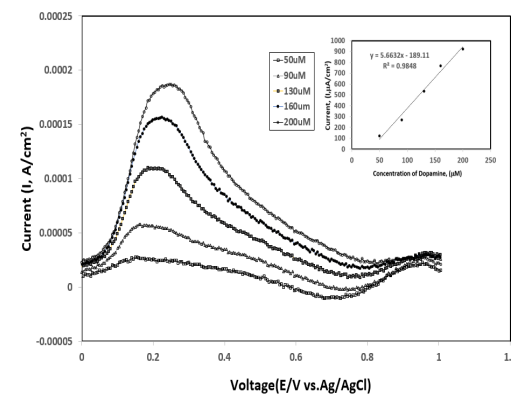


Figure 7c. Differential pulse voltammograms for different concentration of dopamine using aMWCNT_24_BP electrodes.

Table 2. Sensitivity and limit of detection for all biosensors using acid modified BP electrodes

Sample	Sensitivity (microA/micro M/cm2)	Limit of Detection(LOD) (µM/L)
aMWCNT_2 BP	3.16	55.8
aMWCNT_8 BP	3.82	10.6
aMWCNT_24 BP	5.86	25

CONCLUSION

Acid modified MWCNT buckypaper samples have shown electrocatalytic properties towards dopamine and can be used effectively for electrochemical biosensors. Amongst all the acid modified BP samples, aMWCNT_8_BP has shown better characteristics as electrode and have lowest limit of detection.

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