Directed Covalent Assembly of Nanodiamonds into Thin Films

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Abstract. The wide-spread use of polycrystalline diamond thin films is limited by the costs associated with chemical vapor deposition, high growth temperature, and poor substrate adhesion. Here, a solution-phase method to grow nanocrystalline diamond films is demonstrated through carbodiimide-mediated cyclic attachment of carboxylated nanodiamonds and a diamine linker on amine-functionalized substrates. XPS and Raman spectroscopy confirm formation of the desired amide bonds and incorporation of the linker to form the covalently-bonded nanoparticle network. The assembly process was demonstrated in solution phase as well as via spin coating with both methods resulting in similar film morphology as observed using SEM and AFM. The assembly process leaves the films amine-terminated, which is convenient for application-specific surface modifications. The thermal conductivity of the covalently assembled NDs as measured via the 3ω method ranged between 2-20 W m⁻¹ K⁻¹, which is

comparable to those of CVD nanocrystalline diamond films of similar grain size. Future strategies to reduce porosity during the directed covalent assembly strategy holds strong potential for applications requiring thermal dissipation or mechanical and chemical stability.

1. Introduction

Polycrystalline diamond thin films are composed of a mixture of sp³- and sp²-hybridized carbon atoms, inheriting some of the superlative properties from its single crystalline form, specifically the high Young's modulus,¹ increased resistance to wear,² chemical stability,³ low coefficient of friction,⁴ low coefficient of thermal expansion,⁵ wide optical transparency,⁶ and biocompatibility.⁷ These properties make diamond thin films ideal for applications in microelectromechanical systems to reduce wear, stiction, and thermal expansion, in harsh environments to prevent corrosion, or in medical implants such as the artificial heart or the bionic eye to improve biocompatibility.⁸ These films are most commonly grown via chemical vapor deposition (CVD). Studies examining the variation in seeding process, growth conditions, and growth species have enabled depositing CVD diamond films with controlled film morphology, mechanical strength, and electrical conductivity.⁹⁻¹² The commercialization of the CVD process has driven costs down to ~\$700 per 100-mm-wafer for a 1-2 µm thick film. However, the CVD growth is restricted to substrates that can resist melting, reaction with process gases, and carbon dissolution at high temperatures (~700 °C).¹³ Further, the requirement of a specialized growth chamber, vacuum conditions, precursor gases, and large power requirement impede the reduction of cost and thus wide-scale adoption. Transfer printing of CVD diamond films onto flexible substrates has been demonstrated;¹⁴⁻¹⁵ however, this process is limited to feature sizes smaller than 1 mm and the resulting films are prone to breakage upon flexing of the substrate.

An alternative solution is to assemble nanodiamonds (NDs) into continuous thin films. NDs are 1 to 100 nm wide particles or aggregates, which were first reported in the late USSR in the 1960s using controlled detonation.¹⁶ Modern techniques for ND synthesis include ball milling of high-pressure, high-temperature microdiamonds, plasma-assisted CVD, and laser ablation. The development of environmentally friendly purification processes now allow low-cost production of several hundred grams of high-purity ND (~95%) at a time with controlled surface chemistry. The applications of NDs have, as a result, grown via the development of a variety of liquid and gas phase methods to tailor their surface chemistry. The assembly of NDs up to a monolayer has been extensively studied using sonication,¹⁰ electrophoretic deposition,¹⁷⁻ ²⁰ layer-by-layer assembly,²¹⁻²² inkjet printing,²³ and micro-contact printing²⁴ for the purposes of growing CVD diamond thin films. A monolayer fluorinated ND coating has also been demonstrated on a glass slide by reacting fluorinated NDs with aminosilanized glass surfaces.²⁵ Thicker ND films have been electrostatically assembled via layer-by-layer assembly using poly(diallyldimethylammonium chloride),²⁶ poly-L-lysine,²⁷ and bovine serum albumin,²⁸ as an electrostatic glue. Cyclic dip coating of glass slides in ND solutions of pH 3.5 and pH 7.5 with intermittent drying have also shown electrostatic assembly of ND films where the resulting film morphology was controlled using the pH of the second dip coating solution.²⁹ The drying of aqueous ND solutions also result in films when the ND-ND, ND-water, and ND-substrate interactions are controlled using pH and temperature.³⁰ The thick ND films demonstrated thus far rely on the electrostatic or van der Waal attractions, which are weak compared to a covalent bond; as a result, films assembled using these methods are not mechanically or chemically robust. Although NDs have been covalently incorporated into polymers,³¹ matrix-free covalently assembled ND film have not yet been reported. Such a covalent assembly process holds promise to overcome the high cost, high growth temperature, and poor substrate adhesion issues faced by CVD to-date.

Following this motivation, we present here a room temperature assembly process for achieving covalent assembly of polycrystalline diamond films through cyclic attachment of carboxylated ND aggregates (ND-COOH) and a diamine using a carbodiimide cross-linker as shown in Figure 1. The process begins with an amine functionalized surface. In most cases, this can be achieved by hydroxylation with oxygen plasma, followed by silanization with 3aminopropyltriethoxysilane. The primary amines on the substrate were then reacted with an oacylisourea active ester form of ND-COOH. This form was realized using 1-Ethyl-3-(3dimethylaminopropyl) carbodiimide hydrochloride (EDC). Because the half-life of the acylisourea active ester is close to an hour at 20 °C, the reaction was limited to 30 min. The unreacted active ester groups on the substrate-bound ND-COOH were then quenched with a diamine linker, resulting in an amine-terminated surface. Here, we chose a short-chain length linker, ethylene diamine, to reduce the spacing between ND aggregates. Further addition of ND-COOH was achieved by cyclic exposure to freshly activated form of ND-COOH and ethylene diamine. Besides outlining the assembly process, we also examine the morphology of the covalently assembled ND films using atomic form microscopy (AFM) and scanning electron microscopy (SEM), their chemical nature suing X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy, and their thermal transport properties via microfabricated test devices.



Figure 1. Reaction scheme for directed covalent assembly of NDs: (A) Oxide surfaces were hydroxylated via piranha cleaning, RCA-1 clean or oxygen plasma, and (B) then reacted with 2-aminopropyltrimethoxysilane to form an amine terminated surface. (C) ND-COOH were reacted with EDC to form the acylisourea ester, which were then reacted with the amine group on the oxide surface to tether the ND-COOH. (D) The unreacted acylisourea ester groups on the surface-tethered NDs were then reacted with ethylenediamine to form an amine terminated surface. (E) The further addition of EDC activated ND-COOH and ethylene diamine in a cyclic manner allowed achieving a full surface coverage and an increase in film thickness.

The *sp*³-hybridized tetrahedral diamond cubic crystal structure of the as-received ND-COOH was confirmed using X-ray diffraction and Raman spectroscopy (see **Supporting Information Figure S1**). Photon correlation spectroscopy showed bath sonication of ND-COOH powder in deionized water resulted in two particle size distributions, ~20% 14 ± 3 nm and ~80% 83 ± 20 nm. The ζ -potential measurements confirmed the negative charge on ND-COOH suspended in

deionized water. For the rest of the work reported here, 1 mM KCl (pH 6.5) was chosen as the media to suspend ND-COOH as this facilitated reliable measurement of ζ-potential. The directed covalent assembly of ND-COOH was carried out in scintillation vials as shown schematically in **Supporting Information Figure S2** and detailed in the methods section. The film deposition was carried out by cyclic exposure to activated ND-COOH and EDA, while the spent activated ND-COOH were recovered through a regeneration process, which included hydrolysis of the unreacted esters and precipitation using HCl and resuspension in fresh 1 mM KCl (pH 6.5). The regenerated ND-COOH solutions were found to have similar average particle size and zeta potential as that for freshly-prepared (see **Supporting Information Figure S3**). In order to avoid a significant drop in ND-COOH concentration due to reuse, a maximum of two regeneration cycles were used and a fresh ND-COOH suspension was used every fourth deposition cycle.

2. Experimental Section

Nanodiamond film deposition by incubation was carried out on 1 cm x 1 cm chip made of polished silicon, borosilicate glass or fused silica using a standard 20 ml scintillation vial. For either substrate, cleaning involved a sequential rinse of DI, acetone, and 2-propanol followed by drying under a gentle stream of air. The surfaces were then hydroxylated using an oxygen plasma for 1 min using a Technics reactive ion etching chamber with 50 sccm O₂ flow rate, chamber pressure of 240 mTorr, and radio frequency power of 100 W at 13.56 MHz. The surfaces were immediately reacted with (3-aminopropyl)triethoxysilane in the gas phase using a vacuum desiccator for 1.5 h at 20 °C. The silane coated substrates were then soaked in DI for 5 min and baked at 150 °C for 10 min to crosslink the silane layer. A solution containing amine-reactive O-acylisourea form of the ND-COOH was prepared by first bath sonicating (40 kHz, 185 W) 1 mg/ml of ND-COOH in 1 mM KCl (pH 6.5) for 1 h, followed by addition of 0.3 mg/ml EDC. This amount of EDC is expected to activate 10⁶ carboxyl groups per ND aggregate.

The amino-silane coated substrates were then dipped for 30 min in the solution containing amine-reactive form of ND-COOH. Next, the substrates were soaked in 1 mM KCl (pH 7) for 2 min, and agitated in the same solution for another 2 min using a vortex mixer at low rpm. Substrates were then dipped in EDA for 30 min at room temperature. The lifetimes of O-acylisourea intermediate is less than an hour on an average, and if this intermediate does not encounter an amine, it will hydrolyze and regenerate the carboxyl group. Thus the whole process of EDC mediated coupling to the surface as well as the EDA was carried out in nearly an hour. The EDA-reacted substrates were soaked with DI for 2 min and agitated in the same solution for another 2 min using a vortex mixer at low rpm.

Regeneration of ND-COOH solution. Every time after a ND deposition cycle, 1 mM HCl in 500:1 (v/v) ratio was added to the ND-COOH solution to precipitate the ND-COOH. The solution was further centrifuged at 720 rcf for 5 min and then most of the supernatant was replaced with fresh 1 mM KCl (pH 6.5). The solution was bath sonicated for 1 h to suspend the ND-COOH and ready for addition of EDC for the next deposition cycle. Each batch of ND-COOH solution was used for a maximum of 3 cycles.

Nanodiamond film deposition by spin-coating was carried out on 1 cm x 1 cm silicon chips. Piranha cleaning, followed by RCA I and RCA II cleaning, and oxygen plasma (as explained above) for 5 min to clean and hydroxylate the chips. The chips were immediately reacted with (3-aminopropyl)triethoxysilane vapors in a vacuum desiccator for 30 min at room temperature. The silanized chip was baked at 90 °C followed by drying under a gentle stream of air. Activated ND-COOH solution containing amine-reactive O-acylisourea was prepared by first bath sonicating (40 kHz, 185 W) 1 mg/ml of ND-COOH in 1 mM DI for 1 h, followed by addition of 1 mg/ml EDC. Covalent assembly of ND-COOH was carried out by cyclically spin-coating 100 μL activated ND-COOH solution once, 100 μL DI twice, 100 μL of ethylenediamine once, and 100 μL DI twice. Each time, the spin-coating was done at 3000 RPM for 1 min. With a cycle time of 6 min, a total of 5 cycles could be done within half an hour. The recollection and regeneration of ND-COOH was not possible due to the small amounts of reactants used.

Apparent porosity (ϕ_{app}) was calculate using high resolution (<10 nm) AFM images that were leveled by mean plane subtraction, aligned rows with the median method, corrected for horizontal scars, and had minimum data value shifted to zero using the Gwyddion package. The mean height (H_{mean}) and RMS roughness (R_{rms}) for image were calculated using statistical functions. Following, the image data above $H_{mean} + R_{rms}$ was capped at $H_{mean} + R_{rms}$. The new mean height ($H_{corrected mean}$) obtained from the corrected image was then used to calculate ϕ_{app} as follows.

$$\Phi_{app} = 1 - \frac{\text{Total grain volume after rejecting spikes in the data}}{\text{Total volume of the image after rejecting spikes in the data}}$$
(2)
$$\Phi_{app} = 1 - \frac{H_{corrected mean}}{H_{mean} + R_{rms}}$$
(3)

Pore-size distribution was obtained after thresholding images at different values, either (H_{mean} + R_{rms}), H_{mean} , or (H_{mean} - R_{rms}). Watershed segmentation of the resulting image was performed in ImageJ to calculate area and perimeter values for each pore. This data was then used to generate the frequency distribution of the pore radius (2*area/perimeter).

The cross-plane thermal conductivity κ of covalently assembled UNCD films supported on single-crystal silicon was measured using the well-established 3 ω method ³²⁻³⁴, specifically the 3 ω implementation which applies to substrate-supported thin films ³⁵⁻³⁶. This approach has been utilized previously by other groups to study κ of ultrananocrystalline diamond thin films synthesized from various CVD methods ³⁷⁻³⁹ and thus allows for direct comparison between those results and κ values obtained for the covalently assembled ND-COOH films in this work. Briefly, a four-probe dual-purpose heater/thermometer line 50 μ m in width was first patterned on top of the UNCD film of interest using standard photolithography. After confirming all the desired features were successfully resolved by observation under an optical microscope, a 10 nm-thick chromium (Cr) adhesion layer and a 200 nm-thick gold (Au) layer were sequentially deposited using DC magnetron sputtering. Photoresist lift-off was performed which resulted in a 3ω line and four contact pads as shown in the inset of Figure 4A. The resultant microdevice was then placed within a commercial 16-pin ceramic chip carrier and wire-bonded to make electrical connections from the carrier to the contact pads.

The ceramic chip carrier package was loaded into a continuous flow cryostat (Janis Research ST-100) with a stage-mounted precision silicon diode temperature sensor. This sensor served as the input to a PID temperature controller (Lake Shore Cryotronics 335) which maintained the steady-state stage temperature to within 0.01 K of stability for each setpoint. For all measurements, the cryostat was maintained at a vacuum of at least 10⁻⁵ torr via a turbomolecular pump (Leybold TMP-361C) backed by a mechanical pump (Edwards RV12) to prevent convection heat loss from the sample. Radiation between the chip surface and its environment was minimized via a thermally-coupled radiation shield which surrounded the sample space. The data collection process was executed using a computer with LabVIEW software to control the frequency of the AC signal from a low-distortion function generator (Stanford Research Systems DS360) and to record the 3w signal via a lock-in amplifier (Stanford Research Systems SR830). During a 3ω measurement, the 1ω signal component was removed via the use of a tunable potentiometer and a pair of differential amplifiers (Analog Devices AD524). This approach as well as all post-processed through which κ is extracted from the resulting 3ω signals is similar to as in other descriptions of the 3ω method $^{32-36,40}$. Measurements of the fourprobe resistance of the thermometer/heater line as well as the 1ω and the 3ω voltages on the metal line as a function of frequency were taken for stage temperatures between 100 K and 425 K. The four-probe electrical resistance was measured using a small AC sensing signal of 50 µA to avoid Joule heating. This resistance value was used to determine the change in electrical resistance of the metal line with temperature, dR/dT, which is important in extracting κ from the raw 3ω data. A representative example of the in-phase and out-of-phase raw 3ω obtained from one of the UNCD samples is given in **Figure S15A** in the Supplementary Information and is consistent with other examples from literature of a properly functioning 3ω measurement. To further validate the implemented 3ω setup, the temperature-dependent κ of a 200 nm-thick thermal oxide (SiO₂) thin film on silicon substrate was measured and compared to literature values ³². The results of this experiment are given in **Figure S15B** and show very good agreement with published data with less than +/- 9% difference.

Via the 3 ω method and its associated data processing, the total thermal resistance $R_{th,total}$ of the sample, i.e. the temperature rise of the heater/thermometer line per unit of Joule heating, is found from the raw frequency-dependent 1 ω and 3 ω voltages in addition to the calibrated dR/dT of the specific microdevice under test. The thermal resistance of the thin film and its associated heater line and substrate interfaces ($R_{th,FilmInterfaces}$) is found after subtraction of the substrate temperature rise as described in ³⁷⁻³⁹. The as-measured cross-plane thermal conductivity of the thin film κ_{AM} follows via

$$\kappa_{AM} = \frac{t}{2bLR_{th,FilmInterfaces}} \tag{4}$$

where *t* is the film thickness, *b* is the heater line half-width, and *L* is the heater line length. Thus, the uncertainty of κ_{AM} includes both the inherent uncertainty of the 3 ω measurement as well as the non-negligible uncertainty in the film thickness as measured via AFM, whereas $R_{th,FilmInterfaces}$ only includes the former. This point can be observed in the as-measured thermal resistance and thermal conductivity data presented in **Figure S16** within the Supporting Information.

As noted above, there are thermal resistances at the heater-thin film and thin filmsubstrate interfaces which contribute to the measured $R_{th,FilmInterfaces}$ values and thus prevent direct measurement of the thermal resistance of the thin film alone. These represent thermal resistances in series, that is,

$$R_{th,FilmInterfaces} = R_{th,Heater-Film} + R_{th,Film} + R_{th,Film-Substrate}$$
(5)

where $R_{th,Heater-Film}$ and $R_{th,Film-Substrate}$ are the interfacial thermal resistance at each of the two interfaces as labeled and $R_{th,Film}$ is the thermal resistance of the thin film itself. In many thin film 3 ω works, the sum of the interfacial resistances ($R_{th,Heater-Film} + R_{th,Film-Substrate}$) is experimentally determined by performing measurements of identical films of varying thickness t and linearly extrapolating the slope of the resulting t-dependent thermal resistance to zero thickness. This thermal resistance intercept then represents $R_{th,Heater-Film}$ + Rth,Film-Substrate, which can be subtracted from the measured $R_{th,FilmInterfaces}$ to isolate $R_{th,Film}$ and, finally, obtain the intrinsic thermal conductivity κ of the thin film via Equation 1. For the UNCD thin films in this work, the range of t obtainable via the deposition technique employed was very narrow (see Supporting Information Figure S10) and thus a reliable zero-thickness interface was not able to be obtained via the linear extrapolation method described above. Instead, the surface area normalized total interfacial resistance value obtained by Mohr et al 39 (3.4 ± 0.7 m² K W⁻¹) was utilized throughout this work to extract the thin film thermal resistance $R_{th,Film}$ from the measured $R_{th,FilmInterfaces}$ and obtain the intrinsic κ of the covalently assembled UNCD thin films. The value of interfacial resistance taken from Ref.³⁹ was for CVD-synthesized nanocrystalline diamond on silicon substrate and a gold heater line, which is a very similar scenario as in this work. The relative uncertainty associated with this interfacial resistance value was propagated into the resulting $R_{th,Film}$ and κ values along with the other sources inherent to our measurement including those from 3ω voltage, 1ω voltage, film thickness, and dR/dT calibration. Of these contributors, uncertainty in film thickness t and $R_{th,FilmInterfaces}$ were found to dominate the overall uncertainty in κ .

3. Results and Discussion

3.1. Film Morphology and Composition



Figure 2. Characterization of morphology and composition of ND-COOH films obtained via directed covalent assembly. (A) Optical image of ND film deposited using 5 cycles on a borosilicate glass or silicon chip. (B) Atomic force microscopy images of ND films deposited on a borosilicate or silicon chip after 5 cycles. The average and root-mean-squared roughness for each film is denoted as R_a and R_q , respectively. Apparent porosity (ϕ_{app}) for silicon and borosilicate sample were found to be 0.31 and 0.35, respectively. (C) Scanning electron microscopy images showing of ND films deposited after 1, 3, 5, and 20 cycles on a silicon chip. (D) XPS spectrum of N_{Is} (bottom left) could be deconvoluted into peaks at 402 and 399 eV representing the HN-C=O, and $C-NH_2$ bonds, respectively. Red line indicates the experimental data and the shaded curves indicate the deconvoluted peaks. XPS spectra for C_{Is} , O_{Is} , and Si_{2p} is provided in Supporting Information Figure S9. (E) Left panel and right panel shows micro-Raman spectra in the 1050-1800 cm⁻¹ and 2600-3100 cm⁻¹ range. Blue dots indicate the data and the red curves indicate the deconvoluted peaks.

The ND films obtained by directed covalent assembly were observed to be relatively soft and prone to scratching by stainless steel tweezers used for substrate handling (scratch on silicon substrates shown in **Figure 2A**). In addition, the obtained ND films were optically transparent as can be seen in Figure 2A as well as **Supporting Information Figure S4**. Quartz substrates

coated with up to 5 cycles demonstrated >90% transmittance in the 390-790 nm range, resulting in an absorption coefficient between 4000-5000 cm⁻¹. Figure 2B and 2C show the film morphology using an AFM and an SEM, respectively. The AFM images show a disordered stack-like assembly of ND aggregates on both substrates - borosilicate and silicon - resulting in a root-mean-squared surface roughness (R_q) between 16 to 20 nm. The apparent porosity (ϕ_{app}) of the ND films was found to be between 0.3-0.35 for both substrates with majority pores falling between 20 to 70 nm (see Supporting Information Figure S5). The SEM images (see Figure 2C) of substrates after one to three deposition cycles shows a Volmer-Weber mode (islandtype) of film-assembly, where particle-particle cohesive force is stronger than particle-surface adhesive force. This was further verified with an AFM study (see Supporting Information Figure S6). The islands were difficult to visually discern after four deposition cycles and a complete surface coverage was observed starting at five deposition cycles onwards. Film morphology at the millimeter scale shows even deposition and no film cracking after drying, but as noted above the films were easily prone to scratching from handling of the chips in and out of the vials (see Supporting Information Figure S7). We were able to completely release one of the 200 nm thick ND films by etching the silicon substrate (see Supporting Information Figure S8). The film stayed intact following release, which indicates the mechanical integrity of these films and the inherent low residual stress.

The chemical composition of the ND film as analyzed using high resolution XPS and confocal micro-Raman spectroscopy confirms the formation of the amide bonds during directed covalent assembly. The XPS spectra for N_{1s} (**Figure 2D**) could be deconvoluted to two peaks. A peak at 399 eV could be attributed to the unreacted primary amines (C- NH_2) of the EDA whose other end is tethered to ND-COOH. A peak at 402 eV could be attributed to the amide (HN-C=O) bond linking the EDA to the ND-COOH. The complimentary C_{1s} and O_{1s} spectra confirm the formation of the amide linkage (see **Supporting Information Figure S9**). The Raman spectra (see **Figure 2E**) shows peaks at about 1250 and 1300 cm⁻¹ arising from the Amide III band.⁴¹

The peaks at 1332 cm⁻¹ and 2728 cm⁻¹ could be attributed to the sp^3 core of ND-COOH and the graphitic content on its surface, respectively.⁴² The *C*=*O* content of the linker chemistry can be seen at 1734 cm⁻¹ and 1300 cm⁻¹. The C-C and C-N stretching vibrations in the linkages can be seen at 1147 cm⁻¹ while the peak at 1452 cm⁻¹ could be attributed to the bending and scissoring vibrations of it CH₂ content. The peaks at 2869, 2924 and 2965 cm⁻¹ could be attributed to C-H stretching vibrations within the linkages and the ND surface.

Similar to layer-by-layer processing,⁴³ the directed covalent assembly procedure can be significantly sped up by spin coating. This was also found to decrease the amount of reaction solution needed and removed the need to regenerate ND-COOH solutions. However, the decreased reaction time associated with spin coating reduced the film assembly rate per cycle. With spin coating it was seen that a minimum of 10 deposition cycles were needed for a complete surface coverage and the use of 25 cycles resulted in 88 ± 11 nm thick films (See **Supporting Information Figure S10**). The AFM measurements confirm that the surface roughness, porosity, and pore size distribution of the spin cast films were similar ($\phi_{app} = 0.32$ -0.37 see **Supporting Information Figure S11**) to those obtained via the solution method (Supporting Information Figure S5). The ND films obtained by directed covalent assembly can be conveniently left amine terminated, allowing it to be decorated with proteins to run antigen capture assays as shown in **Supporting Information Figure S12**. The recorded capture densities and specificities were similar to those obtained on polycrystalline CVD diamond films in our past experience.^{3, 44-45} This shows that the increased surface area arising from the porosity of the ND films did not negatively impact the ability to perform pathogen capture assays.

3.2. Thermal Characterization



Figure 3. Substrate and heater line thermal interface resistance compensated (A) thermal resistance and (B) thermal conductivity of the UNCD thin films realized through differing numbers of deposition cycles. The inset of (A) shows a representative optical microscope image of one of the patterned 3ω lines used in this work.

The temperature-dependent cross-plane thermal resistance and thermal conductivity (κ) values obtained via the 3 ω method for the covalently assembled ND films in this work are shown in **Figure 3**. A full description of this method as well as the associated data processing can be found in the Experimental section. No clear dependence on the number of deposition cycles was observed, although the two samples with the larger number of deposition cycles did demonstrate higher κ values than those with fewer deposition cycles. The observed values of κ are insensitive to temperature (T) below 300 K within experimental uncertainty. Given diamond's high Debye temperature of 1860 K ⁴⁶, the lattice specific heat *C* should increase within this temperature range. Thus, the observed behavior suggests that - taking the very simplistic phonon kinetic model result of $\kappa = \frac{1}{3}Cvl_{ph}$ ⁴⁶ with temperature-insensitive phonon velocity *v* - the phonon mean free path l_{ph} decreases with increasing temperatures, the behavior varies between samples. The 15- and 20-cycle film samples demonstrated a strong decrease in κ with increasing temperature, which is typically associated with increasingly dominant phonon-phonon scattering and a mean free path no longer limited by boundary scattering effects.

Conversely, the 10-cycle sample showed a strong increase in κ with increasing temperature albeit within the span of the point-to-point uncertainty level. Via film morphology methods discussed above, the 10-cycle sample was found to have the highest variation in film thickness and the lowest overall film quality; thus, the observed increasing κ with temperature may be tied to structural changes incurred during the measurement that the other higher-cycle samples are insensitive to. However, further investigation into low-cycle sample behavior versus temperature would be required to say conclusively and is a candidate for future work.

First principles calculations have previously shown that 80 % of the heat in bulk crystalline diamond is carried by phonons with mean free paths between 500 nm and 3.5 µm at room temperature ⁴⁷. As a result, crystalline diamond structures with characteristic dimensions comparable to or smaller than this range would experience significant phonon boundary scattering and a suppressed thermal conductivity compared to bulk. Thus, compared to the extremely high thermal conductivity values of 2,000-3000 W m⁻¹ K^{-1 48-49} for high-quality single crystal diamond near 300 K, the range of κ for polycrystalline diamond films as well as the nanocrystalline films of this work is expected to be significantly lower. Li et al.'s calculations ⁴⁷ show that for a diamond nanowire with diameter comparable to the crystalline domain size of the NDs in this work (10 nm), the expected thermal conductivity would be approximately 65 W m⁻¹ K⁻¹. For a diamond nanowire with diameter comparable to the range of film thicknesses measured in this work (see Supporting Information Figure S10), the expected thermal conductivity would be 150-400 W m⁻¹ K⁻¹. The differing degrees of confinement associated with these structural forms, i.e. particle vs. nanowire vs. thin film, makes these length scale comparisons indirect. However, these values provide some order-of-magnitude guidance for geometrically constrained pristine crystalline diamond by which to compare the observed κ values as opposed to bulk experimental data, and can serve as a reasonable upper bound as to what might be achievable in the limiting case of pristine crystallinity.

With this in mind, the observed magnitude of the measured κ values are well below these ranges for single crystal diamond nanostructures. This also is to be expected, however, given the large number of particle-particle interfaces and voids within the assembled ND films, as well as the presence of phonon-scattering internal defects within individual particles. It is important to note that the substrate and heater line interface-compensated values of κ presented in Figure 3B still include the negative effects of film porosity. However, it is this version of κ which is most appropriate to consider when evaluating the thermal conduction potential of these films as they are today for applications such as electronics thermal management or MEMS integration as it is indicative of their true as-deposited performance. From this viewpoint, the UNCD films represent roughly a 2x to 15x improvement in thermal conduction over commonly used dielectric thin film materials like silicon dioxide or silicon nitride, but may have comparable or even lower thermal conductivity than certain high quality crystalline thin films such as from III-V semiconductor compounds. However, it should also be noted that these solutionprocessed thin films may be significantly lower cost or have superior ease of integration than many crystalline thin films with higher thermal conductivity. Thus, whether the UNCD thin films described in this work would be of net benefit to a given application depends on more than just thermal conductivity alone and must be evaluated for each specific scenario.



Figure 4. (A) Porosity-compensated thermal conductivity. (B) Room temperature porositycompensated thermal conductivity values measured for the UNCD thin films in this work (solid squares) compared to grain-size dependent thermal conductivity data for CVD diamond compiled from literature ^{37-39, 50-63}.

Future work should seek to minimize porosity and improve interface quality through chemical functionalization, post-deposition annealing, or other strategies. The best evaluation of the thermal conduction potential of covalently assembled UNCD thin films is to compare against reported thermal conductivity values for polycrystalline diamond of comparable grain size from various CVD processes. Thus, to estimate the thermal conductivity associated with conduction within the solid fraction of the measured films (κ_{solid}) and make for as direct a comparison as possible with literature thermal conductivity for solid CVD polycrystalline films, we utilized the established relation ⁶⁴⁻⁶⁶.

$$\kappa_{solid} = \frac{\kappa}{1-\phi} \tag{1}$$

where, ϕ is the pore volume fraction of the film. **Figure 4A** shows the values of κ_{solid} calculated from the κ data from Figure 3B using Equation 1 and ϕ value estimated using high resolution atomic force microscopy. This shows that reduction of porosity may lead to a 30 % to 61 % upshift in thermal conductivity. **Figure 4B** shows the near room temperature κ_{solid} values plotted for each of the four UNCD films from this work against the data compiled from literature ^{37,39,50,63} for CVD diamond thermal conductivity near room temperature as a function of reported grain size. As can be seen, the range of κ_{solid} observed in this work falls within the data scatter found in literature for CVD diamond thin films of comparable grain size. This is a significant finding, as it suggests that these low cost, covalently assembled nanodiamond thin films may be able to perform comparably well to those obtained by more costly CVD processes. The results of this work compare especially well with those recently reported by Mohr *et al.* ³⁹ for CVD diamond at similar grain sizes, where they presented thermal conductivity ranging from 0.6-40 W m⁻¹ K⁻¹ for grain sizes of 6-15 nm. However, even at the current thermal conductivity values observed here with pore inclusions, it appears that covalently assembled UNCD thin films are at least competitive with CVD when grain size is the same.

3.2. Significant Implications

A versatile approach to covalent assembly of nanomaterials has been implemented to synthesize a continuous film of nanodiamond. Conceptually, this room temperature process can be carried out on a variety of substrates that can be terminated with carboxyl or amine groups. The latter has been widely achieved using silane chemistry, thiol chemistry, or reactive plasma treatment. Further, all the chemicals used here were compatible with commonly used substrates used for MEMS fabrication including silicon, Pyrex®, quartz, flexible polyimide, PEEK and transparent conductive polyester film. CVD diamond coating cannot be performed on Pyrex®, polyimide, PEEK or transparent conductive polyester film. In addition, the proposed process costs about \$7 worth of chemicals and supplies (purchased in small quantities) to put down an ND film that is 100 nm thick on a 1x1 cm² substrate. Significant cost reductions can be anticipated from bulk purchase. Detonation-synthesized NDs post extensive chemical purification and size separation are already available worldwide from Carbodeon, Dynalene, and Microdiamant. The carboxylated NDs 67-70 are obtained simply by heavy oxidation of the purified NDs in air. Further, the direct assembly does not require expensive instrumentation and can be carried out in a wet lab with a fume hood. The process can be scaled up using robotic dip coaters, similar to those used in layer-by-layer self-assembly, or using roll-to-roll processing. The process uses mostly aqueous solvents and thus presents low work hazard. The most harmful chemical used here was ethylene diamine, which has an NFPA rating of 3 and an oral toxicity of 1200 mg/kg. Ethylene diamine was used in a fume hood in a closed vial and it was reused. The carboxylated NDs have been shown to be benign in in-vitro studies, which is promising in terms of lower toxicity and environmental risks.⁷¹⁻⁷⁴ Further, the proposed chemistry is simple yet versatile. The choice of diamine linker length and chemistry can be further tailored to impart novel functionality such as adsorption selectivity and pH-sensitivity for energy and health applications. Ethylene diamine was chosen as the linker molecule for MEMS applications to keep the distance between NDs to ~8 Å. Patterning of the ND films can also be envisioned through selective surface functionalization or reactive ion etching in an oxygen-rich plasma.

4. Conclusion

In summary, we demonstrate the feasibility to assemble polycrystalline diamond films in solution phase through carbodiimide-mediated cyclic attachment of ND-COOH and a diamine on amine-functionalized substrates. The formation of the desired amide bonds and incorporation of the diamine to form the nanoparticle network was confirmed using XPS and Raman spectroscopy. The assembly process was demonstrated in solution phase as well as via spin coating; in either case a minimum number of cycles were required for complete surface coverage. The films assembled via the two methods showed similar porosity, between 0.3 and 0.37. Further, we showed that the assembled ND films could be adapted with relative case for conducting pathogen or bead capture assays resulting in similar performance as that on CVD diamond films. The thermal conductivity measured via the 3ω method ranged between 2-20 W m⁻¹ K⁻¹, which is comparable to those of CVD nanocrystalline diamond films of comparable grain size. Future strategies to reduce porosity during the directed covalent assembly of the NDs hold potential for increased thermal conductivity.

Supporting Information

Supporting Information provides Figures S1-16 referenced in the main text as well as details of materials and methods in addition to those listed in the experimental section.

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TOC Graphics



Directed Covalent Assembly of Nanodiamonds into Thin Films

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Supporting Information



Figure S1. Characteristics of ND-COOH in powder and solution form. (A) X-ray diffraction pattern obtained using the ND-COOH powder. The spectra shows peaks at 43.94° and 77° degree that reflect <111> (d = 2.059 Å, a = 3.566 Å) and <220> (d = 1.262, a = 3.571) plane in diamond structure. Peaks evident at 38.16, 43.94°, 64.84°, 77.84°, and 82.14° correspond to the <111> (d = 2.356 Å), <220> (d = 1.437 Å), <311> (d = 1.226 Å), and <222> (d = 1.172 Å) plane of the underlying aluminum sample carrier. Lattice constant of A1, a = 4.064 Å. (B)

Micro-Raman spectrum of the ND-COOH powder using a 532 nm excitation source shows peaks at 1327.89 cm⁻¹ and 1585.46 cm⁻¹ that reflect its sp^3 and sp^2 content, respectively. (C) Zeta potential measurement of ND-COOH dispersed in DI water and 1 mM KCl solutions of pH 6.5, 7.5 and 8.5. Bars reflect the average value from three solutions and the error bars reflect the standard error of mean. (D) Particle size of ND agglomerates measured in DI water and 1 mM KCl solution was increased, the size of the NDs agglomerates was found to increase. Precipitation of NDs occurred within 10 mins at pH 7.5 and 8.5. The difference in the size of NDs agglomerates seen for pH 8.5 and pH 7.5 was due to the variation in time it took to go from the sonication bath to the photon correlation spectroscopy setup. The 1mM KCl pH 7.5 and pH 8.5 were heterogeneous solution. Smallest ND agglomerate sizes after sonication were observed in DI water.



Figure S2. Schematic representation of the directed covalent assembly of ND-COOH and its regeneration for reuse. A sample is cleaned using DI water, isopropyl alcohol, and acetone. (A) Cleaned sample is put into an oxygen plasma chamber for 1 min with 50 sccm O₂ flow rate, chamber pressure of 240 mTorr, and radio frequency power of 100 W at 13.56 MHz. (B) After oxygen plasma, the sample is put into a vacuum desiccator with vaporized (3-aminopropyl)triethoxysilane for 1.5 h at 20 °C. (C) Meanwhile, a solution containing amine-reactive ND-COOH is generated by bath sonicating 10 mg ND-COOH in 10 ml of 1 mM KCl (pH 6.5) and adding 3.4 mg of EDC. The silanized substrate is dipped in this solution for 30 min. (D) Then substrate is washed with 1mM KCl (pH 7) for 4 min. (E) The substrate is dipped into EDA for 30 mins. (F) The substrate is washed with DI water. (G) The nanodiamonds are precipitated using 1 mM HCl to adjust pH to 4, and centrifuge at 720 rcf for 5 min. (H) The supernatant is removed from the solution. (I) The ND-COOH are suspended in fresh 10 ml of 1 mM KCl (pH 6.5) using the bath sonication for 1 hr.



Figure S3. Impact of regeneration on the ND agglomerate size (graphs on the top) and zeta potential (graphs on the bottom) for up to 5 cycles. Red, blue and green columns correspond to data from ND-COOH suspensions after 1 h of sonication right before the deposition, 30 min after adding EDC into ND solution (after deposition), and after regeneration (includes the 1 h of bath sonication before next cycle). Note, the green column for cycle *n* is the same as the red column for cycle n+1. The presented manner allows changing the upper limit for y-axis for individual cycle. The increase in particle size and reduction of zeta potential is evident after addition of EDC to a freshly or regenerated solution of ND-COOH. This is believed to be due to hydrochloride content of the EDC that reduces the pH and the zeta potential, which is responsible for keeping the ND-COOH suspended. It is also evident that the regeneration cycle is able to restore the zeta potential and particle size of the ND-COOH.



Figure S4. Optical characterization of a quartz substrate coated after each cycle of directed covalent assembly of ND-COOH. (A) Per cent transmission of light as a function of wavelength. Data as obtained directly from the instrument. (B) Linear absorption coefficient as a function of light wavelength. The linear absorption coefficient ($\alpha = A/(0.4343 z)$) was calculated by first converting the transmittance data into absorbance values ($A = 2 - log_{10} \% T$), followed by using the Beer-Lambert's law, the transmittance data, and the thickness (z) of the quartz substrate as 1 mm. Linear absorption coefficient is large when the beam is quickly absorbed as it passes through the film, and the absorption coefficient is small when the medium is relatively transparent to the beam.



Figure S5. (A) Equivalent pore size distribution and **(B)** particle size characterization for ND films deposited on borosilicate glass (shown in Figure 2B). The pore size and particle size were corrected for AFM tip radius (~10 nm in this case). With H_{mean} as the threshold, the average pore radius was 44.9 ± 7.6 nm and the average particle size was 41.1 ± 19.4 nm. With $H_{mean+RMS}$ as the threshold, the average pore size was 60.4 ± 16.7 nm and the average particle size was

 36.6 ± 16.4 nm. With $H_{mean-RMS}$ as the threshold, the average pore size was 39.5 ± 7.1 nm and the average particle size was 48.8 ± 24.8 nm.



Figure S6. AFM imaging of polished silicon substrate coated with 1-5 cycles of directed covalent assembly of ND-COOH. Imaging performed using a standard Si tip to understand growth mechanism.



Figure S7. Low magnification SEM images of polished silicon substrate coated with 1-5 cycles of directed covalent assembly of ND-COOH.



Figure S8. Freely-floating 500 nm-thick ND film in water. The film was grown on a silicon chip first and then released by overnight etching of silicon substrates with 3:7 (v:v) mixture of HNO₃ (70% in water) and HF (49% in water).



Figure S9. XPS analysis of the ND films obtained via 5 cycles of directed covalent assembly. (A) Survey spectra highlight (in green) the C_{1s} , N_{1s} , O_{1s} and Si_{2p} peaks that were further analyzed. Using these peaks, the atomic % in the spectra are estimated to be 45% C, 2.2% N, 32% O, and

21% Si. (B-E) are high resolution spectra of the C_{Is} , N_{Is} , O_{Is} and Si_{2p} peaks. (B) XPS spectrum of C_{Is} could be deconvoluted into peaks at 285.2±1.3 (center ± FWHM), 286.8±2, 287.7±1.3, and 289.2±1.3 eV representing the sp^2 C, sp^3 C, C=O and C-N bonds, respectively;⁷⁵⁻⁷⁶ their concentrations were estimated to be 14.3%, 73.4%, 2.8%, and 9.6%, respectively. (C) XPS spectrum of O_{Is} could be deconvoluted into peaks at 532.7±2.4 and 533.2±1.6 eV representing O=C and HO-C bonds, respectively;⁷⁷ their concentrations were estimated to be 25.8% and 74.2%, respectively. (D) XPS spectrum of N_{Is} could be deconvoluted into peaks at 400.7±1.9 and 401.8±4.6 eV representing the $C-NH_2$, and HN-C=O bonds, respectively; their concentrations were estimated to be 55.5% and 44.5%, respectively. (E) XPS spectrum of Si_{2p} could be deconvoluted into peaks at 101.9±0.8 and 103.9±1.7 eV representing the Si-C and SiO₂ bonds, respectively;⁷⁸ their concentrations were estimated to be 1.6% and 98.5%. Red line indicates the experimental data and the shaded curves indicate the deconvoluted peaks.



Figure S10. Thickness and roughness of spin cast ND films using AFM. (A) Average film thickness measured by scratching the film with an AFM tip. (B) Root-mean-squared and average surface roughness measured with increasing number of deposition cycles.



Figure S11. Porosity and pore size distribution analysis using atomic force microscopy (AFM). Samples were prepared via spin coating the solutions as described in the method section. Each panel corresponds to data from ND films deposited either via 10, 15, 20, or 25 cycles. In each panel, the AFM image is shown at the top with the analyzed pore size distribution below it. The pore size distribution was calculated after thresholding the AFM image at different heights – mean height (H_{mean}), mean height plus root-mean-squared roughness ($H_{mean+rms}$), and mean height minus root-mean-squared roughness ($H_{mean-rms}$). The graphs are annotated with the apparent porosity (ϕ_{app}).



Figure S12. Biofunctionalization of covalently assembled ND film and its application to biosensing. (A) The unnormalized fluorescent intensity recorded on an ND film with and without Cy3-labeled mouse IgG immobilized. (B) Bead capture density obtained when PBS containing FITC-labeled goat anti-mouse IgG functionalized beads at various concentrations was exposed to ND films with and without immobilized mouse IgG. (C) The *E. coli* O157:H7 capture density obtained when PBS containing DiOC₆(3)-labeled live *O157:H7* at various concentrations was exposed to ND films on a silicon chip with or without anti-*E. coli* O157:H7 tethered to the surface. (D) The *E. coli* O157:H7 capture density obtained when PBS containing DiOC₆(3)-labeled live *O157:H7* at various concentrations was exposed to ND films on a silicon chip with or without anti-*E. coli* O157:H7 tethered to the surface. (D) The *E. coli* O157:H7 capture density obtained when PBS containing DiOC₆(3)-labeled live *O157:H7* at various concentrations was exposed to ND films on a silicon chip with or without anti-*E. coli* O157:H7 tethered to the surface. (D) The *E. coli* O157:H7 capture density obtained when PBS containing DiOC₆(3)-labeled live *O157:H7* at various concentrations was exposed to ND films on a borosilicate chip with or without anti-*E. coli* O157:H7 tethered to the surface. Example fluorescence images for (B) provided in **Supporting Information Fig. S13-14**.



Figure S13. Example fluorescence microscopy images showing FITC-labeled *E.coli O157:H7* captured on nanodiamond coated silicon chip with and without anti-*E.coli O157:H7* immobilized when exposed to solutions containing 10^5 , 10^6 or 10^7 cfu/ml.



Figure S14. Example fluorescence microscopy images showing FITC-labeled *E.coli O157:H7* captured on nanodiamond coated borosilicate glass substrate with or without immobilized anti-*E.coli O157:H7* when exposed to solutions containing 10^5 , 10^6 or 10^7 cfu/ml, respectively.



Figure S15. Validation of 3ω experimental procedure. (A) Representative raw 3ω in-phase and out-of-phase data. The larger magnitude, frequency-dependent in-phase component and the smaller, frequency-insensitive out-of-phase component are indicative of a properly functioning measurement per literature. (B) Comparison of results obtained for thermally grown 200 nm-

thick SiO₂ on silicon substrate in this work versus accepted literature values also obtained via a 3ω measurement ³².



Figure S16. As-measured (A) thermal resistance and (B) thermal conductivity of the UNCD thin films realized through differing numbers of deposition cycles. It is important to note that the thermal resistance does not include the propagated uncertainty associated with the respective film thickness measurements, whereas this uncertainty is included in the thermal conductivity data.

MATERIALS AND METHODS

Materials. Carboxylated nanodiamonds (ND-COOH, 98% purity) with average 3-4 nm particle size and 50 nm aggregate size were purchased from International Technology Center (Raleigh, North Carolina). 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), a water-soluble carbodiimide crosslinker was used for zero-length conjugation of carboxyl groups on ND-COOH to the amine group on ethylene diamine. EDC was purchased from Thermo Scientific Pierce. Ethylenediamine (EDA, 99% purity) was purchased from Alfa Aesar. Acetone (CMOS), 2-propanol (CMOS), (3-Aminopropyl)triethoxysilane (99%, ACROS Organics), potassium chloride (ACS), hydrochloric acid (ACS Plus) and sodium hydroxide (ACS) were obtained from Fisher Scientific. Deionized water (DI) with a minimal conductivity of 18 MΩ-cm was obtained using a Millipore deionization system.

XRD was performed with a Bruker D8 Discover using an X-ray wavelength of 1.54056 nm generated from copper anode, a step time of 240 s with a step size of 0.02°, a Ni filter and a 0.5 mm tube.

Particle size and zeta potential measurements were carried out using photon correlation spectroscopy ($\lambda = 660$ nm) on a Brookhavens Instruments ZetaPlusTM. Average particle size

distribution was obtained from 10 measurements using an angle of incidence of 90° degree. The zeta potential calculations were performed using the Smoluchowski equation because the ND-COOH particles were of wide size range (10 - 200 nm). Use of the Huckel approximation did not change the trend seen in the zeta potential measurements. All calculation were based on properties of water at 25 °C (viscosity of 0.890 cP, refractive index of 1.330 and dielectric constant of 79.63).

XPS analysis was performed with a Kratos Axis Ultra spectrometer (Kratos Analytical, Manchester, UK) equipped with a monochromatized aluminum X-ray source (powered at 10 mA and 13 kV). Instrument was calibrated to $Cu_{2p3/2}$ (932.7 eV) and $Au_{4f7/2}$ (84 eV). The samples were attached on a conductive multi-specimen holder using Cu-Be clips and screws, in order to avoid differential charging. The pressure in the analysis chamber was about 10^{-7} Pa. The angle φ between the normal to the sample surface and the direction of photoelectrons collection was 0°. Analysis was performed in the hybrid lens mode with the slot aperture; the analyzed area was 700 µm × 300 µm. The pass energy was set at 160 eV for the wide scan and 40 eV for narrow scans. Charge stabilization was achieved by using the Kratos Axis device. The following sequence of spectra was recorded: survey spectrum, C_{1s}, N_{1s}, O_{1s}, and Si_{2p}. The C1s peak of carbon was fixed to 284.5 eV to set the binding energy scale. Data treatment was performed with the Kratos Vision software. Atomic concentration ratios were calculated using peak areas normalized on the basis of acquisition parameters after a linear background subtraction, experimental sensitivity factors and transmission factors provided by the manufacturer.

Raman spectroscopy was performed using a 532 nm source on a Horiba XploRATM Plus confocal system with a 1800 gr/mm grating, 100 μ m slit, a 500 μ m hole, and a 20 s integration time on a deep cooled open electrode 1024 x 256 CCD Camera (Syncerity, Horiba).

SEM images were recorded with a Hitachi S-4800 Field-Emission Electron Microscope using an accelerating voltage of 1kV to obtain balance between electrical charging and resolution.

AFM images were recorded on an Agilent 5420 Atomic Force Microscope using a standard silicon probe. Scanning rate and resolution was set to 0.2 lines/s and 512 points respectively. In case of measuring porosity, high resolution probes with a sharp diamond-like-carbon spike (Budget Sensors SHR75) were used in tapping mode.

UV-Vis Transmissibility was measured using a Shimadzu UV-1650PC UV-Vis Spectrophotometer with a 10 mm x 1 mm beam scanning the wavelength in increments of 0.1 nm at 160 nm/min and recording signal using a silicon photodiode.

Optical characterization was performed using a Filmetrics F10-RT with a regulated tungstenhalogen light source and a probing spot size of 6 mm.

Antibody Immobilization of Amine-terminated ND Films: The amine-terminated ND film obtained after EDA reaction was rinsed with DI water and reacted with glutaraldehydride in a sodium cyanoborohydride coupling buffer by reductive amination at room temperature for 4 h to yield an aldehyde terminated surface, which was then rinsed with DI water, dried with nitrogen, and incubated with a 100 μ g/ml antibody solution for 18-22 h at 4 °C. The antibody immobilized surface was then washed with phosphate buffered saline (PBS) containing 0.05 %(v/v) Tween 20 (T20) twice, and PBS once to remove non-specifically adsorbed antibodies. The non-specific binding sites were blocked with a casein and BSA blocking buffer mixture for 1 hour at room temperature. The sample was then washed again with PBS-T20 twice and PBS once to remove excess blocking solution.

Fluorescent labeling of *E. coli O157:H17* **bacteria.** The live culture of *E. coli O157:H7* was inoculated in Luria-Bertani broth (LB) at 37 °C for 12 h. Based on plating culture at the 12th hour, all bacteria were found to reach a stationary phase of growth. Live culture was used for work in this paper. Fresh culture (1 ml in 1.5 ml centrifuge tube) was washed with phosphate saline buffer (PBS) via centrifuge at 12k rpm for 2 minutes. The supernatant (0.9 ml) was removed, and the culture was resuspended in PBS (0.9 ml). The washing procedure was done

two times. A 2 μ l green fluorescent DiOC6(3) (5mg/ml) was added in the washed culture and vortexed to mix properly. The labeling was performed in a 37 °C incubator for 30 minutes. Excess labeling dye was removed by centrifuging the culture at 12k rpm for 3 minutes, followed by removing the supernatant (0.9 ml) again. The labeled culture was then resuspended in PBS (0.9 ml). The concentration of the labeled culture was estimated by agar plating of the 10⁻⁵ and 10⁻⁶ dilution. The average concentration was found to be 10⁹ colony forming units per ml (cfu/ml).

Functionalized Microspheres and Bacteria capture experiment. Live DiOC6(3) labeled bacteria or latex microspheres (4 μ m) decorated with FITC-labeled goat anti-mouse IgG were used in this experiment. A 100 μ l aliquot of 10⁵, 10⁶ and 10⁷ cfu/ml was deposited in the 7 mm diameter PDMS wells, which were attached on the antibody-functionalized nanodiamond surface. A cover slip was placed on the top of the PDMS well to prevent evaporation. The surface exposed to the bacterial or microsphere solution was placed in a 37 °C incubator for 1 h. Later the solution was removed using a vacuum aspirator and the surface was washed with PBS (thrice) to remove non-specifically bound bacteria or microspheres. The surface captured bacteria or microsphere were imaged using an Olympus BX41 fluorescence microscope equipped with a Photometrics Coolsnap K4 camera and enumerated using ImageJ. Five locations were imaged for each sample.