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PAPER

## Resorcinarene amine stabilized nanodiamond dispersions in organic solvents: applications in diamond film growth†

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Nanodiamonds of widely differing sizes (4 to >100 nm), shapes, and origin could be extracted from aqueous dispersions into toluene by a multidentate resorcinarene amine surfactant, in the absence of any elaborate covalent functionalization or extreme conditions. Resorcinarene amine encapsulated nanodiamonds displayed excellent dispersion stability in non-polar organic solvents for several months. The IR spectral analysis of these extracted and further precipitated nanodiamonds suggests that the carboxylic acid groups present on the nanodiamond surfaces are electrostatically stabilized by the resorcinarene amine surfactant. Such nanodiamond dispersions can also act as nucleation sources for the fabrication of continuous diamond films by CVD growth. Notably, this process resulted in diamond films with better uniformity, smaller grain size and reduced surface roughness when compared to the films prepared with unmodified nanodiamonds as nucleating agents.

## Introduction

Nanodiamonds,<sup>1</sup> exhibiting several attributes of bulk diamonds such as hardness, chemical stability and wide band gap to name but a few, have attracted a lot of attention. These properties lead to their wide use in diverse applications ranging from quantum computing, biological and electronic devices, to composite materials.<sup>2</sup> To harness the unique properties of nanodiamonds, as with any other nanosized material, it is necessary to disperse them in suitable media. The low stability to sedimentation of liquid dispersed nanodiamonds is well-documented in the literature.<sup>1c</sup> The problem is further exacerbated by the fact that there are no universal materials such as nanodiamonds; and nanodiamonds supplied are vendor specific, depending on their synthesis, and purification conditions.<sup>1c</sup> Diverse approaches employing surfactants, mechanical treatments or combinations thereof have been developed to address this issue with various levels of success.<sup>1c,3</sup> Functionalization approaches have also been developed in the past, which have aided the dispersion stabilization of nanodiamonds.<sup>1c,4</sup> Though both covalent and non-covalent strategies have been adopted for dispersing nanodiamonds in aqueous media,<sup>4a-c</sup> primarily covalent

functionalization methods are adopted for dispersing nanodiamonds in organic media.<sup>4d,e</sup> Recently, Li and coworkers reported a non-covalent strategy for dispersing nanodiamonds that used oleylamine in non-polar organic solvents and involved the air oxidation of the nanodiamonds at 420 °C.<sup>5</sup> The current approaches for the functionalization of nanodiamonds often involve toxic reagents such as acids or fluorine gas, moisture sensitive conditions, high temperature, longer reaction durations *etc.*<sup>1b,c,5</sup> In this context, simpler functionalization approaches and processing strategies are needed to fully realize the untapped potential of nanodiamonds.

Nanodiamonds have been used as nucleation seeds in chemical vapor deposition (CVD) of diamond films.<sup>1a,6</sup> Diamond films and coatings have found wide ranging applications in electronic and electrochemical devices,<sup>7</sup> sensors,<sup>8</sup> protective coatings,<sup>9</sup> optical windows<sup>10</sup> and so on. In spite of the notable progress in recent years, there are still problems plaguing the development of diamond based electronics, and currently there is a need to decrease diamond film roughness.<sup>1a</sup> In order to fabricate diamond films on non-diamond substrates, nucleation or seeding is required prior to growth.<sup>1a</sup> Regardless of the technique employed to fabricate the diamond films such as hot filament CVD<sup>11</sup> and microwave plasma CVD,<sup>12</sup> one of the most significant factors influencing the surface roughness and grain size of the diamond film is the initial nucleation density and size. One major problem with the use of smaller nanodiamonds (4–5 nm sizes) as nucleation seeds is that they often form larger 100–500 nm aggregates, which require additional treatments such as ultrasonic breaking prior to CVD film growth.<sup>1a</sup> In addition to ultrasonic treatment, abrading the surface with diamond particles is another widely employed mechanical nucleation technique.<sup>13</sup> Micro- to nano-scale

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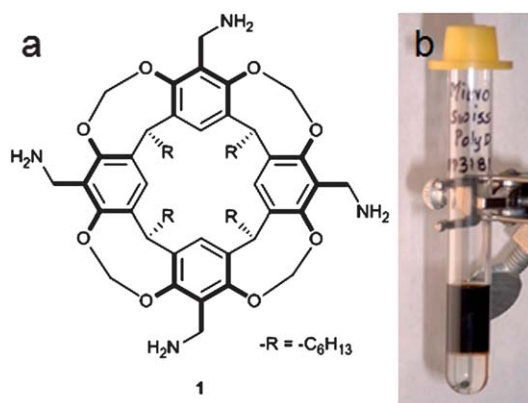
scratches or pits are created on the surface of the substrate to trap diamond particles as seeds.<sup>14</sup> Consequently, the process damages the substrate surface along with any topographical features that might have already been manufactured onto the surface.<sup>15</sup> Bias enhanced nucleation<sup>16</sup> is another widely used electrical method, where the nucleation density is relatively low and limited to metallic or semiconducting substrates in order to apply bias voltage for bombarding the surface with carbon ions. Thus, carbide-rich surfaces are created to enhance diamond nucleation. However, the bombardment also produces damage to the surface. A new non-damaging spray nucleation technique has been published recently, nevertheless, the control and stability of the technique is still uncertain.<sup>17</sup>

We demonstrate the utility of a multidentate resorcinarene amine surfactant (**1**, Fig. 1a) in phase-transferring nanodiamonds from aqueous to organic phase (Fig. 1b) and aiding the dispersion of nanodiamonds in non-polar organic solvents. Resorcinarenes, a class of macrocyclic molecules, are an established building block in supramolecular chemistry.<sup>18</sup> Here we show that resorcinarene amine **1** can extract commercially available nanodiamonds of various sizes and shapes at room temperature, in the absence of any extreme conditions. Further, we have developed a non-intrusive nucleation technique for diamond film growth with resorcinarene encapsulated nanodiamond dispersions as precursors.

## Experimental

### General remarks

Prior to their use all solvents employed in this study were dried and distilled following standard procedures. Nanodiamonds obtained from various sources were used as received. Polycrystalline liquid diamond (<30 nm) from Microdiamant, Altai from Ultradiamond Technologies, NB90-Semiconductor Grade PSD 5 nm from Dynalene, and Mypolex N-6 (polycrystalline diamond from DuPont, currently Microdiamant) will be referred to as Microdiamant, Altai, Dynalene and DuPont nanodiamonds respectively in this article. Operations involving nanodiamonds were typically carried out in silanized glassware.



**Fig. 1** Resorcinarene amine (a) mediated phase-transfer of Microdiamant nanodiamond (b) from aqueous to organic phase (THF/toluene).

### Characterization

<sup>1</sup>H-NMR analysis of organic compounds was carried out in a Varian Oxford 400 MHz instrument. IR analysis of solution drop cast samples was carried out on a Thermo Electron Nicolet 370 DTGS spectrophotometer operating in transmission mode. HRMS analysis was carried out in a Bruker 12 Tesla APEX-Qe FTICR-MS equipped with an Apollo II ion source in a positive electrospray ionization mode.

TEM analysis of nanodiamond dispersions was carried out in a JEOL JEM-2100F field emission microscope operating at 200 kV equipped with a Gatan SC1000 ORIUS CCD camera (11 megapixel). Diluted nanodiamond dispersions (5× volume) were sonicated for 5 minutes prior to their deposition on a formvar-carbon coated copper grid for TEM analysis. SEM images of diamond films grown on silicon substrates were obtained using a JEOL JSM-6060LV scanning electron microscope operating at 5–30 kV. Atomic force microscopy was carried out on a Veeco diNanoscope 3.

### Resorcinarene amine (1) synthesis

Tetraphthalimide resorcinarene cavitand was synthesized from 2-methylresorcinol in 4 steps by modified literature procedures.<sup>19</sup> To a solution of tetraphthalimide resorcinarene cavitand (0.950 g, 0.629 mmol) dissolved in THF (9 mL), excess EtOH (90 mL) and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (0.630 mL, >20 equiv.) were added and refluxed under argon atmosphere for 4 h. The reaction mixture was allowed to cool, acidified with HCl (0.8 mL), and refluxing continued for another hour. To the residue obtained after removal of volatiles under reduced pressure, excess sodium hydroxide (aqueous solution) was added, and the precipitate obtained was filtered and dried to yield **1** (522 mg, 84%) as a white solid.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3373 (N–H), 2928 (C–H), 1586 (C=C), 969 (C–O–C);  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>): 7.04 (s, 4H), 5.92 (d, *J* 6.8 Hz, 4H), 4.76 (t, *J* 8 Hz, 4H), 4.35 (d, *J* 6.8 Hz, 4H), 3.60 (s, 2H), 2.21 (q, *J* 8 Hz, 2H), 1.5–1.2 (m), 0.90 (t, *J* 6.8 Hz, 3H);  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>): 152.96, 138.12, 129.10, 118.97, 99.28, 36.92, 36.15, 31.82, 30.12, 29.47, 27.87, 22.61, 14.02; *m/z* (FTICR-MS, ESI) 1011.6180 (M + Na)<sup>+</sup>.

### Nanodiamond extraction and precipitation

In a typical extraction experiment, aqueous nanodiamond dispersions were mixed with an equal volume of resorcinarene amine surfactant (6 mM) solution in tetrahydrofuran (THF). The dispersion was sonicated briefly for 20 s, at regular intervals of 15 min, for over an hour. Addition of an equal volume of toluene followed by vigorous mixing for 30 s led to the immediate and complete transfer of the nanodiamonds from the aqueous to organic phase.

Extracted nanodiamond dispersions (in THF–toluene mixture) were precipitated by adding excess ethanol (9× volume) and centrifuged on a Sorvall Legend 23R Centrifuge at 9000 rpm (~8000 g) for 30 minutes. The precipitate obtained could be redispersed in toluene, chloroform, dichloromethane or THF–toluene mixtures.

### Diamond films by CVD growth

The 2-inch p-type silicon wafers were ultrasonically cleaned in acetone for 10 minutes, then flushed in DI water and blow-dried.

All the wafers were spin-coated with resorcinarene amine encapsulated (Microdiamant) nanodiamond dispersions. Another wafer was coated with the unmodified (as received Microdiamant) nanodiamond dispersion as a control. All nanodiamond dispersions were spin coated at 500 rpm for 5 seconds and then at 4500 rpm for 30 seconds. Coated samples were baked at 100 °C for 2 minutes.

A microwave CVD system (AsTex) with automatic pressure, temperature, and gas flow controllers was used to grow the diamond films.<sup>8</sup> Growth experiments were conducted with 1% methane in hydrogen gas with a substrate temperature of 750 °C and 1000 W microwave power. The gas flow rates were 891 and 9 SCCM for hydrogen and methane respectively. The growth chamber was pumped down to 1 mTorr or lower with a turbo pump before heating the substrate to 750 °C and striking the microwave plasma. Diamond films were grown for 90 min.

## Results and discussion

### Resorcinarene amine mediated extraction and dispersion of nanodiamonds

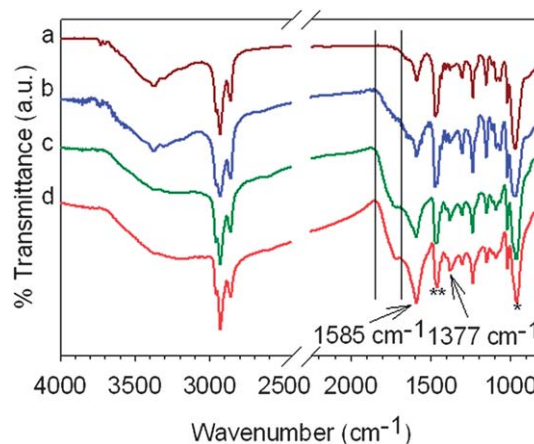
The aqueous Microdiamant nanodiamond dispersion was treated with an equal volume of resorcinarene amine surfactant (**1**, Fig. 1a) solution in THF (6 mM) and the suspension was periodically agitated for an hour at room temperature. Addition of toluene, and vigorous mixing resulted in the immediate and complete transfer of nanodiamonds to the organic phase, which could be readily monitored visually (Fig. 1b). The extraction process described in the experimental section is flexible as neither sonication nor the use of silanized glassware is critical for a successful extraction. However, the surfactant concentration played a crucial role, as lowering the resorcinarene amine concentration from 6 mM to 4 mM resulted in only partial extraction. In the absence of the resorcinarene amine surfactant, there was no nanodiamond extraction.

Remarkably, such phase transferability of nanodiamonds was limited to the multidentate resorcinarene amine surfactant, as other resorcinarene derivatives such as the parent resorcinarene and resorcinarene cavitand (Fig. S1†) were not effective in extracting the nanodiamonds under identical conditions. Also, amino compounds such as benzylamine, hexylamine, and dimethylaminopyridine were not effective in extracting Microdiamant nanodiamonds from aqueous to organic phase. With cetyl trimethylammonium bromide surfactant, nanodiamonds were briefly extracted into the organic phase (Fig. S2a†). However, such dispersions were not stable as they began to settle down in the interface within a few minutes and were completely in the interface in ~1 hour (Fig. S2b†). Note that the experiments involving small molecules were carried out at higher surfactant concentrations (48–50 mM). These experiments clearly indicate the importance of both the amine functionality and the macrocyclic resorcinarene skeleton in effecting the nanodiamond extraction.

Notably, the Microdiamant nanodiamonds extracted into the organic phase could be completely evaporated and redispersed in organic solvents such as tetrahydrofuran and toluene. Such dispersions were stable for months without any noticeable sedimentation (Fig. S3†). Further, nanodiamonds extracted into the

organic phase could be precipitated by solvent-induced precipitation. Precipitation of the nanodiamond dispersions was carried out by adding excess ethanol and then isolating the precipitate by centrifugation at ~8000 g for 30 minutes. The precipitate could be redispersed in toluene or chloroform. Excess resorcinarene amine surfactant could be removed after two precipitation/redispersion cycles, as monitored by the spectroscopic analysis of the supernatant obtained after centrifugation. The redispersed nanodiamonds obtained after removal of excess surfactants, exhibited moderate stability and occasionally some partial sedimentation was observed after the second round of precipitation.

Not surprisingly, the infrared spectra of extracted and subsequently precipitated nanodiamonds correlated reasonably well with the resorcinarene amine surfactant (Fig. 2). However, a closer look at the FTIR spectra from various stages revealed noticeable gradual differences, providing clues about the nature of the interaction between the resorcinarene amine surfactant and the nanodiamonds. The key observations from the IR spectra of the precipitated nanodiamonds are: (a) the appearance of a new peak at 1377 cm<sup>-1</sup>, (b) the increased intensity of 1585 cm<sup>-1</sup> peak (c) the appearance of a shoulder at 1720–1730 cm<sup>-1</sup> (in between the lines in Fig. 2), and (d) a broad peak centered around 3200 cm<sup>-1</sup>, while the peaks at 968 cm<sup>-1</sup> from C–O–C stretching<sup>20</sup> (represented as \* in Fig. 2) and 1460 cm<sup>-1</sup> (represented as \*\* in Fig. 2) essentially remained constant. The first three observations can be explained by symmetric (expected ~1400–1310 cm<sup>-1</sup>), antisymmetric (expected ~1610–1560 cm<sup>-1</sup>) and C=O stretching of the COO<sup>-</sup> group of the nanodiamonds and the very broad peak centered around 3000 cm<sup>-1</sup> could be due to O–H (from carboxylic acid on nanodiamond) or N–H (of the resorcinarene amine due to the –NH<sub>3</sub><sup>+</sup> antisymmetric) stretching.<sup>21</sup> At first sight these observations were rather surprising, as these commercially available nanodiamonds were not oxidized in this study and were used as received. However, it is well-documented in literature that nanodiamonds can have a wide-variety of surface functional groups such as carboxyl, hydroxyl, keto, anhydride and lactones.<sup>1c,22</sup> It is possible that the phase-transfer is promoted by the electrostatic stabilization of the carboxylic



**Fig. 2** FTIR spectra of resorcinarene amine **1** (a), resorcinarene amine encapsulated Microdiamant nanodiamond (b), and once (c) and twice (d) precipitated resorcinarene amine encapsulated Microdiamant nanodiamonds.



acid groups present on the nanodiamond surfaces by the amine groups of the multidentate resorcinarene amine surfactants.

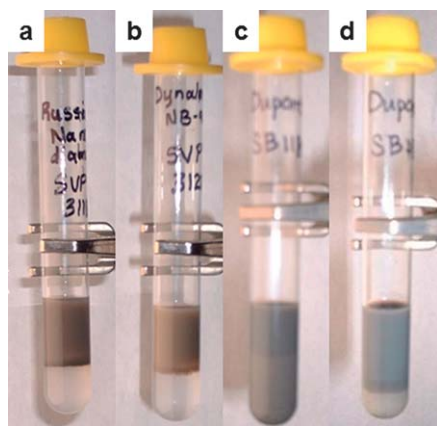
### General applicability

This simple surfactant mediated phase-transfer approach was successful in extracting a number of commercially available nanodiamonds (such as Microdiamant, Altai, Dynalene and DuPont) into organic solvents (Fig. 3). In the case of DuPont nanodiamonds, initially an emulsion formation and partial extraction of the nanodiamonds was observed (Fig. 3c). However, over a period of two months, almost complete transfer of the DuPont nanodiamonds into the organic phase was observed (Fig. 3d).<sup>23</sup>

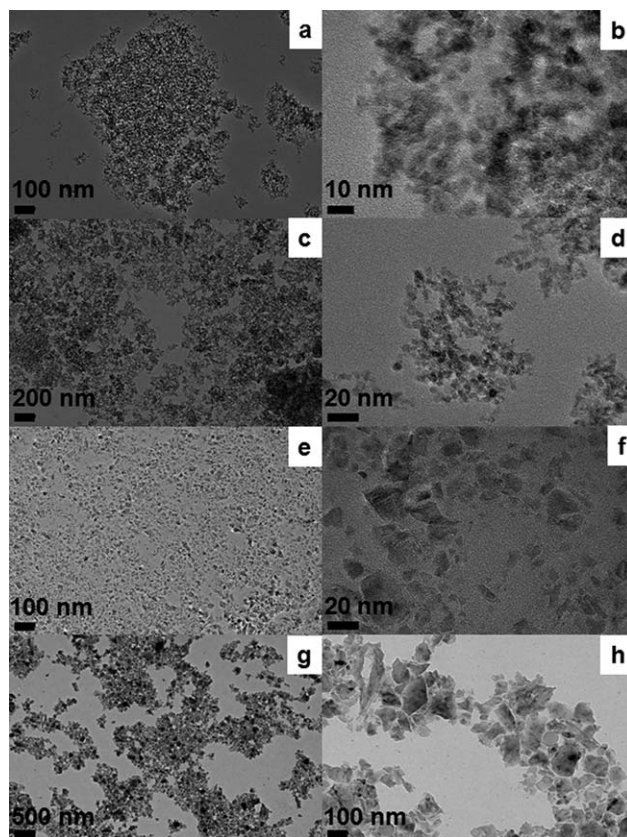
TEM analysis of the extracted nanodiamonds (Fig. 4) showed that nanodiamonds of various sizes and shapes could be effectively dispersed in non-polar organic medium by the resorcinarene-amine surfactant. Smaller detonation nanodiamonds (with typically ~4 to 5 nm diameter) from Altai and Dynalene sources appeared almost spherical in shape, in contrast to those obtained from Microdiamant (up to 30 nm) and DuPont (>100 nm). Given the established dependence of nanodiamond structure on their production conditions,<sup>1b,c</sup> it is remarkable that resorcinarene amine **1** can act as an excellent surfactant for extracting nanodiamonds from widely differing origins. Also, it is impressive that the resorcinarene amine surfactant **1**, with relatively shorter C6 chains, is capable of extracting nanodiamonds with dimensions much larger than 100 nm. In this regard it is worth noting that a structurally similar resorcinarene-thiol surfactant,<sup>24</sup> with longer C11 chains, has been known to phase-transfer gold colloids up to 87 nm from aqueous to organic phase depending on the experimental conditions.<sup>25</sup>

### Diamond film growth

Resorcinarene-amine encapsulated nanodiamonds spin coated on a silicon wafer were used as nucleation seeds to grow diamond films by CVD for 90 min. Spin coating does not damage the substrate. To understand the influence of the resorcinarene amine surfactant in the growth process, identical films were also



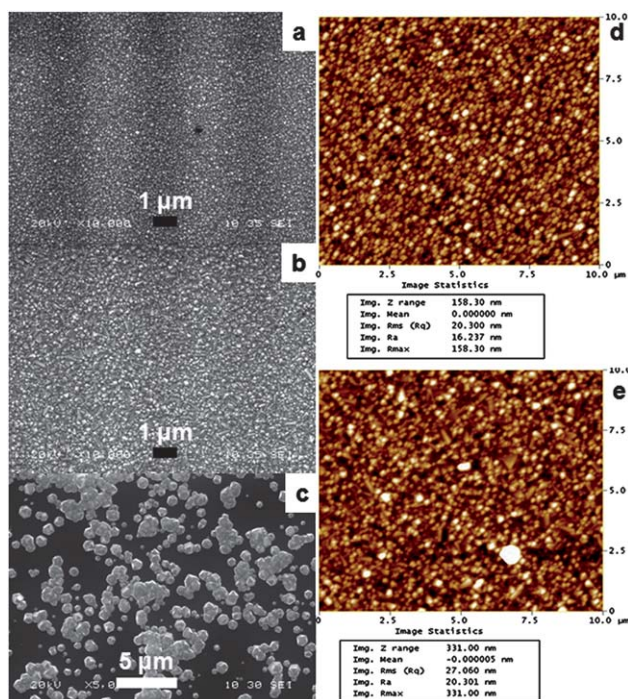
**Fig. 3** Resorcinarene amine extracted nanodiamonds from various sources: (a) Altai, (b) Dynalene, (c) DuPont (immediately) and (d) DuPont (after 2 months).



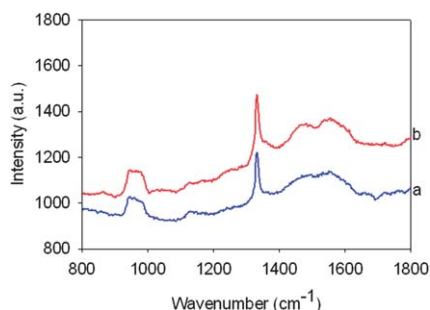
**Fig. 4** TEM images of resorcinarene amine extracted nanodiamond dispersions: (a and b) Altai (c and d) Dynalene (e and f) Microdiamant and (g and h) DuPont.

grown with unmodified (as received) nanodiamond dispersions or a bare silicon substrate. Continuous diamond films of about 500 nm thickness were observed in both cases with the resorcinarene amine encapsulated nanodiamonds (Fig. 5a) and the unmodified nanodiamonds (Fig. 5b) as nucleation seeds. The grain size of the diamond film in the former (Fig. 5a) is much smaller and more uniform compared to the latter (Fig. 5b). The SEM of a diamond film grown under identical condition but without the nanoseeding method (Fig. 5c) shows only sporadic growth of the diamond crystals. The AFM analysis of the diamond films (Fig. 5d and e) further confirmed the SEM results (Fig. 5a and b). Remarkably, the root mean square value of the surface roughness of the nanodiamond nucleated diamond films increased substantially from 20.3 nm to 27 nm when the resorcinarene amine surfactant was not used. These results clearly demonstrate that resorcinarene amine extracted nanodiamonds are useful as a new seeding method to grow continuous, smooth diamond films. A detailed investigation of this observation is currently under way in our laboratories.

The Raman spectra of the diamond films grown with the nanodiamond nucleating agents are shown in Fig. 6. The diamond peaks at  $1332\text{ cm}^{-1}$  are clearly seen in both cases. These  $\text{sp}^3$  peaks have similar FWHMs around  $10\text{ cm}^{-1}$ , indicating the good quality of the films.<sup>12c</sup> The small broad peaks centered around  $1450\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$  are indicative of non-diamond carbon in the films that can be reduced by either lowering the methane concentration or adding oxygen containing gas.<sup>12c</sup>



**Fig. 5** Microscopic analysis of diamond films grown under different conditions. SEM (a–c) and AFM (d and e) images of diamond films grown with resorcinarene amine encapsulated nanodiamonds (a and d), and unmodified (as received) nanodiamonds from Microdiamant as nucleating agents (b and e) and without a nucleating agent (c).



**Fig. 6** Raman spectra of diamond films grown with resorcinarene amine encapsulated Microdiamant nanodiamonds (a) and unmodified (as received) Microdiamant nanodiamonds (b) as nucleation seeds.

## Conclusions

We have demonstrated the utility of a multidentate resorcinarene amine surfactant in extracting nanodiamonds from aqueous to organic phase. Resorcinarene amine stabilized nanodiamond dispersions in non-polar organic solvents, such as toluene or tetrahydrofuran, were found to be stable for at least several months. Notably, the simple extraction procedure described here for dispersing nanodiamonds in organic solvents does not require elaborate covalent functionalization approaches or extreme conditions. Further, this extraction procedure could be applied to nanodiamonds from a variety of commercial sources with varying sizes and shapes. We have demonstrated their utility as nucleation sources in the CVD growth of diamond films without

damage to the substrate surface. Diamond thin film with small grain size and low surface roughness could be grown by using resorcinarene encapsulated nanodiamonds as nucleating agents. Since the technique is compatible with semiconductor processing methods, the process developed could help integrate diamond films with silicon for MEMS and several other applications.

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- 25 As noted in ref. 24a, in toluene–THF mixture, gold colloids up to 42 nm could be extracted into the organic phase. However, in chloroform–THF mixture with excess tetraoctylammonium bromide, gold colloids up to 87 nm could be extracted.