

Supplementary Information

Robust, Directed Assembly of Fluorescent Nanodiamonds.

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S1 Nanodiamond self-assembly:

Substrates were sonicated in acetone and isopropyl alcohol followed by cleaning in Piranha (3:1 H₂SO₄: H₂O₂) solution. The substrates were then introduced into the vacuum chamber of a FEI Sirion XL30-FEG SEM and exposed to an oxygen plasma (50W, 1 Torr) for 2 hours to remove residual carbon contamination. For EBID of carbon seeds, naphthalene precursor (C₁₀H₈, Sigma Aldrich, 99%) was heated to 30 °C inside the Gas Injection System (GIS) installed on the SEM to deliver vapor through a needle positioned 200 μm above the surface. The samples were then transferred to a Reactive Ion Etching (RIE) system for amination of EBID carbon. Following evacuation to base pressure of 1.5×10⁻⁶ Torr, a pure ammonia (NH₃) plasma was generated at a pressure of 0.05 Torr using a Radio Frequency power supply operating at 13.85 MHz. Samples were exposed to the NH₃ plasma for 45s.

To achieve nanodiamond self-assembly, the EBID-patterned silicon substrates were immersed in an aqueous mixture of varying concentrations of 35 nm nanodiamonds (35-nm brFND

supplied by Academia Sinica, containing on average ~ 15 NV/particle) and EDC with the constant ratio of ND:EDC (1:10). The samples were kept in the solution for 6 hours to complete the self-assembly process, then washed with water and nitrogen-dried after removal from solution. Figure S1 shows assembly of NDs on a Si_3N_4 substrate. The self-assembly procedure results in the attachment of 1-5 nanodiamonds on each seed in the array, as shown in the insets of Figs. 1 and S1.

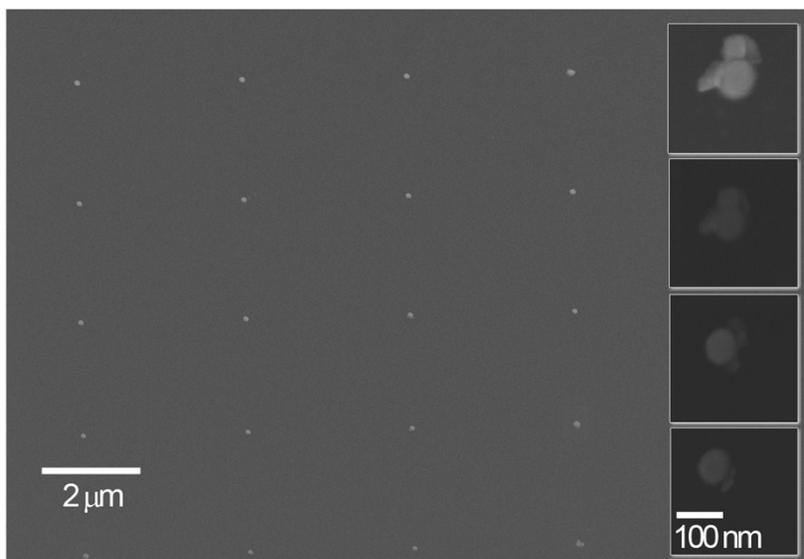
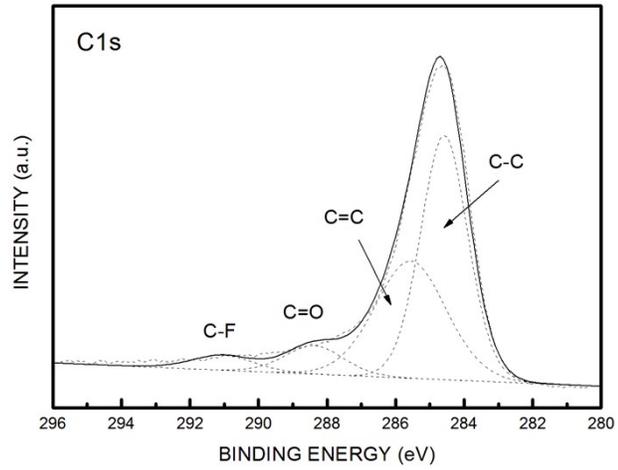


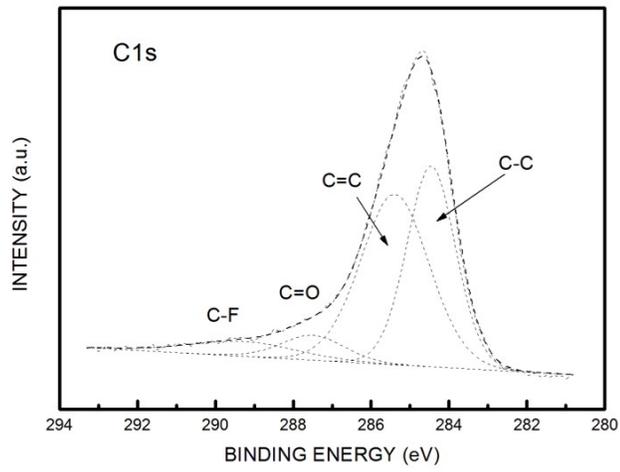
Figure S1. Self-assembly of NDs on a Si_3N_4 substrate. The insets are magnified images (fixed magnification) of a few carbon seeds on the pattern showing the successful attachment of NDs.

S2 X-ray photoelectron spectroscopy (XPS):

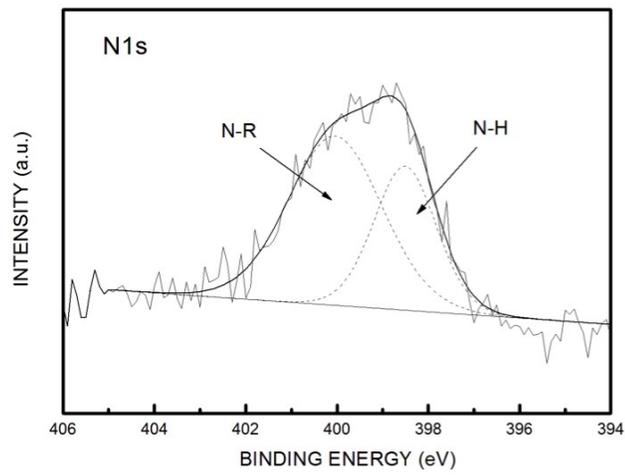
XPS was used to establish the effectiveness of the plasma process for amination of the carbon surface. The chemical bonding of the surfaces were assessed by using a Specs 150 SAGE instrument operated with a Mg $K\alpha$ X-ray source (Mg anode operated at 10 keV and 10 mA). The C1s peak at 284.6 eV was used as a reference to compensate for any surface charging.



(a)



(b)



(c)

Figure S2. Surface modification of sputtered carbon with plasma treatment (a) C 1s XPS spectrum of deposited carbon, (b) C 1s XPS spectrum of deposited carbon after plasma treatment, (c) N 1s XPS spectrum of deposited carbon after ammonia plasma treatment.

An oxidized silicon substrate was sputtered with carbon and the sample was exposed to NH_3 plasma for 30 seconds. XPS measurement was performed on both the clean SiO_2/Si and carbon-coated surface. Fig S2 shows the deconvolution of the XPS C1s peaks obtained from the surface modification of sputtered carbon without (Fig S2a) and with (Fig S2b) ammonia plasma treatment, along with the XPS N 1s peak (Fig S2c), which was observed only for the sputtered carbon after ammonia plasma treatment. The C1s spectrum of both samples show four peaks with bonding energies of 284.6 eV, 285.2 eV, 287.9 eV and 290.1 eV, which were assigned to C–C, C=C, C=O and C–F, respectively. For both samples a single F1s peak was also observed at 686 eV (data not shown), which is consistent with the C–F bond and likely results from prior processing under fluorine gas in the same chamber). The N 1s spectrum after ammonia plasma treatment clearly shows the presence of amino groups at the surface of the plasma treated carbon. The XPS data demonstrates that this procedure is highly selective, resulting in amine functionalization only of the sputtered carbon, while the surrounding SiO_2/Si surface remains oxygen-terminated. In addition, XPS reveals that the ammonia plasma treated carbon contains both amine and amide groups, both of which are suitable for coupling to carboxyl groups on the nanodiamond surface using carbodiimide conjugation.

S3 Optically Detected Magnetic Resonance (ODMR):

ODMR measurements were conducted on the patterned nanodiamonds using a microwave (MW) generator coupled to a 20mW amplifier. A 30 μm copper wire placed close to the pattern served as the MW antenna. The ground state in the nitrogen vacancy defect consists of a singlet $m_s = 0$ state separated by 2.87 MHz from the doublet $m_s = \pm 1$ state (Figure S3-a). In principle, an external magnetic field can be detected through the induced energy shift in the Zeeman sublevels¹. A 50 μW continuous green laser (523nm) focused using a 0.9 NA objective lens has been used to excite NV centers in nanodiamond. Photoluminescence (PL) was collected with and

without microwave excitation at wavelength ranges from 2.78 to 2.95 GHz. The ODMR signal was obtained by subtracting the MW-off from the MW-on data, and fitted using Lorentzian curves (Figure S3-b). Under continuous MW excitation, substantial ODMR peak broadening is observed with increasing MW power (Figure S3-c).

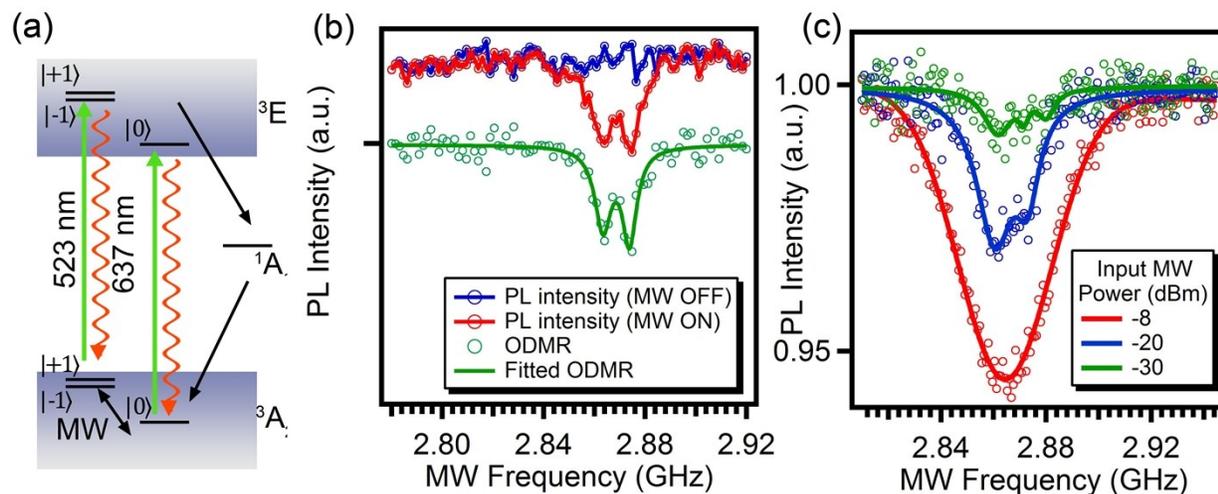


Figure S3. ODMR measurement of nanodiamond array. (a) Band structure of NV defect in diamond. (b) ODMR data fitted with Lorentzian curves. (c) Peak broadening of ODMR as a function of input microwave power from -8 to -30 dBm.

References:

1. Rondin, L. et al. Magnetometry with nitrogen-vacancy defects in diamond. *Rep Prog Phys* **77**, 056503 (2014).