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Electronic Supplementary Materia

Microscopic imaging and tuning of electrogenerated chemiluminescence with boron-doped diamond nanoelectrode arrays

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Microfabrication of the markers on the MNEAP

The markers generated on BDD in order to easily locate the arrays with the microscope were obtained as follows. A PMMA 671.05 layer was spin-coated at 5000 rpm for 1 minute on a BDD substrate and subsequently annealed at 170 °C for 15 minutes. In Table S1 are listed relevant experimental conditions.

Table S1 Experimental parameters used for the markers exposure

Dose	400 μC/cm^2
Aperture	300 μm (mag 220)
Bake	170 °C for 15 minutes
Current	310 pA
Developer	MIBK:IPA=3:1
Temperature	RT

After development, samples were evaporated with 30 nm of chromium, followed by lift off in hot $(CH_3)_2CO$ in order to obtain BDD substrate with metallic markers.

Fig.S1a reports the identification key of the NEAs in the platform and Fig. S1b shows the scheme of the whole sample area fabricated for ECL experiment, including the markers.

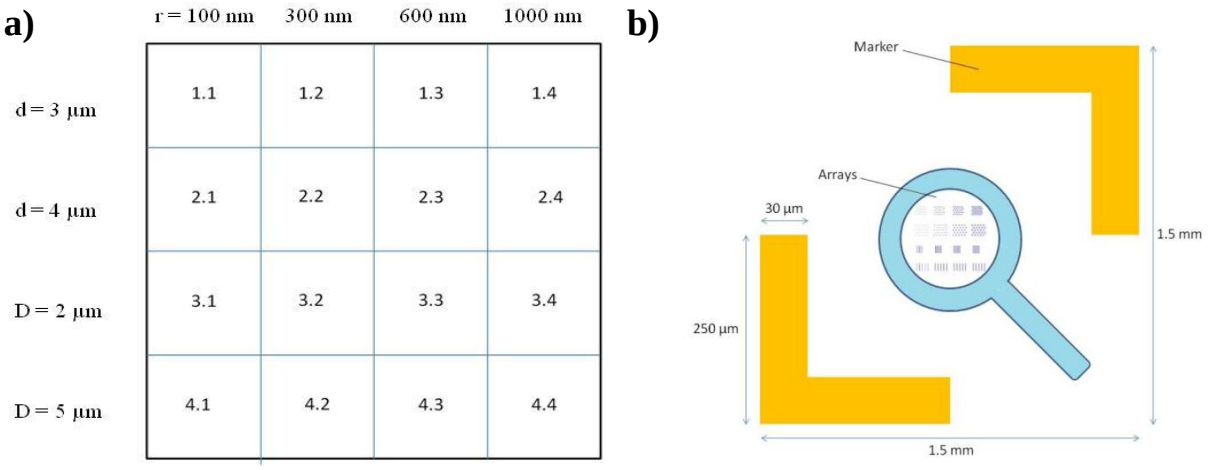

Fig. S1 a) Identification key of the NEAs in the platform; b) Scheme of the whole sample area

After treatment with O_2 plasma for 15 seconds and deposition of a layer of PC by spin coating, the structures were exposed by EBL following the scheme shown in Fig. S2, using the parameters reported in Table S2.

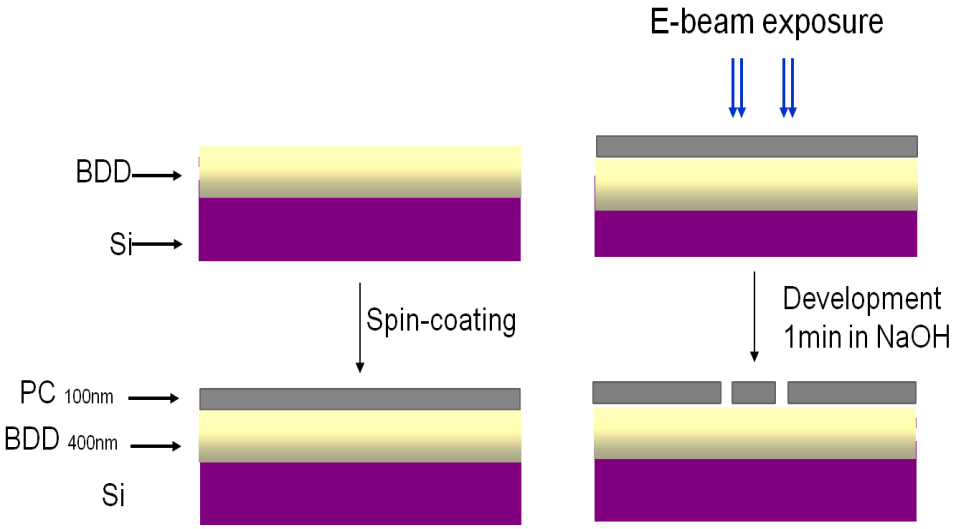

Fig. S2 Schematic representation of the e-beam writing steps of BDD nanodisk arrays

Table S2 Conditions used for the microfabrication of the MNEAP

Resist	PC 3% in Cyclopentanone
Spin Speed	2000 rpm
Annealing	180 ºC for 30 minutes
Dose	8000 µC/cm^2
Development	1 min in 5M NaOH at 35 ºC

Optical microscopy characterization of the MNEAP

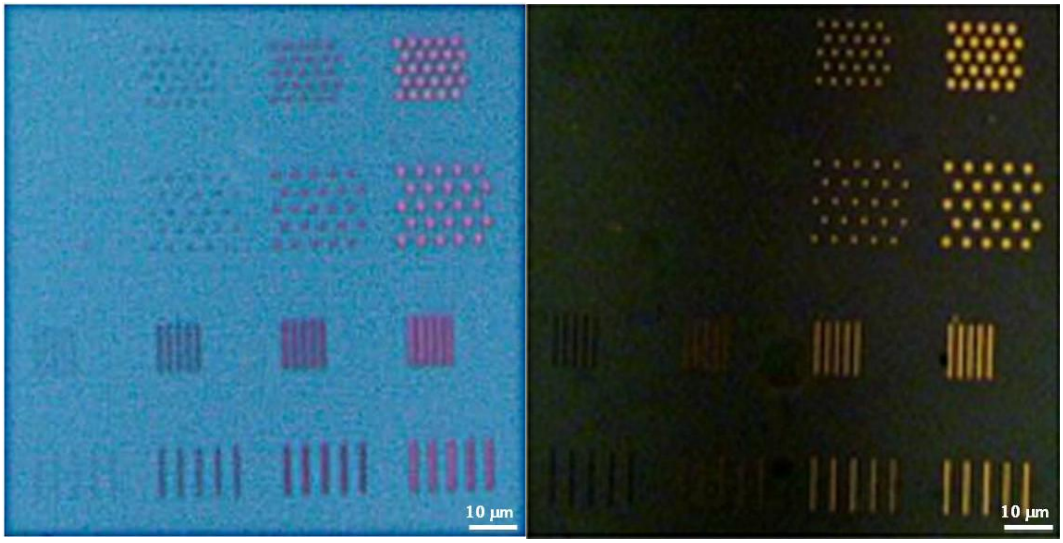

Fig. S3 Optical microscope images of the MNEAP in bright field (left) and in dark field (right)

Calculation of the thickness of the ECL reaction layer

Table S3 Thickness μ of the ECL reaction layer calculated for different TPrA concentrations and different disk radii using Eq. 6

	Thickness of the ECL reaction layer (µm)			
[TPrA] (M)	**r = 100 nm**	**r = 300 nm**	**r = 600 nm**	**r = 1000 nm**
0.001	0.098	0.28	0.53	0.81
0.003	0.096	0.27	0.48	0.71
0.005	0.095	0.26	0.46	0.66
0.01	0.093	0.25	0.42	0.58
0.03	0.089	0.22	0.34	0.44
0.085	0.082	0.18	0.26	0.32