Supplementary Materials for

Surface transfer doping can mediate both colloidal stability and self-assembly of nanodiamonds

Materials and Methods

Materials

Detonation nanodiamonds (NDs) were provided by the Nanocarbon Research Institute. Hydrochloric acid, sulfuric acid and sodium hydroxide (Sigma-Aldrich) were used as received.

Plasma hydrogenation of nanodiamonds

80-100 mg of NDs were deposited in a quartz tube and inserted in a plasma Downstream source (Sairem). High purity research grade N9.0 hydrogen gas was injected in the tube at a pressure of 15 mbar and plasma was generated in the quartz tube with a microwave power of 300 W (2.45 GHz). During the plasma, the tube was air cooled and a smooth rotation is applied in order to mix the particles in the plasma. NDs were exposed to hydrogen plasma for 15 minutes and were cooled down under hydrogen, leading to H-NDs.

Oxidation of nanodiamonds

NDs-COOH were prepared by annealing under air as described elsewhere (*1*). Annealing treatments in air were performed at atmospheric pressure in a tubular furnace for 4 h at 673 K. The temperature was controlled using a thermocouple in the tube and the crucible was introduced into the tube when the targeted temperature was reached.

Preparation of nanodiamonds dispersions

NDs-H were dispersed in ultrapure water by sonication (Hielscher UP400S, 300W, 24 kHz) for 2h under cooling. Larger aggregates were removed from the solution by 1h centrifugation at 4000 rpm. An example of resulting dispersion is plotted on Figure S2.

Preparation of nanodiamonds self-assembled structures

Self-assembled structures of NDs-H were obtained after addition of acid into water-based dispersion of NDs-H using a Malvern autotitrator module (MPT-2). Initial NDs-H concentration of 0,5 to 1 mg/ml for a volume of 6 ml were used. Self-assembly occurs during addition of HCl (0.1 M) or H_2SO_4 (0.05 M) under mild magnetic steering at room temperature. The acid volume needed to increase the acid concentration in the solution by steps of 2 mM (1 mM for H_2SO_4) was automatically added by the autotitrator module.

In order to observe the self-assembled structures formed in solution by Scanning Electron Microscopy, a drop from the suspension after acid addition was deposited on a silicon substrate and dried at room temperature. Largest structures could be observed directly by eye in solution.

Nitrogen adsorption

Nitrogen adsorption measurements were performed on 30 mg of NDs at 77 K with a gas adsorption system ASAP 2000 (Micromeritics). Before measurement, samples were outgassed under secondary vacuum at 573 K for 12 h.

Water adsorption

Water adsorption isotherms were performed at 298 K by thermogravimetry using a SETARAM microbalance. The samples (30 mg of NDs) were out-gassed under secondary vacuum at 573 K for 6 h and cooled down to 298 K prior to the sorption measurements. The water pressure was then increased step by step in order to obtain the entire adsorption isotherm. For each uptake, the equilibrium was reached and the mass recorded versus time.

X-ray Photoelectron spectroscopy

A drop of NDs dispersed in water was deposited on a silicon substrate for XPS measurements. Annealing treatment at 400°C during 1h was performed in a ultra-high vacuum (UHV) system connected to the XPS setup. The temperature was measured using a thermocouple and the pressure maintained below 5×10^{-9} mbar. Samples could be transferred to the XPS setup *in vacuo* avoiding air exposure. A monochromatized Al Kα anode (1486.6 eV) was used calibrated versus the Au 4f7/2 peak located at 84.0 eV. The spectrometer was equipped with an EA 125 hemispherical analyzer. The path energy was 20 eV, corresponding to an absolute energy resolution of 0.6 eV. The detection limit of our XPS setup is of 0.5 at. %. Areas of XPS core levels were extracted after a Shirley correction of the background and atomic contents are calculated after correction by the photoionisation cross-sections. A curve fitting procedure was performed to extract the components in the C1s spectra using Voigt functions with a Lorentzian width of 0.4 eV.

Zeta Potential/Titration

Size and Zeta potential (ZP) measurements of NDs-H suspensions were performed in ultrapure water on a Nanosizer ZS (Malvern) in the back scattering configuration (173°). pH-titration of the ZP was monitored using a Malvern autotitrator module (MPT-2) with HCl 0.1 M and NaOH 0.1 M as acidic and basic titrants. Acid titrations where also performed using the same autotitrator module with HCl 0.1 M and H_2SO_4 0.05 M under mild magnetic steering. For each pH value or acid concentration, three independent ZP and size measurements were made after recirculating the solution.

Scanning Electron Microscopy

The self-assembled structures were observed by Field Emission Scanning Electron Microscopy (FE-SEM) carried out with a ZEISS SUPRA 40 microscope. By using an in lens detector, a high lateral resolution close to 3nm was achieved. Pictures were recorded at acceleration voltages of the incident primary electron beam of 2 to 20 kV.

Supplementary Text

Specific surface area

The specific surface areas of ND-H and NDs-COOH are determined from nitrogen adsorption isotherms (Figure S1). The BET method was used in the linear region $0.05 < P/P_0 < 0.3$ (*2*). Specific surface area of NDs-H and NDs-COOH are estimated to 351 m^2/g and 307 m^2/g, respectively.

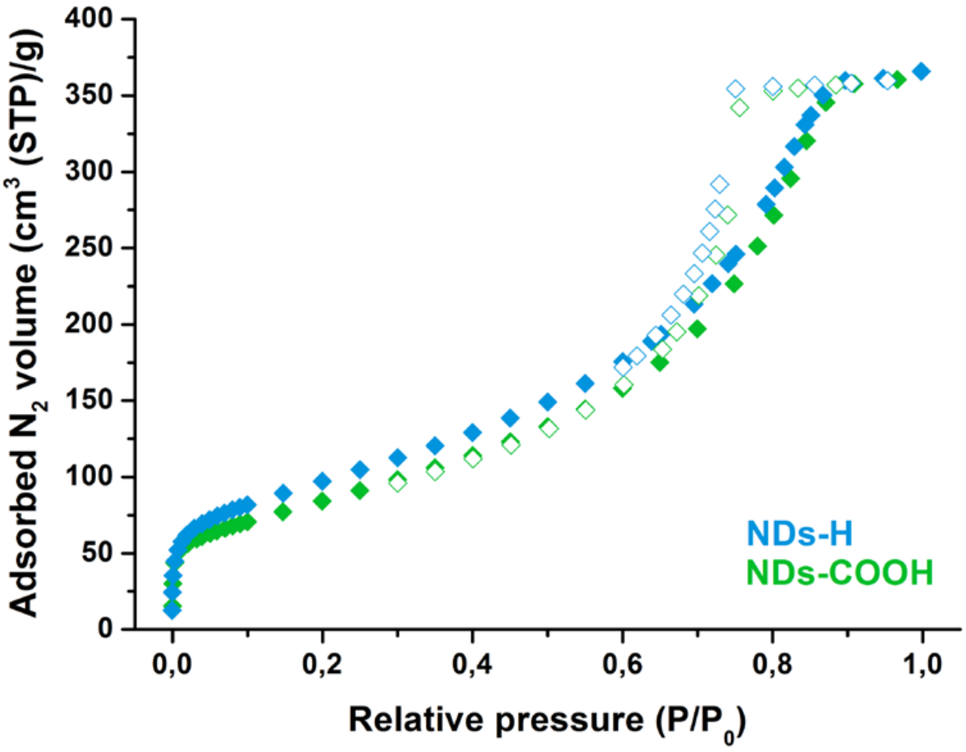

Figure S1 : Nitrogen adsorption-desorption isotherms of hydrogenated (blue) and oxidized (green) nanodiamonds.

Hydrophilic site density calculation

Hydrophilic sites density was estimated by the number of water molecules adsorbed in the linear region for $0.05 < P/P_0 < 0.35$, corresponding to a monolayer coverage. Correction by the specific surface area calculated from nitrogen adsorption isotherms indicates the surface density. Hydrophilic site densities of 1.4 and 1.7 sites/nm^2 are obtained for NDs-COOH and

NDs-H, respectively. For comparison, densities ranging from 0.7 to 5.3 hydrophilic sites/nm^2 have been reported for mesoporous silica surfaces with tunable hydrophobicity under the same experimental conditions *(16).*

Figure S2 : Water-based dispersion of NDs-H at 2 mg/ml.

DLS measurements

After hydrogenation and dispersion in ultrapure water, size distribution measurements by DLS show a narrow peak centered on 30 nm. Compared to NDs-COOH measured at 10 nm, a slight aggregation occurs after hydrogenation treatment which remains very limited.

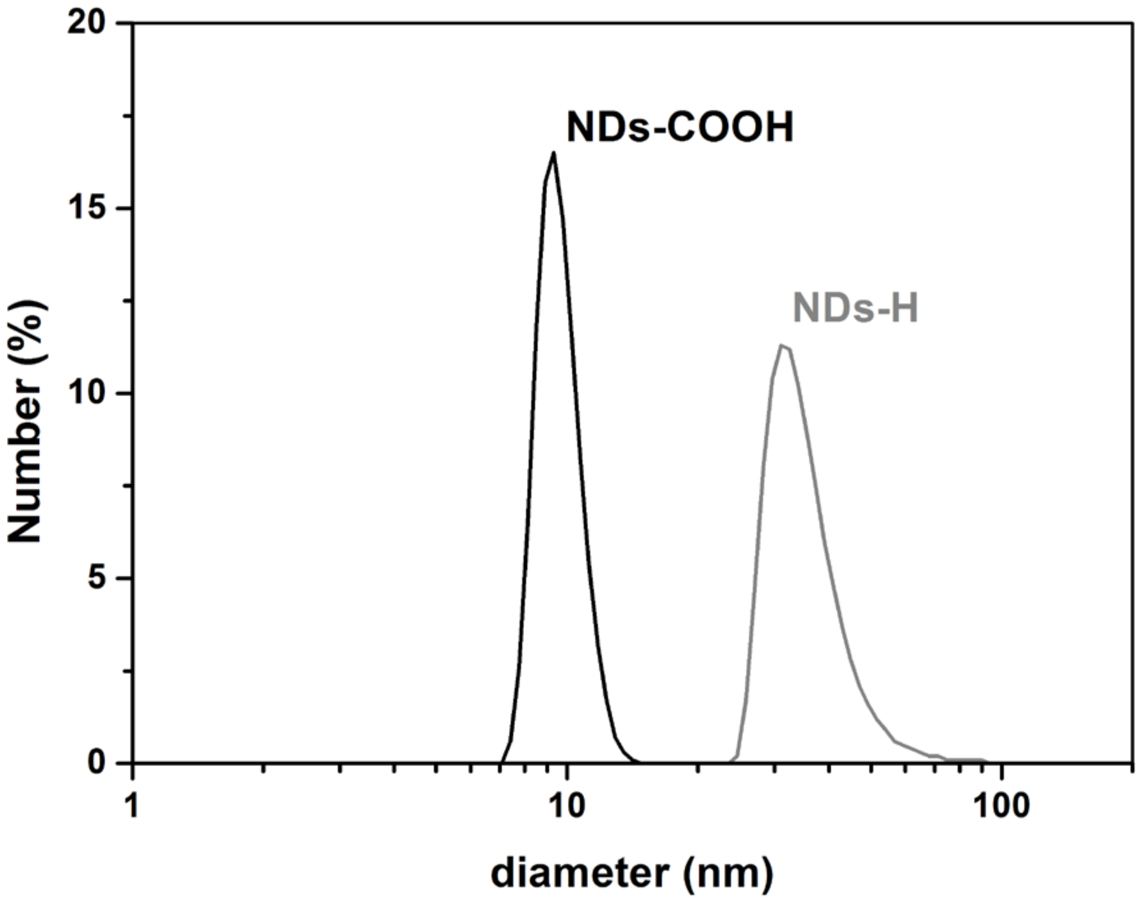

Figure S3: DLS size distribution of NDs-H and NDs-COOH dispersed in ultrapure water at 25°C

Self-assembly using sulfuric acid

Hydrochloric acid was replaced by sulfuric acid (H_2SO_4) to observe the role of counter-ion valence on the shape of the self-assembled structure. In the case of H_2SO_4 addition in the NDS-H dispersion, the following redox reaction occurs:

$$4(e^{-}h^{+})_{NDs-H} + O_{2,air} + 2H_2SO_4 \rightleftharpoons 4h^{+}_{NDs-H} + 2SO^{2-}_{4,aq} + 2\,H_2O$$

Similarly to the case of HCl addition, self-assembled structures were observed by SEM but having different shapes (Figure S3). Self-assembled structures were obtained at lower acid concentration than after HCl addition since one H_2SO_4 molecule leads to two holes at the NDs-H surface instead of one in the previous case. At low concentration, diamond shapes are observed (Figure S3 A), which are then assembled into rod-like structures of length up to millimeter scale (Figure S3 B-E).

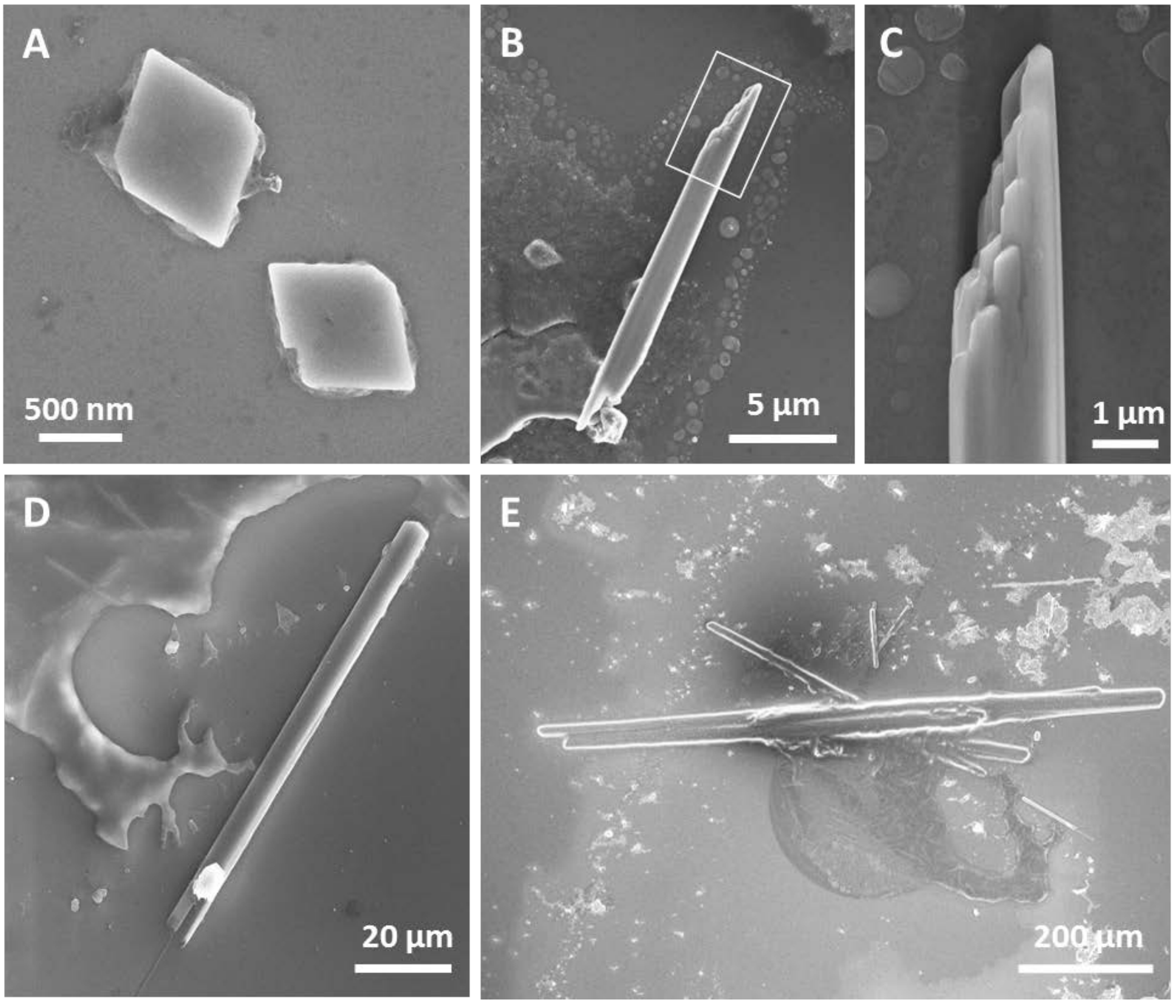

Figure S4 : Self-assembled structures from NDs-H/SO_4^{2-} complexes. (A-D) SEM images of various structures obtained after addition of H_2SO_4 at a concentration of 0.05 M in water-based dispersion of NDs-H. (C) Magnified view of the squared region in (B), showing that the self-assembled structure is composed of several rod-like assemblies.

References

32. Osswald, S.; Yushin, G.; Mochalin, V.; Kucheyev, S. O.; Gogotsi, Y. *J. Am. Chem. Soc.* **2006**, *128*, 11635.

33. Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938,** *60*, 309.