Supporting Information for:
Block Copolymer-Nanodiamond Coassembly in Solution: Towards Multifunctional Hybrid Materials

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1 Characterizations

1.1 Spectroscopy and X-ray diffraction

Fourier-transform infrared (FTIR) spectra of pristine and oxidized NDs were acquired using a Bruker VERTEX 80v FTIR spectrometer. The ND powders were vacuum dried at 60 °C before the measurements to remove moisture and then ground mixed with potassium bromide (KBr) on an agate mortar before pelleting using a hand press kit. Each measurement was performed in vacuum with 64 scans and 4 cm⁻¹ resolution. The obtained absorbance spectra was baseline corrected and smoothed using OPUS 7.5 software, and then normalized with respect to the maximum intensity using sklearn.preprocessing package in Python.

For Raman spectroscopy, samples were prepared by casting 30–60 µL ND dispersion onto a cleaned Si wafer. The samples were air dried at an ambient temperature overnight, followed by overnight vacuum annealing in an oven at 100 °C. The measurements were carried out on a Tokyo Instruments Nanofinder 30 system using a 5 mW laser (532 nm wavelength), which was 100× magnified and focused onto a sub-micrometric spot size on the sample using an objective lens with a numerical aperture of 0.95. An Andor DU920P BR-DD couple charge device operated at −60 °C was used to capture the emitted light from the sample in a 180° scattering geometry with a grating of 1200 grooves per mm and a 50 µm pinhole. Recorded data were baseline corrected, smoothed, and normalized in Python. The baselines were obtained using asymmetric least square smoothing with an asymmetric factor $1 \times 10^{-4}$, threshold 0.03, smoothing factor 4, and 10 iterations. The baseline-subtracted spectra were then smoothed by employing the Savitzky–Golay method (20 points of window, polynomial order 2).

UV-Vis spectra of the nanocomposite films were probed using a Shimadzu UV-2600 spectrophotometer equipped with a deuterium light source, Czerny–Turner monochromator, and photomultiplier R-928 detector. The measurements were performed in transmittance mode using 1.0 nm slit width, 1.0 nm resolution, 0.1 s accumulation time, and ambient air as the reference. The films used for UV-Vis spectroscopy measurements were prepared using UV-grade fused silica glasses as substrates.

The X-ray diffraction (XRD) analysis was carried out by means of a Bruker D8 Discover diffractometer, equipped with a copper line focus tube and a Göbel mirror that together produce a beam of Cu Kα radiation of 0.15418 nm average wavelength. On the primary beam side, a 1.2 mm divergence slit was used. Along the secondary beam path, a fully open detector slit preceded a 0.2° Soller slit in front of a scintillation counter detector. To enhance the contribution from the surface, the measurements were performed in grazing incident (GI) configuration in the form of 2θ scans, with the primary beam impinging on the sample surface at an angle of 0.5°, slightly above the critical angle for total reflection from a diamond film. The acquisition range was set around the expected position of the diamond (111) Bragg peak, which is the most intense reflection according to structural factors for bulk diamond.
1.2 Film thickness and water contact angles

The film thicknesses were measured based on spectral interferometry using a Hamamatsu Optical NanoGauge Thickness measurement system C13027 equipped with a halogen light source. The measurements were performed for wavelengths in the range between 400 to 1100 nm using the FFT analysis method utilizing polystyrene refractive index (RI) for the BCP-ND film, SiO$_2$ glass RI for fused silica, and RI 1.526 for Lotus glass substrate.

Water contact angles (WCAs) of the films were analyzed on a KRÜSS DSA100 drop shape analyzer using the sessile drop method with 2 $\mu$L dosing volume and 2$^\circ$ camera inclination angle. The acquired WCAs are the average of at least three different spots on each sample.

1.3 Dynamic light scattering (DLS)

The particle size distributions of the BCP-ND nanocomposite micelles were measured using CUMULANT method on a 3D LS Spectrometer from LS Instruments equipped with a He–Ne laser (632.8 nm wavelength) and two avalanche photodiode (APD)-based photon detectors. Around 1–1.5 mL of the sample was first filtered through a PTFE syringe filter (pore size 5 $\mu$m) and then loaded into a cylindrical glass cuvette, which was previously cleaned thoroughly with acetone and blown dried with nitrogen. Before inserting into the spectrometer, the cuvette surface was further cleaned with acetone or isopropanol using a low-lint-release wipe to avoid dust contamination. The measurements were performed in 2D scattering geometry with a pseudo-cross correlation, an automated intensity attenuator, a controlled temperature of 25 $^\circ$C, varying scattering angles of 30–120$^\circ$ in 15$^\circ$ step, and averaging time of 60–120 s for each measurement.

In DLS measurements, the particle Brownian motion causes fluctuating scattered intensity, which is measured as the normalized intensity correlation function in the spectrometer. Using Siegert relationship, the normalized electric field correlation function can be obtained and analyzed using the CUMULANT analysis. The CUMULANT method fits a polynomial of third degree to the logarithm of the field correlation function, yielding the particle decay rate $\Gamma$ and diffusion coefficient $D$ defined through

$$\Gamma = q^2 D,$$

where $q$ is the scattering vector determined in terms of the sample refractive index $n_0$, laser wavelength $\lambda$, and scattering angle $\theta$ by

$$q = \frac{4\pi n_0}{\lambda} \sin \frac{\theta}{2}.$$

Furthermore, the second order cumulant was used to yield the particle average hydrodynamic radius $\bar{R}$ and its distribution width. The computation of $\bar{R}$ was conducted using the Stokes–Einstein relation

$$\bar{R} = \frac{kT}{6\pi \eta D},$$

where $k$ is the Boltzman constant, $\eta$ the sample viscosity, and $T > 0$ is absolute temperature. The probability density function of $\bar{R}$ obtained from the DLS measurement at 60$^\circ$ scattering angle was plotted according to the Gaussian distribution using the distribution width obtained from the second order cumulant.

The particle zeta potentials were determined using an electrophoretic light scattering technique on an ELSZ-2000 Zeta-Potential & Particle Size Analyzer (Otsuka Electronics Co., Ltd.) equipped with a semiconductor laser source and an APD detector. The measurements were performed using a flow cell at 25 $^\circ$C based on Laser Doppler method.

1.4 Microscopy

Transmission electron microscopy (TEM) images were probed using a JEOL JEM-1230R at an operating voltage of 100 kV. A small drop of the BCP-ND dispersion (5 $\mu$L) was placed on a carbon-coated copper grid. Upon dropping the dispersion, the solvent was immediately blotted by a filter paper underlying the grid and the sample was further dried in air under a fumehood. The sample was then stained using OsO$_4$ vapor before imaging to selectively stain the polyisoprene block. The atomic resolution TEM images of oxidized NDs were acquired using a JEOL JEM-ARM 200F in a Scanning TEM (STEM) mode at 200 kV operating voltage. Prior to measurements, the oxidized ND powders were vacuum dried in an oven overnight at 60 $^\circ$C to remove contamination. A small amount of oxidized-ND powder was deposited on a carbon-coated copper grid by gently touching the grid onto the powder, followed by a gentle shaking to remove the excess.
Scanning electron microscopy (SEM) was performed on an FEI Quanta 250 FEG or a JEOL JSM-7900F microscope operating at 5–10 kV and 4–5 mm working distance. The samples were sputter coated with Pt-Pd and mounted on an aluminium stub before imaging to avoid charging. For cross-sectional analysis, the BCP-ND films were carefully fractured in liquid nitrogen using tweezers, followed by air drying, sample mounting on a copper stub, and Pt-Pd coating before imaging.

Atomic Force Microscopy (AFM) was performed using an Agilent 5500 scanning probe microscope (SPM). The samples were scanned in the tapping mode using a MikroMasch SPM probe (HQ:NSC18) with a silicon cantilever, 75 kHz resonance frequency, and 2.8 N/m force constant. The acquired images were post-processed and analyzed in Gwyddion data analysis software to obtain the mean square roughness $S_q$, the mean roughness $S_a$, and the maximum height value.

## 2 Raman and XRD spectra

![Raman spectra and XRD scans](image)

**Fig. S1:** a) Raman spectra of pristine ND and oxidized NDs with oxidation temperature of 450 and 525 °C plotted without baseline correction and normalization. The dashed line is used as a guide to emphasize the diamond peak shifts with respect to the single crystal diamond (111), attesting the decreasing degree of tensile strain as the oxidation temperature increases. b) GI-XRD $2\theta$ scans around the diamond (111) Bragg peak of ND samples obtained by drop casting on a silicon substrate suspensions of (black curve) pristine NDs dried in vacuum at 100 °C, (blue curve) NDs annealed at 450 °C and (orange curve) NDs annealed at 525 °C. Peak broadening is caused by crystallites’ finite size and/or micro-strain. The decrease of the peak's FWHM upon oxidation at 525 °C is likely due to a reduction of the micro-strain and suggests an enhanced homogeneity of the materials system.

## 3 Properties of ND dispersions

**Table S1:** Properties of ND and ISV1-ND dispersions in DMAc: ND concentration before ($C_o$) and after ($C_f$) centrifugation, average hydrodynamic radii of NDs in DMAc after centrifugation ($\bar{R}_{ND}$) along with its full width at half maximum (FWHM$_{ND}$), and ND weight fraction ($\phi_{ND}$) in the corresponding ISV1-ND dispersion at 10 gL$^{-1}$ ISV1 concentration.

| $C_o$, gL$^{-1}$ | $C_f$, gL$^{-1}$ | $\bar{R}_{ND}$, nm | FWHM$_{ND}$, nm | $\phi_{ND}$, wt% |
|-----------------|-----------------|-------------------|-----------------|-----------------|
| 5               | 3               | 14.10 ± 0.09      | 5.65 ± 0.05     | 22              |
| 10              | 5               | 15.04 ± 0.05      | 6.12 ± 0.05     | 34              |
| 15              | 8               | 16.95 ± 0.33      | 6.83 ± 0.17     | 44              |
| 20              | 10              | 18.04 ± 0.11      | 7.41 ± 0.18     | 50              |
| 30              | 13              | 19.68 ± 0.03      | 9.84 ± 0.02     | 55              |
| 40              | 17              | 35.06 ± 0.35      | 18.25 ± 0.16    | 63              |
4 Solvent and polymer Hansen solubility and Flory-Huggins interaction parameters

Table S2: Hansen solubility parameters ($\delta_D$, $\delta_P$, and $\delta_H$) of the solvents and the polymers along with the Flory-Huggins interaction parameters between the polymer block and the solvent ($\chi_{i,s}$) computed from equation 4.

| Component | $\delta_D$, MPa$^{1/2}$ | $\delta_P$, MPa$^{1/2}$ | $\delta_H$, MPa$^{1/2}$ | $\chi_{i,DMAC}$ | $\chi_{i,acetone}$ | $\chi_{i,ethanol}$ |
|-----------|-----------------|-----------------|-----------------|----------------|----------------|----------------|
| DMAc      | 16.8            | 11.5            | 10.2            |                |                |                |
| Acetone   | 15.5            | 10.4            | 7               |                |                |                |
| Ethanol   | 15.8            | 8.8             | 19.4            |                |                |                |
| PI        | 16.6            | 1.41            | -0.8            | 2.1            | 1.1            | 2.7            |
| PS        | 18.5            | 4.5             | 2.9             | 1.1            | 0.7            | 1.9            |
| P2VP      | 19.1            | 9.6             | 9.2             | 0.2            | 0.4            | 0.9            |

The Flory-Huggins interaction parameters ($\chi_{i,s}$) between polymer (i) and solvent (s) listed in Table S2 were calculated by equation 4.

$$\chi_{i,s} = \frac{V_m A_{i,s}}{RT},$$ (4)

where $V_m$ is the molar volume of the solvent, $A_{i,s}$ is the Hansen solubility parameter (HSP) distance computed from the dispersion ($\delta_D$), polar ($\delta_P$), and hydrogen bonding ($\delta_H$) terms of the HSP as in equation 5. $R$ is the gas constant (8.3145 Jmol$^{-1}$K$^{-1}$), and $T$ is temperature (K).

$$A_{i,s} = (\delta_{D,i} - \delta_{D,s})^2 + 0.25(\delta_{P,i} - \delta_{P,s})^2 + 0.25(\delta_{H,i} - \delta_{H,s})^2$$ (5)
Fig. S2: Angular dependency of the DLS data of various ISV1-ND patchy hybrid micelles in DMAc represented by the reduced decay rate ($\Gamma/q^2$) or diffusion coefficient $D$ versus squared scattering vector $q^2$. The weak $q$-dependency of the curves can be interpreted as the presence of nearly spherical shape of the ISV1-ND micelles. The curved profile of pristine ISV1 (0 wt%) indicates the presence of particle anisotropy. This could be because in the absence of NDs the solvated P2VP corona are more stretched and the repulsion between the P2VP chains contribute to the detection of particle anisotropy in the DLS measurements.
Fig. S3: TEM images of the superstructures formed by a) ISV1-ND at $\phi_{ND} = 22$ wt%, b) ISV1-ND at $\phi_{ND} = 50$ wt%, c) ISV2-ND at $\phi_{ND} = 22$ wt%, and d) ISV3-ND at $\phi_{ND} = 22$ wt% after dialysis against acetone. The BCP self-assembly guide the NDs to form interconnected strings stabilized by P2VP along PS matrix (gray phase) with embedded PI domain (dark phase). For each line, the most-left and center images are in-focus images in which NDs appear as dark spots, while the most right column is an overfocus image where NDs appear as bright spots (partially highlighted by dashed red lines) to provide a better contrast with the dark PI phase.
Fig. S4: Scattering vector ($q$) dependency of the diffusion coefficient $D$ ($\Gamma/q^2$) of various ISV-ND aggregates in acetone obtained after passing through a 5-µm pore size syringe filter. A small deviation observed at low $q^2$ is presumably due to the aggregate polydispersity and anisotropy.
Fig. S5: TEM images of a) ISV1 and b) ISV1-ND at φ_{ND} = 22 wt% after dialysis against ethanol (EtOH) along with their c) particle size distribution and d) diffusion coefficient D versus squared scattering vector q^2. The angular dependency (d) of ISV1 in EtOH at low q^2 is probably affected by the formation of merged micelles as shown in the TEM image (a) and the highly solvated P2VP chains which may contribute to the particle anisotropy. Meanwhile, the ISV1-ND in EtOH show bigger aggregates with a broader size distribution.
References

[1] C. M. Hansen, *Hansen Solubility Parameters: A User's Handbook*, CRC press, Boca Raton, 2007, pp. 345–505.