## Supplementary Information to the paper:

Colloidal Properties and Behaviors of 3nm Primary Particles of Detonation Nanodiamond in Aqueous Media

N. O. Mchedlov-Petrossyan, N. N. Kamneva, A. I. Marynin, A. P.Kryshtal and E. Ōsawa

## Contents

- 1. Conductivities and pH values of ND hydrosols of different concentrations.
- 2. The IR spectra of the solid samples obtained from the ND hydrosols.
- 3. The EDX spectrum of the dried sample.
- 4. The absorption spectra of dyes in the presence of ND nanoparticles.
- 5. The table of absorption maxima shifts of the dye double-charged anions.
- 6. Coagulation by electrolytes: dependences of absorption at 525 nm vs. time and vs. concentration of NaCl.
- 7. Size distribution on coagulation by NaCl: DLS and SLS methods.
- 8. Coagulation by NaOH and HCl.
- 9. Photo: restoration by HCl of the ND hydrosol after coagulation by NaOH.
- 10. Coagulation by  $K_3Fe(CN)_6$ ,  $K_3Fe(CN)_6$ , NaBr, CTAB, SDS,  $C_{14}H_{29}OSO_3Na$ , and  $C_{16}H_{33}OSO_3Na$ : dependences of absorption at 525 nm vs. electrolyte concentrations.
- 11. Transmission electron microscopy images.

TABLE I. The resistance, specific conductance, and pH values of the ND hydrosol at different concentrations (wt./vol.%); 25  $^{\rm o}{\rm C}$ 

| No. | w, %  | R, kOhm | κ, S/cm                | $\kappa^* = \kappa - \kappa (H_2O), S/cm$ | <b>к*</b> /w           | pН   |
|-----|-------|---------|------------------------|---|------------------------|------|
| 1   | 0.020 | 6.67    | $8.069 \times 10^{-6}$ | $5.052 \times 10^{-6}$                    | $2.526 \times 10^{-4}$ | 6.17 |
| 2   | 0.099 | 2.57    | $2.094 \times 10^{-5}$ | $1.792 \times 10^{-5}$                    | $1.810 \times 10^{-4}$ | 6.12 |
| 3   | 0.19  | 2.32    | $2.320 \times 10^{-5}$ | $2.018 \times 10^{-5}$                    | $1.062 \times 10^{-4}$ | 4.76 |
| 4   | 0.50  | 1.21    | $4.448 \times 10^{-5}$ | $4.146 \times 10^{-5}$                    | $8.293 \times 10^{-5}$ | 4.78 |
| 5   | 0.70  | 0.92    | $5.850 \times 10^{-5}$ | $5.548 \times 10^{-5}$                    | $7.926 \times 10^{-5}$ | 4.77 |
| 6   | 1.00  | 0.75    | $7.176 \times 10^{-5}$ | $6.874 \times 10^{-5}$                    | $6.874 \times 10^{-5}$ | 4.65 |
| 7   | 2.50  |         |                        |   |                        | 4.78 |

 $\kappa$  (H<sub>2</sub>O)= 3.017 × 10<sup>-6</sup> S cm<sup>-1</sup>



Figure I. Conductance of the ND hydrosol: the dependence of  $\kappa^*/w$  on w for the successively diluted solutions.



Figure II. The size distributions of 1.0 % ND hydrosols obtained by dilution of sample 1 (empty circles, measured in the Aalto University, Espoo, Finland) and sample 2 (filled squares, measured in the National University of Food Technology, Kiev, Ukraine); both measurements have been made in six months after preparation of the sols.



Figure III. The IR spectra of solid ND on diamond plate obtained from the 0.603 % hydrosol: the sample was obtained by drying of the colloidal system [the upper curve] and by drying the deposit after coagulating by  $6.7 \times 10^{-4}$  M NaOH with further centrifugation [the lower curve].



Figure IV. The EDX spectrum after drying the 5.0 % ND solution (Si originates from the silicon wafer).



Figure V. The absorption spectra of bromophenol blue in water (1) and in ND 0.048 % solution, without subtracting the blank (2).



Figure VI. Absorption spectra of fluorescein dianion in water (1) and in ND 0.048 % solution (2), with subtracting the blank.



Figure VII. Absorption spectra of bromocresol green dianion in water (1) and in ND 0.048 % solution (2), with subtracting the blank.



Figure VIII. Absorption spectra of pseudoisocyanine cation in water (1) and in ND 0.048 % solution (2), with subtracting the blank.

TABLE II. The positions of the absorption bands of the dyes dianions,  $R^{2-}$ , in water and in 0.048 % ND hydrosol, 25 °C or room temperature

| Anionic dye         | $\lambda_{\max}^{W}/nm$ | $\lambda_{ m max}^{ m ND}/ m nm$ | $\Delta \lambda_{\max} = \lambda_{\max}^{ND} - \lambda_{\max}^{W}$ |
|---------------------|-------------------------|----------------------------------|--|
|                     |                         |                                  |  |
| Fluorescein         | 490                     | 504                              | 14   |
| 5'-Aminofluorescein | 489                     | 502                              | 13   |
| Sulfonefluorescein  | 496                     | 508                              | 12   |
| Bengal Rose B       | 547                     | 570                              | 23   |
| Bromophenol blue    | 591                     | 601                              | 10   |
| Bromocresol green   | 616                     | 622 <sup>a</sup>                 | 6  |
| Bromocresol purple  | 589                     | 599                              | 10   |

<sup>a</sup> In 0.089% ND



Figure IX. The absorption spectra of methyl orange anion in water (1) and in 0.018 (2) and 0.024 (3) wt./vol. % ND hydrosols, with subtracting the blank.



Figure X. The absorption spectra of the solvatochromic betain dye in water (1) and in 0.024 % ND hydrosols (2), with subtracting the blank.



Figure XI. The spectra of the indicator sulfonefluorescein at different pH in 0.024 % ND: the spectrum of  $R^{2-}$  at pH 10, NaOH (1), without any additives (2), with HCl additives, at pH = 4.10 (3), 3.78 (4), 3.59 (5), 3.39 (6); the spectrum at pH = 3.02, exhibiting the presence of the neutral dye form H<sub>2</sub>R with  $\lambda_{max}$  448 nm (7); the spectrum of the HR<sup>-</sup> form in ND-free acetate buffer solution at pH 5.0 (8).

In the case of sulfonefluorescein, the spectra of  $HR^-$  and  $R^{2-}$  are resolved much poorer as compared with those of sulfonephthaleins. In this case, the monoanionic spectrum was measured in aqueous ND-free solution at proper pH value, while the spectrum at pH 3.04 reflects the presence of an admixture of the H<sub>2</sub>R form (not shown in the scheme).



Figure XII. The time dependence of the absorbance at 525 nm of 1.0 % ND hydrosol at NaCl concentrations/mM of 2.0 (1); 2.5 (2); 3.0 (3); 3.2 (4); 3.5 (5).



Figure XIII. The time dependence of the absorbance at 525 nm of 5.0 % ND hydrosol at NaCl concentrations/mM of 2.0 (1); 3.0 (2); 3.2 (3); 3.5 (4).



Figure XIV. The determination of the critical coagulation concentration of 0.19 % ND by NaCl via spectrophotometric titration: the changes of absorbance at wavelength of 525 nm vs. the NaCl concentration in the optical cell, for the diluted hydrosols prepared from the first (3.81 %) and second (5.0 %) initial samples.



Figure XV. Particle size distribution in 0.036 % ND hydrosol (1) and in 0.024 % sol at NaCl concentration of 2 mM (2) and 3 mM (3); left: DLS, right: SLS.



Figure XVI. The time dependence of the absorbance (at 525 nm) of 0.19 % ND hydrosol at NaOH concentrations/mM of 0.20 (1); 0.30 (2); 0.40 (3); 0.45 (4).



Figure XVII. The determination of the critical coagulation concentration of 0.19 % ND by HCl via spectrophotometric titration at 525 nm.



Figure XVIII. The restoration with HCl addition of the hydrosol previously coagulated via NaOH: the ND hydrosol obtained by peptization of the coagulated sol with HCl (1) and the initial coagulated sol (2). The final NaCl concentration formed after neutralization of the alkali is below the CCC of NaCl.



Figure XIX. The determination of the critical coagulation concentration of 0.19 % ND by  $K_3Fe(CN)_6$  via spectrophotometric titration at 525 nm.



Figure XX. The determination of the critical coagulation concentration of 0.19 % ND by  $K_4$ Fe(CN)<sub>6</sub> via spectrophotometric titration at 525 nm.



Figure XXI. The determination of the critical coagulation concentration of 0.19 % ND by NaBr via spectrophotometric titration at 525 nm.



Figure XXII. The determination of the critical coagulation concentration of 0.19 % ND by CTAB via spectrophotometric titration at 525 nm.



Figure XXIII. The determination of the critical coagulation concentration of 0.19 % ND by SDS via spectrophotometric titration at 525 nm.



Figure XXIV. The determination of the critical coagulation concentration of 0.19 % ND by  $C_{14}H_{29}OSO_3Na$  via spectrophotometric titration at 525 nm.



Figure XXV. The determination of the critical coagulation concentration of 0.19 % ND by  $C_{16}H_{33}OSO_3Na$  via spectrophotometric titration at 525 nm.



Figure XXVI. The TEM image of the 0.036 % ND hydrosol after evaporation of water.



Figures XXVII–XXVIII. The TEM images of the 0.036 % ND hydrosol after evaporation of water.

## FURTHER DILUTION:



Figures XXIX–XXX. The TEM images of the 0.0036 % ND hydrosol after evaporation of water.



Figure XXXI. The TEM image of the 0.0036 % ND hydrosol after evaporation of water.