

# All-optical pH sensing with hybrid sp<sup>2</sup>-sp<sup>3</sup> carbon nanostructures

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## 1. Introduction

Nanodiamonds (NDs) with a hybrid sp<sup>2</sup>-sp<sup>3</sup> shell decorated with oxygen-containing functional groups has attracted much interest as promising materials with high sensing potential for applications in various fields of science and technology. Tunable surface chemistry determines photoluminescent (PL) properties of these nanoparticles which can be adjusted to be sensitive to changes of a desired external parameter. Nano-scale size, chemical stability inherited from the diamond, and biocompatibility allows to extend the use of hybrid sp<sup>2</sup>-sp<sup>3</sup> carbon nanostructures in the field of biomedicine and cell technologies, where accurate, remote, and non-destructive control of such environmental parameters as pH, temperature, and ionic strength, which are of great importance as small shifts in these parameters may lead to dramatic results and cell death.

## 2. Result and discussion

In the present study, all-optical method of pH control with high-purity and high-homogeneity water solutions of NDs (RayND-M, Ray Techniques Ltd), produced by laser synthesis followed by an undisclosed surface modification process is proposed. Based on UV-vis absorption, FTIR, steady-state, and time-resolved fluorescence spectroscopic analysis of NDs it was revealed that NDs exhibit excitation-dependent fluorescence originating from hydroxyl, carbonyl, and carboxyl groups. The latter ones are sensitive to pH changes through protonation-deprotonation which is reflected in the decrease of PL with excitation at  $\lambda_{\text{ex}} = 371$  nm and emission at  $\lambda_{\text{em}} = 456$  nm (see Fig.1a) and simultaneous increase of PL when excited with  $\lambda_{\text{ex}} = 470$  nm with emission centered at  $\lambda_{\text{em}} = 553$  nm (see Fig.1b). Both excitations/emissions were used to obtain calibration curves which allow determining the pH values of water solutions by PL measurements (see Fig.1b). Ratio of normalized PL intensities  $I_{553}$  and  $I_{456}$  (with excitation at 470 nm and 371 nm, respectively) is well approximated with linear function ( $R^2 = 0.97$ ) (see Fig.1c).

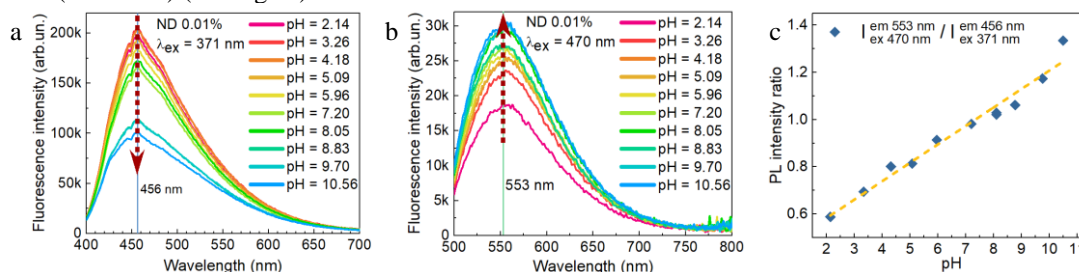


Fig. 1. pH screening with NDs with two-wavelength excitation and two-wavelength emission detection

Intensities ratio allows to avoid errors caused by the laser power fluctuations, ND-concentration dependence of the detected signal, increasing reliability of all-optical approach of  $[\text{H}^+]$  detection. Based on the obtained calibration, pH value can be calculated using the following formula:

$$pH = 12.8 \cdot \frac{I_{553}^{\text{norm}} I_{456}^{\text{max}}}{I_{456}^{\text{norm}} I_{553}^{\text{max}}} - 5.5,$$

where  $I_{553}^{\text{norm}} I_{456}^{\text{max}}$  and  $I_{456}^{\text{norm}} I_{553}^{\text{max}}$  are PL intensities when excited with  $\lambda_{\text{ex}} = 470$  nm and  $\lambda_{\text{ex}} = 371$  nm and normalized on the maximum values of the PL measured for the calibration solutions with pH 10 and pH 2, respectively; '12.8' and '5.5' are empirically obtained coefficients.

## 3. Conclusions

Diamond-like NDs produced by laser synthesis decorated with carboxylic functional groups are demonstrated to be accurate all-optical sensors of pH values of solutions. pH can be easily recalculated from the PL intensities with two-wavelength excitation/emission approach, avoiding undesirable errors caused by hardware and fluctuations in NDs concentrations used for measurements.

## 4. Acknowledgements

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