Luminescent carbon nanodots stabilized by a polymer matrix for pH-sensing

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With the development of technological capabilities and present scientific advancements, there is a need to develop smart materials, which combine simplicity of synthesis with the main improvements, such as cheapness and environmental concern, unique selectivity and sensitivity. Luminescent carbon nanodots (CNDs) are one of modern smart materials. They are of high promise for catalysis, optics, sensor systems, and medicine. The undeniable advantage of CNDs are the low cost and wide availability of raw materials for synthesis.

The aim of the work was to design, characterize and study of the chemical-analytical properties of carbon nanodots in solution and modified polymer hydrogels.

Samples of CNDs were synthesized by heating a mixture of citric acid and urea in a quartz reactor at 165°C. The mixture obtained after heating was dissolved in isopropyl alcohol and acidified with a solution of hydrochloric acid. The precipitate formed in an acidic medium was filtered off and dried in air at a temperature of 120°C.

Characterization of CNDs

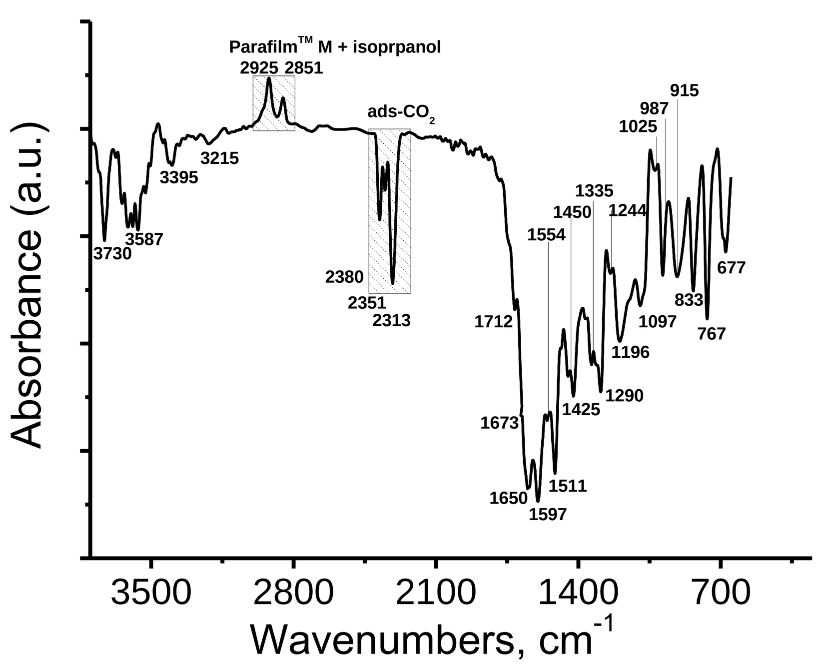


Fig. 1: FTIR ATR spectrum of CNDs

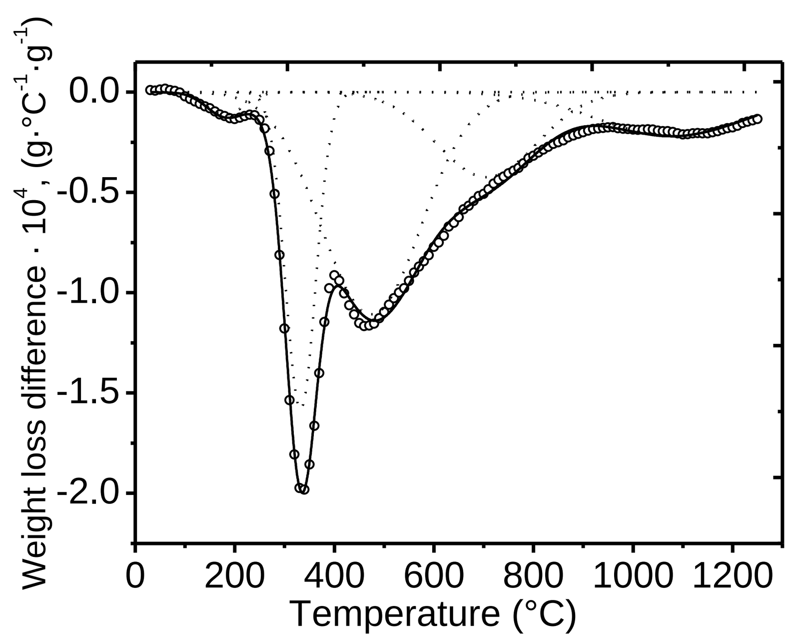
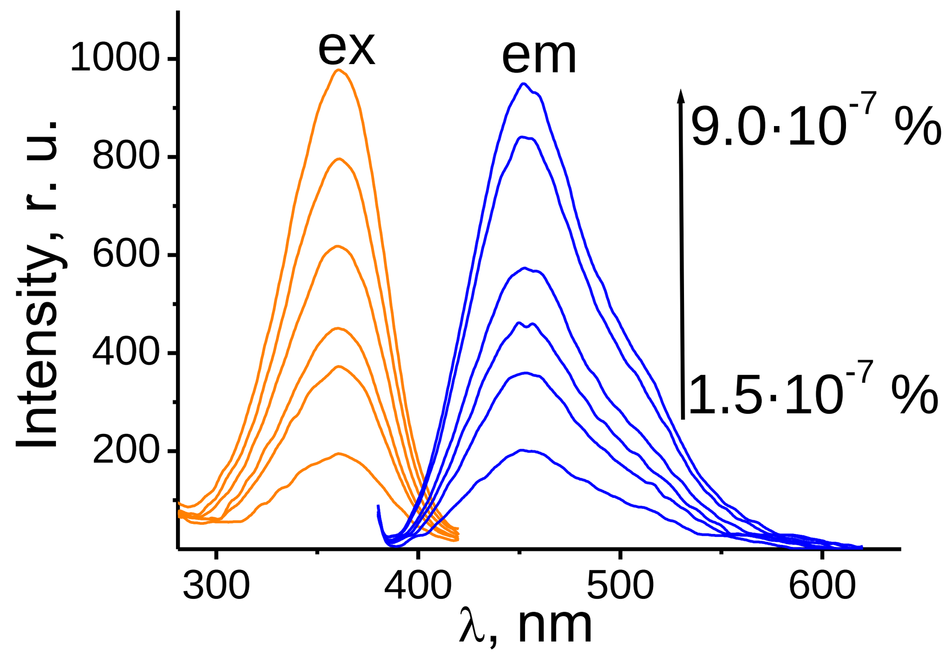


Fig. 2: DTG of CNDs.

CNDs were examined with thermal analysis and FTIR ATR. In fact, FTIR ATR spectroscopy confirms the presence of numerous different functional groups (Fig. 1).

The total weight loss effect is very significant of 58.7%. Thus, the CNDs consist of thermally unstable groups, on more than half, and they are easily removed by heating (Fig. 2).

Luminescence of CNDs in water solutions



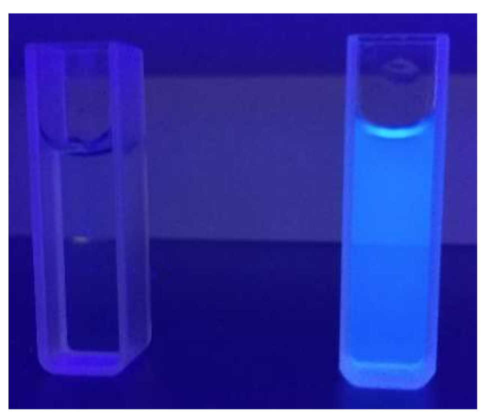


Fig. 3: Excitation and emission spectra at different contents of CNDs in water solution. λ_{ex} = 360 nm, pH = 7.0, l = 1.00 cm.

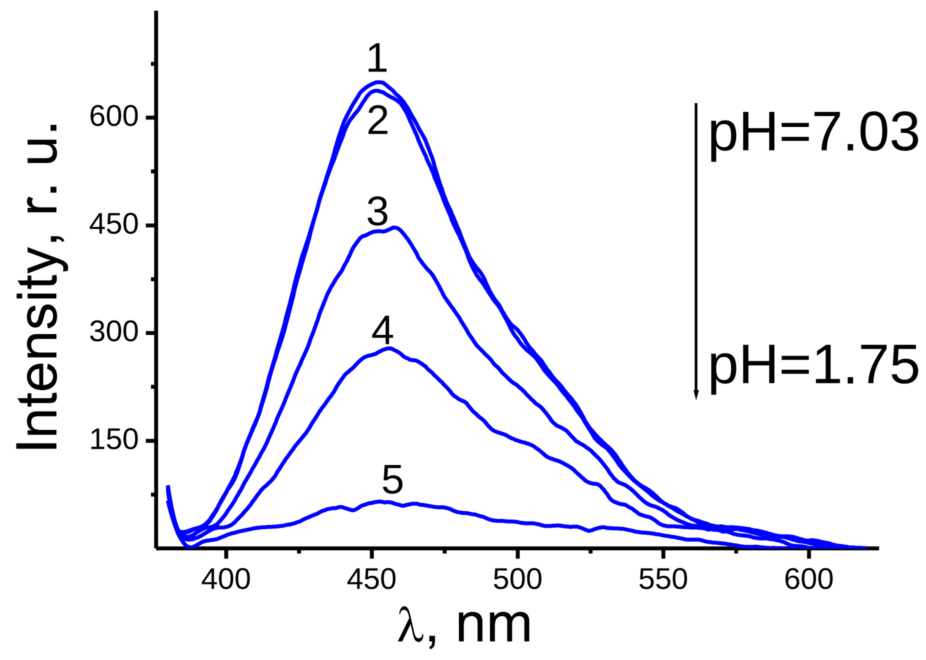
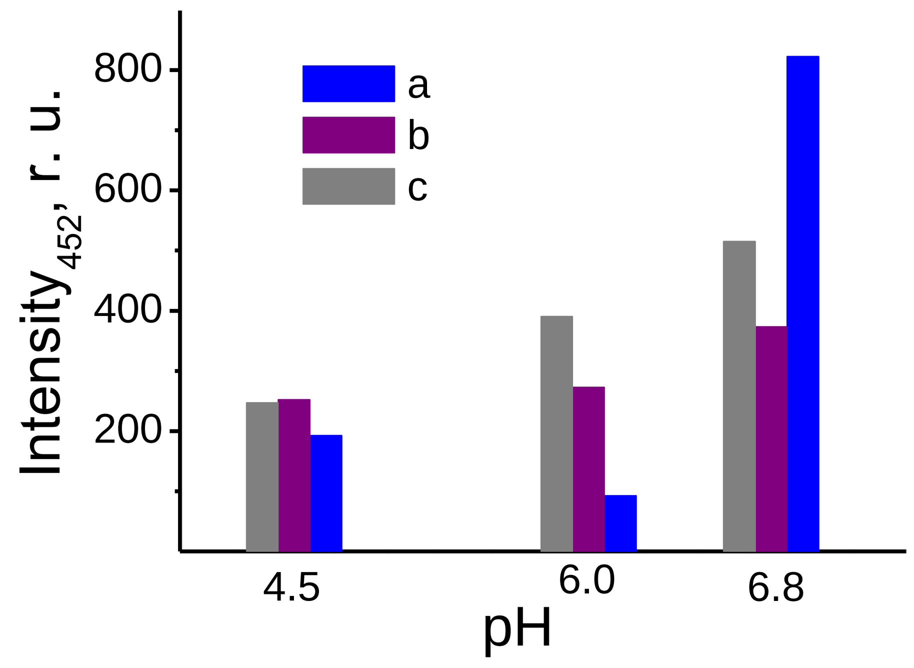


Fig. 4: Luminescence spectra of CNDs in a Krebs solution at different acidity, pH: 7.03 (1), 6.08 (2), 4.46 (3), 2.76 (4), 1, 75 (5). λ_{ex} = 360 nm, l = 1.00 cm

The maximum emission is observed at 452 nm, which corresponds to a blue luminescence (Fig. 3). The calculated quantum yield of CNDs is 26%.

The luminescence of CNDs solutions enhances with acidity decreasing and reversibly diminishes in the range of pH from 2 to 7 (Fig. 4).

Luminescence of CNDs in polymer matrix



PP hydrogels modified with CNDs

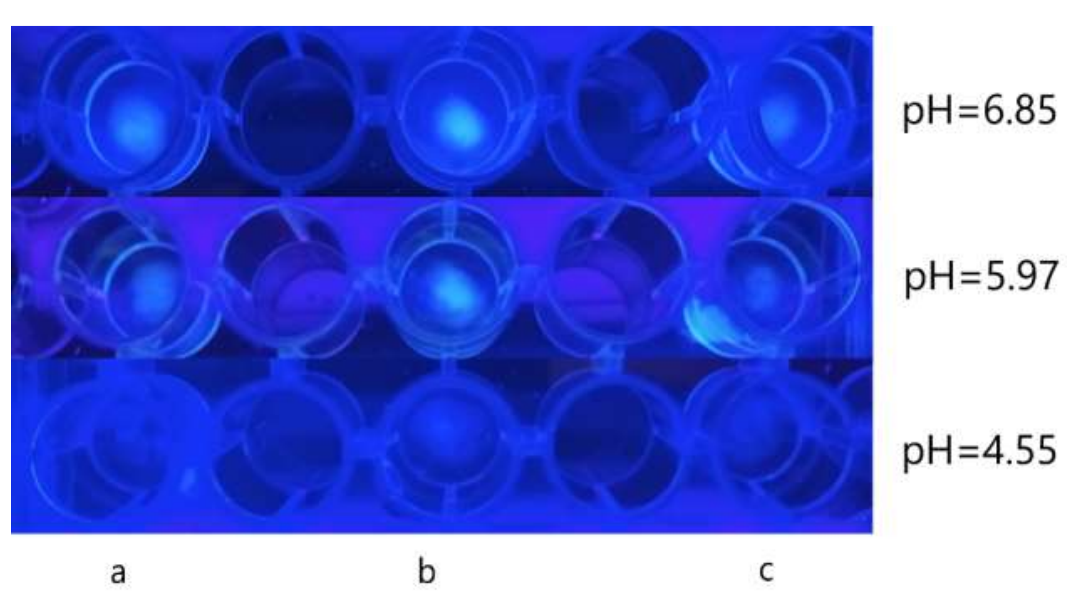


Fig. 5: Diagram of the luminescence intensity of PP hydrogels modified with CNDs (**a-c**) in a Krebs solution at different acidity.
λ_{em} = 452 nm, λ_{ex} = 345 nm, l = 1.00 cm

Polyacrylamide-based polymeric (PP) hydrogels are good candidates for wound dressings in modern medicine. In our work, the PP hydrogels (**a-c**) were impregnated with CNDs. It was shown that electrolyte and water solutions could not remove the CNDs from the PP hydrogels.

There is a general tendency for the immobilized CNDs to luminescence quenching as the pH of the solution decreases, in particular, in the range of pH 6-7 (Fig. 5). Notably, that sample (**a**) showed the most prominent (highest) change in luminescence intensity. So, this composite is the most attractive for a visual test screening.

The CNDs were examined with thermal analysis and FTIR ATR. Water solutions of CNDs were studied with IR and PL spectroscopies. From the thermal analysis of CNDs, they contain significant amounts of O- and N-containing surface groups. These CNDs show blue luminescence in water solutions. The photoemission intensity reversibly decreases with the pH of solutions, and complex multicomponent matrices, for example, a Krebs solution, have no impact on the luminescent properties. The CNDs were also used as modifiers for PP hydrogels. The prepared composites maintain their sensitivity to pH changes and can monitor the acidity of polymer-contacted surfaces.