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Surface modification of finely dispersed NaCl

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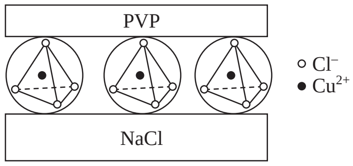
The first successful surface modification of finely dispersed NaCl particles was achieved during their synthesis *in situ* in the presence of $CuCl_2$ and polyvinylpyrrolidone. Obtained layered structure is stable to washing with polar organic solvents and to environmental moisture.



Surface modification of nanoparticles, which is a common tool for their stabilization and size regulation is widely applied to metals,[1–3] metal[4–6] and nonmetal[7,8] oxides, chalcogenides – $A^{II}B^{VI}$ semiconductors,[9–11] insoluble metal fluorides[12] and other classes of chemical compounds. In contrast, synthesis and surface modification of finely dispersed alkali metal halides is slightly studied in materials science.[13,14] At the same time, finely dispersed NaCl is not an exotic object, in the form of aerosol it is used in medicine (halotherapy) and plays significant role in atmospheric processes,[15] in this field the growth,[16] hygroscopicity[17] and chemical transformation[18] of these particles are intensively studied. From practical point of view, nanosized NaCl may be utilized to generate microwave (giga- and terahertz) radiation,[19] which in turn may be used for nonlinear bio imaging and spectroscopy,[20] ultra-high-speed optical communications,[21] time and frequency metrology,[22] *etc*.

Previously, we studied different methods of producing NaCl finely dispersed particles,[23] *viz*., synthesis from organic precursors in organic solvents, mechanical and ultrasonic dispersion, cryochemical method, spray pyrolysis and a solvent substitution technique. The latter method proved to be the most simple and convenient to obtain finely dispersed NaCl.

Surface modification of alkali halide crystallites is a non-trivial problem. Standard methods of modification applied to metal, metal oxide or $A^{II}B^{VI}$ semiconductor nanoparticles involve coordination bonding of organic ligands, like amines, phosphines, thiols, citric acid, *etc*., or electrostatic bonding of ionic surfactants, like cetyltrimethylammonium bromide (CTMAB). We tested various modifiers for alkali halide crystallites, including crown ethers. All of them, if sorbed, were easily eluted from the surface under washing with polar organic solvents.

Here we report the successful modification of the surface of NaCl with inorganic modifier – $CuCl_2$, polymer molecules of polyvinylpyrrolidone (PVP) and their mixtures.

Surface modification was achieved in the process of NaCl particles formation by the method of solvent substitution. This method is based on a dramatic decrease of NaCl solubility under water replacement with acetone excess, providing supersaturation and precipitation. The variation of NaCl concentration from 5.0 to 0.5 M led to a decrease in average particle size from 5.1 to 1.5 μm. However, the yield of the target product fell proportionally, so all further studies we carried out using 2.5 M aqueous solutions of NaCl.[†]

Addition of $CuCl_2$ or PVP modifiers resulted in the pronounced decrease of average particle size (Figure 1), the combination of $CuCl_2$ and PVP caused the maximal effect. This is due to the

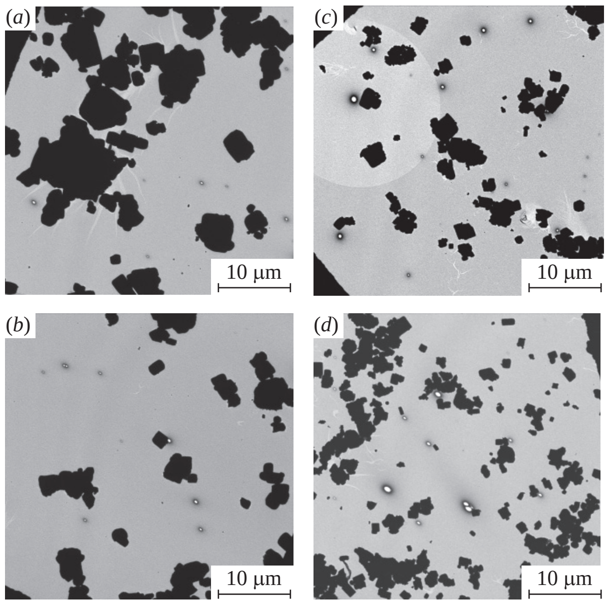


Figure 1 TEM images of NaCl powders prepared (*a*), (*b*) without PVP, (*c*), (*d*) by addition of PVP solution in acetone (0.15 wt%); (*a*), (*c*) without $CuCl_2$, (*b*), (*d*) in the presence of 0.25 M $CuCl_2$.

[†] *Synthesis of modified NaCl particles (typical procedure)*. PVP (0.01 g, MW 25000–30000, Merck) was dissolved in the mixture of aqueous 2.5 M NaCl solution (2 ml) and aqueous 0.25 M $CuCl_2$ solution (2 ml). Then 0.2 ml of the resulting mixture was added dropwise to 0.15 wt% PVP solution in acetone (4 ml) under ultrasonic agitation. The resulting particles were centrifuged, washed with acetone and dried in air.

TEM images were obtained with a LEO912 AB OMEGA transmission electron microscope. XRD measurements were carried out on a Stoe Stad P powder diffractometer (CuKα radiation). FTIR spectra were recorded on an IR200 Thermonicolet spectrometer. All reaction mixtures were agitated with a MELFIZ ultrasonic disperser (frequency 22 kHz) placed directly in the reaction medium.

surface modification, which prevents the further growth of NaCl crystals.

XRD studies of all synthesized samples showed reflections corresponding to sodium chloride only. This confirms just surface modification of the particles.

Preparation of NaCl powders in the presence of PVP was accompanied by the formation of a thin polymer film on the crystals surface according to TEM. Combustion analysis gives 4.4 wt% of carbon in the sample. Considering average particle size ~1 μm, specific surface of this powder is about 2.3 $m^2 g^{-1}$ and the thickness of the polymer film needs to be about 25 nm.

The combination of $CuCl_2$ and PVP in the reaction medium reduces resulting NaCl crystals size to 0.4–1.2 μm [Figure 1(*d*)]. In such a sample, copper content is 1.361 mg per 1 g of NaCl and carbon content is 7.86 wt%. Simple calculations provide the value of specific surface of 3.5 $m^2 g^{-1}$, Cu^{II} content of 3.6 Cu^{II} ions per 1 nm^2 of NaCl surface and thickness of polymer film of about 30 nm. The content of Cu^{II} ions is very close to monolayer filling of NaCl crystal surface.

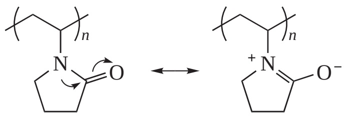
Samples of NaCl, obtained in the presence of copper ions, had the bright yellow color. It may be caused by the sorption of yellow tetrachlorocuprate(II) complexes,[24] which are formed in excess of chloride anions in solutions:

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \leftrightarrow [CuCl_4]^{2-} + 6H_2O. \qquad (1)$$

These surface complexes have rather low stability, the modified NaCl samples lost their color when dried in air. Apparently, this is due to the sorption of water vapor from air, which moves left the reversible reaction (1).

NaCl samples obtained in the presence of both copper ions and PVP also had the bright yellow color, but powders thus prepared retain the color for many months. So, the adsorbed tetrachlorocuprate(II) complexes, as well as NaCl surface, are effectively protected from environmental moisture by the polymeric layer and cannot be eluted by polar organic solvents from the surface when washing.

It is well known from IR spectroscopy data,[25–27] that PVP can interact with inorganic anions and cations. This interaction can be with nitrogen atoms or carbonyl oxygen of a flat and polar peptide bond in the lactam ring that exists in two resonance states (Scheme 1).[28]



Scheme 1

The results of such interaction are manifested, as a rule, in the change of the shape of the band in IR region, its broadening, shift of the maximum, and change of intensity. Therefore, we investigated FTIR spectra of the powder of pure PVP (sample 1), NaCl formed in the presence of PVP (sample 2), NaCl obtained *via* the addition of $CuCl_2$ and PVP to the reaction medium (sample 3), and a specially prepared powder of PVP–$CuCl_2$ without sodium chloride (sample 4). The significant shift of ν(C=O) of PVP from 1668 to 1622 cm^{-1} occurs for sample 4, while for samples 2 and 3, the broadening of this band is observed. In addition, shift of scissoring band of CH_2 group in PVP, adjacent to N and C=O, from 1462 to 1468 cm^{-1} occurs for sample 4, while there is a splitting of the band 1462 cm^{-1} for samples 2 and 3. At last, for samples 3 and 4, C–N band of PVP is shifted from 1287 to 1291 and 1295 cm^{-1}, respectively, whereas in sample 2 its broadening is observed. Obviously, all these changes are due to the interaction of PVP with $CuCl_2$ as well as with the surface of NaCl crystals.

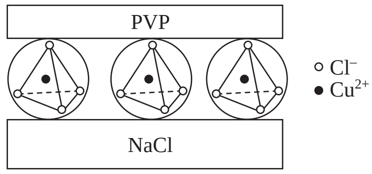


Figure 2 The structure of the surface layer of modified NaCl crystal.

A significant shift of the band of C=O group and more pronounced changes in the vibration frequencies of the C–H and C–N bonds for sample 4 compared with samples 2 and 3 indicate different type of PVP interactions with $CuCl_2$, on the one hand, and NaCl or $[CuCl_4]^{2-}$ surface ions, on the other. In the first case, coordination complexes PVP–$CuCl_2$ are formed.[28,29] In other cases, the interactions of PVP with surface ions are due to weaker electrostatic effects.

Thus, the ability of $CuCl_4^{2-}$ ion to interact with both NaCl and PVP provides the formation of sandwiched structure (Figure 2), where $CuCl_4^{2-}$ ions serve as anchors for strong bonding of PVP molecules to NaCl surface. Surface modification *in situ* decreases average particle size. These modified samples possess high stability to washing with polar organic solvents and to environmental moisture.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.05.035.

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