

Integrated Chemical System Based on Silver Halide Nanocrystals

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Abstract

The theoretical analysis of integrated chemical systems (ICSs) based on molecules of bacteriorhodopsin (bR) adsorbed on silver halide nanocrystals was carried out. The principal possibility for overcoming the electric potential threshold of non-selective reduction of silver halide nanocrystals during actinic flash action was noted [1]. We have shown experimentally [2] that life time of free electric carriers during optoacoustic effect in photoemulsions is in nanosecond time scale. It means that latent image centers (LICs) in silver halide crystals are formed in nanoseconds under certain conditions. In order to transform LICs to development centers in very short time interval we propose to use molecules of bR adsorbed on silver halide crystals.

Introduction

A chemical approach to nanotechnology based on ICSs is actively developed during last years. Concepts considered in the framework of this approach are applied to create different structural materials. These materials are widely used both in information recording systems (including original systems with variable light absorption) and in different microelectronic and photonic devices.

It is well-known that absorption of light triggers a chain of transformations in bR molecule. The protein consecutively passes through intermediate states usually denoted by K,L,M,N and O, this process leading to the change of photoinduced electric potential of bR molecule. The characteristic time of these transformations is about 10 ps and maximum value of electric potential on the individual cellular membrane is 100 mV. Thus, light energy transforms into electrochemical potential difference of protons on the membrane. In the end the system returns to initial state, a time of the photoelectrical cycle being 0.01 s. During this cycle the proton moves from cytoplasm to intercellular space. Therefore the bR molecule acts as a proton pump (the proton eliminates from bR molecule in the state L, the molecule joins a new proton in the state O). To obtain the maximum value of electric potential it is necessary to obtain a big number of identically oriented bR molecules. One of the possible ways to create such orientation is to apply an external electric field. The total change of electric potential of the organized ensembles of

bR molecules can be up to 10 – 12 V under actinic flash action [3]. Taking into account this effect the process of non-selective reduction of small silver clusters (LIC) to big silver particles of colloidal dispersion can be effectively switched on in 10 picoseconds after flash action.

Main features of AgBr nanocrystal reduction in electric field.

Detailed analysis of experimental data about electric field influence on the LIC formation was carried out in [4]. Ultra-fine grained photographic emulsion based on AgBr nanocrystals with 20 nm in diameter is a trigger system. This is a consequence of existence of the thermodynamic barrier between initial and developed states. The lower the barrier the higher is photographic speed. From the other side, a small value of barrier increases a probability of background effects.

The photographic properties of the system under consideration are determined by particular features of AgBr microcrystal synthesis (a big number of the surface particles compared to the volume ones, a low level of chemical sensitization, a small defect concentration, non-typical habit, i.e. microcrystal form is close to spherical).

In paper [4] the phase states of grains are considered as a function of electric potential. There are three areas of stable states on the phase plane: 1 – metallic silver, 2 – silver bromide, 3 – silver oxide and molecular bromine. It was noted that before formation of metallic silver during motion from area 2 to area 1 a thermodynamically non-equilibrium, but meta-stable AgBr state with broken stoichiometry firstly forms. The area of supersaturated silver solution meta-stability ends at electric potential value equal to -300 mV and $\lg a_{Ag} = 5$. Crossing of meta-stability boundary leads to appearing of colloidal silver. Some difficulties in speed regulation by electric potential are connected with the fact that a change of potential in small interval causes big changes in system properties.

Let us estimate a number of ionic pairs in microcrystal with 20 nm in diameter. According to [5] we have a speed of electron injection equal to 3×10^{12} electrons per second for the grain with 1.4 μ m in diameter. Taking into account that the time of full grain reduction is equal 10 ms, we obtain a total number of electrons necessary for it equal to 3×10^{10} . If each injected electron reduces one ion of silver, then this quantity is equal to a number of ionic pairs (Ag^+

and Br⁻) in the crystal. For the 20 nm AgBr nanocrystal we in the same way obtain 10^5 pairs of ions. Thus, time of full reduction for silver bromide nanocrystals is 3×10^5 times less than the same time for X-ray emulsions. The nature of injected electrons can be different (photoelectrons, electrons from the cathode, electrons from the chemical mediators).

We noted many times earlier [1, 5] extraordinary high speed of silver reduction excluding stage by stage process of LIC formation and its further growth up to colloidal particles. Injection speed in these experiments reached the values $10^{11} - 10^{12}$ electrons per second. These data are valid for X-ray and fine grained emulsions. For nanocrystals such speeds of electron injections will lead to the time of full grain reduction equal to $10^{-6} - 10^{-7}$ s (this time refers to the time of LIC formation plus the time of nonselective reduction of the grains).

In photochromic ICS based on AgBr nanocrystals the process of grain reduction both containing and non-containing LICs dominates. Such non-selective reduction starts under potentials equal to -300...-400 mV. Under bigger potential values (-800 mV) disappearing of reduction kinetics difference for both cases of grains is observed.

It was demonstrated that optical density for ICS based on nanocrystals exceeds value $D=1$ in few milliseconds under experimental conditions [6]. Increasing of electric potential of bR molecules can significantly decrease time of appearance of silver colloidal particles in this ICS. Such systems could be useful as effective photochromic inorganic materials or photochromic sensors.

The main properties of ICS under investigation

One of the main properties of ICS under investigation (AgBr nanocrystals with adsorbed bR molecules placed in transparent polymer film) is appearing of photoinduced difference of potential on the surface of nanocrystals. The value of this difference exceeds the threshold of spontaneous fogging. As it was noted earlier, the jump of potential was due to conformation transformation of optical trigger bR molecule in the tens of picoseconds [3]. The process of non-selective reduction of AgBr nanocrystals began in the same period of time. Let us note that it is not necessary to reduce silver ions in the whole microcrystal volume in order to obtain high value of optical density. It is quite possible it will be sufficient to reduce only surface and subsurface silver ions to form silver atom aggregate (e.g. grid or surface fragment) with metallic bond. Thus even on this intermediate stage of non-selective reduction process we can obtain very effective scattering and absorption of actinic light. Earlier we measured [2] the corresponding coefficients with the use of special optoacoustic time resolved techniques. The coefficient values for laser wavelength $\lambda = 530$ nm were correspondingly $\mu_{\text{abs}} = (2.2 \pm 0.4) \text{ cm}^{-1}$ and $\mu_{\text{scatt}} = (2.2 \pm 0.5) \times 10^5 \text{ cm}^{-1}$. The time of final localization of free charge carriers (electrons and holes) in the traps was 2×10^{-8} s.

As a result of these processes we can obtain high values of optical density (e.g. $D=3$ and more) in the time interval

from hundreds of nanoseconds to tens of microseconds. This time is essentially shorter than the one obtained earlier [6] and for AgBr nanocrystals without bR molecules (5 ms for $D=3$ for several emulsion layers). It should be noted that substantial optical densities in the visible part of spectrum have been obtained for AgBr nanosol as well as for some similar objects in nanosecond time interval [7].

Up to last time there existed some difficulties in obtaining homogeneous, optically transparent and stable polymer films with incorporated bR molecules. It was shown recently [8] that bR films with remarkable optical properties could be obtained by incorporation of bR molecules into polyvinyl alcohol.

Let us make hypothetical consideration of model system consisting of chemically sensitized AgBr nanocrystals and possessing reversible photochromism. Let the system be under the joined influence of actinic light and electric field. According to general scheme of chemical sensitization mechanism it leads to appearing of Ag_n microclusters (together with Ag_2S and other compounds) on the AgBr surface. Here n is 1,2,3 For photographic emulsions based on silver bromide nanocrystals with the lowest level of chemical sensitization n does not exceed 2 [9]. Ag_n microclusters can randomly aggregate in bigger particles which can disintegrate both spontaneously and under electric field action.

Another way of appearing of neutral particles of silver is action of actinic light of sufficient intensity. It breaks ionic bonds in AgBr, that leads to appearing of photoelectrons in the conduction band. When concentration of electrons there exceeds the critical value, we have a saturation in the electron subsystem and the phase of metallic silver begins to emerge as Ag_n on the surface. Let us underline that this aggregation process has characteristic velocities determined by the velocities in the electron subsystem.

We believe that all cooperative mechanisms leading to surface metallic phase of silver can be united by the percolation mechanism. The corresponding details are presented in another our report at this conference.

Conclusion

We proposed to use photoinduced states of bR molecules to initiate the ultrafast aggregation of silver clusters. The joined action of actinic light and electric field created by bR molecules leads to photochromic effect that is sufficient to obtain high optical densities in the visible range of spectrum. The characteristic time of this process does not exceed several milliseconds. Further investigation of such ICSs together with new achievements in nanotechnologies will make possible to develop new photochromic and photonic devices

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Biography

Dr. Valery Zakharov is a senior research fellow of the Laboratory of Structural Chemistry, Department of Chemistry, Moscow State University. He is an author and co-author of 85 scientific papers and patents. The fields of scientific interests are theory of photoprocess, metallic clusters, photochromic and electrochromic sensors, ODMR spectroscopy, integrated chemical systems.