Optical and Electrochemical Features of Nanograined AgBr Crystals with Organic Molecules as a Trigger

V.N.Zakharov, L.A.Aslanov, N.N. Alekhin,
I.K.Kudryavtsev, H.Schenk*
Moscow State University, Department of Chemistry
* Amsterdam University, Department of Chemistry
Department of Chemistry, Moscow State University,
Moscow, 119992, Russian Federation
E-mail: zakharov@struct.chem.msu.ru

For the first time the process of ultra fast reduction of nanograined AgBr crystals under actinic flash action was reported in [1]. In order to obtain the high optical densities in full visible spectrum range it was necessary to trigger the nucleation process in the initially transparent system for very short period of time. So the appropriate trigger was needed.

Organic polymer systems doped with strong nonlinear optical functional molecules have emerged in the last decade as a new class of electrooptic materials and have received considerable interest for integrated optical device applications. Macroscopic optical properties of these materials, such as photovoltaic effects, electrooptic effects, harmonic generation, and photorefractive effects, are always associated with microscopic polarizabilities through the molecular orientational distribution. We selected bacteriorhodopsin (bR) as an example of nonlinear optical functional molecule. It is the light sensitive protein found in a crystalline biological membrane and is known to exhibit strong photovoltaic behavior and large optical nonlinearities. However, there is significant difficulty in forming uniform, transparent and stable bR films. It was shown recently [2] that bR films with photovoltaic and electrooptic properties can be obtained by embedding bR molecules in a poly(vinyl alcohol) (PVA) polymer matrix. In these films, the PVA polymer host is doped with a small concentration of bR. When an AC rectangular or sinusoidal external electric field is applied across the resulting material, a modulated photocurrent is observed when a laser beam illuminates the sample.

We propose to modify this material adding nanograined silver halide crystals (20 nm in diameter) into polymer film. In this case molecules of bR adsorbed on the surface of these crystals could be used as electrooptic trigger generating the process of silver nucleation in silver halide matrix under powerful flash action. The main electrochemical features of nanograined AgBr crystals are described in [3]. During the electrolytic reduction process there is no direct injection of electrons from the cathode into the emulsion grains. The role of a “reduction atmosphere” forming in the vicinity of the cathode is specially stressed in [4]. The nature of this “atmosphere” as well as electron carriers have not been clarified. However, even if there is no direct electron transfer, all the results and conclusions remain completely valid from point of view of thermodynamics. The reduction process may develop according to two different schemes:

direct injection

$$e\ (\text{cathode}) + Ag_{Ag}^{+}\ (\text{emulsion grain}) \Rightarrow Ag_{Ag}^{x} \qquad [1]$$

with the aid of a donor-acceptor impurity

$$e\ (\text{cathode}) + A \Rightarrow A^{-}$$

$$A^{-}\ (\text{donor}) + Ag_{Ag}^{+} \Rightarrow A + Ag_{Ag}^{x} \qquad [2]$$

The results of thermodynamic analysis of these two cases coincide. For electrolytic reduction Faraday’s law is valid, i.e. reduction of each silver grain requires the transition of one electron from the cathode. This condition holds sufficiently strictly at small cathode displacement rates, i.e. conditions close to equilibrium.

In a general form the values of electric potentials of emulsion grains are presented in Table 1.

Table 1. Values of electric potentials of emulsion grains

State of the system	*Relative values of electric Potential* [mV]
1. Equilibrium system $Ag_{\infty}AgBr/Ag^{+}$	0
2. Specks of full latent image	-20 : -170
3. Specks of latent subimage	-170 : -270
4. Increase in light sensitivity	-100 : -300
5. Onset of spontaneous fogging	-300 : -400
6. Disappearance of discrepancy between kinetics of unexposed grains and that of grains with latent image specks	-800
7. Oxidation processes (desensibilization, oxidation of latent image and visible blackering)	> 0

It can be seen from this table that in order to overcome the spontaneous fogging threshold and to initiate the full nucleation process it is necessary to apply to the grains negative electric potential exceeding 800 mV.

It is well known that light absorption triggers transformation chain of bR [5]. Protein goes though intermediate states which usually are denoted in alphabetic order: K,L,M,N and O. These transformations and electric potential changes correlated with them occur in ten picoseconds. The value of electric potential photoinduced by bR molecules on single membrane is 100 mV. The energy is stored electrostatically in accordance with the mechanisms of molecular condenser appearing under flash action. To obtain high photopotentials (up to 10-12 V) it is necessary to use packs of oriented membranes or bR molecules.

The system consisting of appropriate polymer and nanograined AgBr crystals with adsorbed bR molecules is practically transparent initially. Under flash action the silver particles nucleation process develops resulting in appearance of colloidal particles. As was shown in [6], the scattering coefficient exceeds the absorption one in 10^5 times.

To summarize, one can conclude that the systems investigated reveal new perspectives for creation of ultrafast electrochromic and photochromic materials.

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