

## **M98-A10 PHOTOADAPTIVE FIBERS FOR TEXTILE MATERIALS**

Investigators: German Mills, B. Lewis Slaten, Royal M. Broughton

Graduate Students: G.A. Gaddy, K. Malone

Undergraduate Students: J. McLain, S. Ruggs

### Goal:

Photoadaptive fibers and films, which experience photoinduced reversible optical and heat reflectivity changes, are being developed. Results from detailed kinetic investigations on the particle formation process carried out on thin films allowed further improvements in the speed of metal crystallite generation. The improvements permitted a reproducible enhancement of the metallization speed exclusively at high intensities of light, as required in our original goals. Furthermore, conditions have been found under which particle oxidation has been achieved. This is an important result that will enable us to fulfill the overall goal for this project to develop reversible particle generation in textile materials.

### Abstract:

Kinetic determinations on the photochemical generation of nanometer-sized Ag crystallites were performed using optically transparent polymeric films in order to optimize the metallization speed. Uniform incorporation of  $\text{Ag}^+$  and  $\text{AuCl}_4^-$  ions into the films, by swelling the films with solutions of these ions, resulted in a fast photogeneration of particles inside the polymeric materials. Films employed initially were made by crosslinking poly(vinyl alcohol) with dimethylsulfoxide in the presence of poly(acrylic acid), which suffered from undesired dark formation of Ag crystallites at high  $\text{Ag}^+$  concentrations. Inhibition of the dark reduction processes was accomplished employing water-insoluble films made with glutaraldehyde as a crosslinking agent with some decreases in the speed of particle photogeneration. Detection of nanometer-sized Ag crystallites as well as  $\text{Ag}_2^+$  and  $\text{Ag}_4^{2+}$  clusters with UV-Visible spectroscopy was possible due to the high optical quality of the films. Formation of the larger Ag particles seems to proceed by fast cluster expansion, rather than cluster-cluster aggregation steps. Despite the effectiveness of the photoreaction, the polymeric films exhibit the desired property of forming metal crystallites exclusively via high light intensity photolysis, but not at ambient intensities. The generated Ag particles decay via a dark reaction when hydrogen peroxide is incorporated into the films. This finding is expected to enable the preparation of systems exhibiting reversible formation of metal crystallites, which is the ultimate goal of this project.

## Introduction:

Metal particles in the nanometer-size range in recent years have received an enormous amount of attention, as their properties are substantially different from those of the bulk metals. Gold and silver crystallites have been extensively studied because their unusual size-dependent properties and are not only of scientific interest but may also have an important role in future electronic devices. Preparation of stable "nanoparticles" of these metals continues to pose a significant problem since the thermodynamic stability of larger (micron sized) particles is the driving force for the fast growth of the small crystallites. For this reason, synthesis of small metal crystallites in systems that inhibit particle growth is a promising procedure for exploiting the unique properties of these "nanomaterials". While most of the interest has been centered on the physical properties of these crystallites, particle generation in such systems has allowed the discovery of some of their novel chemical properties. For instance, illumination of AgBr in silica glasses induces reversible formation of small Ag particles. These photoadaptive (or "smart") systems experience desirable and predictable reversible changes in their chemical properties in response to illumination, and are the basis of photochromic glasses. A model photoadaptive system was developed recently by us, in which  $\text{AuCl}_4^-$  or  $\text{PdCl}_4^-$  ions incorporated into methanol-swollen, crosslinked polymers of diallyldimethylammonium chloride (DADMAC) were photoreduced to form nanometer-sized Au or Pd particles. However, oxidation of the metal crystallites in a dark room temperature process reforms the starting metal ions.

Similar systems based on metal crystallites prepared inside polymeric matrices are of practical interest as adaptive reflectors of intense infrared radiation (IR). The dye-based polymeric photochromic glasses currently available are unsuitable for this purpose due to their limited thermal stability and poor IR reflectivity. Polymeric adaptive fibers were proposed in the present project as IR reflectors. The envisioned fibers were expected to function in a fashion similar to the photoadaptive gels where fast generation of nanometer-sized Ag or Au crystallites would occur only upon exposure to high photon intensities, followed by oxidation of the particles in the absence of light.

The research results of the gel systems served as a starting point for the preparation of photoadaptive IR reflecting fibers. Water-insoluble fibers containing Ag ions that responded to light were prepared during the first year of this investigation by crosslinking poly(vinyl alcohol), PVA, with dimethylsulfoxide (DMSO) in the presence of poly(acrylic acid), PAA. PVA fibers containing poly(DADMAC) or PAA and  $\text{AuCl}_4^-$  ions yielded similar results under photolysis. The next step consisted in a thorough study of the dynamics of particle evolution with the aim at optimizing the speed of the formation and oxidation steps. Preparation of high quality transparent films of the crosslinked PVA polymers was, therefore, necessary since UV-Visible optical detection is the preferred method for such measurements, as the crystallites exhibit strong plasmon bands centered between 380 and 500 nm for Ag, and 520 to 650 nm for Au. Detailed investigations of the particle generation kinetics revealed that the desired light-sensitivity of the fibers existed also in the films. Illumination of the films resulted in a fast formation of metal particles, but several problems were also identified: i.) the polymer films were insoluble in cold water but showed partial solubility at high temperatures, ii) aging of films in the dark for several days decreased drastically the rate of the

photochemical reaction, iii) generation of Au crystallites was more than ten times slower than the corresponding photogeneration of Ag crystallites. Therefore, during the last year efforts were made to improve the long term photochemical as well as physical properties of the polymeric films. The studies were centered on materials containing  $\text{Ag}^+$  ions, which exhibited the most promising properties.

#### Results:

Reaction of PVA (molar mass =  $1.7 \times 10^5$  g/mol) with DMSO for 10 min at 343 K in the presence of PAA (molar mass =  $2 \times 10^3$  g/mol) produced solutions that solidified to gels after 3 days at room temperature. Similar gels were obtained in the presence of  $[\text{AgNO}_3] \leq 0.1$  M, or in the absence of PAA. Films were made after melting the gels at 343 K and coating the solutions onto glass discs. Uniform shrinking and separation of the films from the glass supports was accomplished by exposure to methanol at 77 K. Films free of  $\text{Ag}^+$  ions were cleaned by a 19 hour immersion in methanol; incorporation of metal ions into the polymers was achieved by swelling the films with methanolic solutions containing 0.1 M or less  $\text{AgNO}_3$ . Following a brief cleaning step with  $\text{CH}_3\text{OH}$ , the films were placed between 2 glass disks and dried at room temperature.

An alternative preparation of PVA films employed glutaraldehyde (GA) as crosslinking agent instead of DMSO. In this procedure a hot solution containing PVA, PAA, GA and HCl (the crosslinking catalyst) was placed between glass plates and allowed to react. After a several hours the resulting film was separated from the glass plates and the crosslinking reaction was quenched by exposure to liquid  $\text{CH}_3\text{OH}$ , or by HCl evaporation in a vacuum oven. Incorporation of  $\text{Ag}^+$  ions into the films proceeded with  $\text{AgNO}_3$  solutions in  $\text{CH}_3\text{OH}$  as described above for the films prepared with DMSO. Since GA binds in an irreversible fashion to PVA, all polymers crosslinked with GA were completely insoluble even in hot water. The proposed structure for the crosslinks is presented in Figure 1.

Films of non-crosslinked PVA were also prepared in order to study the effect of DMSO on the generation of Ag particles by non-photochemical reactions. These films were made by depositing an aqueous PVA solution onto glass plates, which after drying were exposing to an  $\text{AgNO}_3$  solution in  $\text{CH}_3\text{OH}$  to incorporate  $\text{Ag}^+$  ions without dissolving them. Alternatively, solutions containing  $\text{AgNO}_3$  in conjunction with PVA were used to prepare the films. Similar results were obtained with both types of films.

Transparent films of good optical quality resulted in all cases, with thickness ranging between 0.1 to 0.2 mm. Irradiations were carried out inside a Rayonet circular illuminator using photons of wavelengths =  $350 \pm 10$  nm, with a light intensity of  $7.0 \times 10^{17}$  mol (photons)/min. Displayed in Figure 2 are typical optical spectra of PVA films prepared with 10 mM  $\text{AgNO}_3$  after illumination for 47 min, the strong signals centered at 460-470 nm correspond to the plasmon band of the crystallites. The top curve corresponds to a non-crosslinked film, the middle curve was recorded for a film crosslinked with DMSO whereas the lower curve was measured for a film made with GA as a crosslinking agent. Signals corresponding to two types of metal clusters,  $\text{Ag}_2^+$  and  $\text{Ag}_4^{2+}$ , were detected after correcting the spectra (by subtraction of the absorptions of the unirradiated films). These clusters are formed as transient intermediates that survive only for fractions of a second, during the reduction of  $\text{Ag}^+$  in solution. The cluster with 4 Ag

atoms is a constituent of the latent image formed by exposure of photographic films to light. This cluster plays a key role in the autocatalytic development process of Ag in photography that results in a  $10^4$  fold amplification step producing visible images. Generation of such clusters is a very interesting and unexpected result for several reasons. In the first place, detection of such species implies that the formation mechanism of Ag crystallites in the films occurs through a process similar to the established mechanism for the  $\text{Ag}^+$  reduction in solution. Furthermore, no change in the optical signal of these species have been detected after illumination is terminated, implying that generation of the clusters in the PVA films is a new way to stabilize such species. This, in turn, may allow the systematic study of these important species, which has not been accomplished in solution because of their instability toward aggregation and growth. Even in photographic films isolation of the clusters has not been possible since they are sensitive to oxidation in the presence of air.

Presented in Figure 3 is the evolution of the optical density (O.D.) at 280 nm corresponding to the Ag clusters within the first 16 min of irradiation. During this period the rate of cluster generation is a linear function of time with similar formation rates in all cases, resulting in photonic efficiencies of about  $6 \times 10^{-3}$ . At longer times the formation rate of the clusters becomes increasingly slower as the photoreaction proceeds. Figure 4 shows the increase in optical density of the metal crystallites at 450 nm, as a function of illumination time for the 3 types of films. Two distinct formation steps can be distinguished: an initial step where O.D. increases linearly with time, for which estimated photonic efficiencies for particle formation are about  $4 \times 10^{-3}$ . A second step follows where a nonlinear increase of the absorbance takes place, the estimated rate of O.D. increase is about 4 times that of the first step. Straight lines were obtained by plotting  $(\text{O.D.})^{1/3}$  as a function of time during the second step. According to known mechanisms of Ag formation, these results indicate that the nanometer-sized particles are generated by deposition of Ag atoms on the existing clusters. During the initial step generation of clusters is the faster process, and metal particles slowly form at the expense of some of the existing clusters. However, at longer times a relatively large concentration of clusters exist, and formation of nanometer-sized particles by addition of silver atoms to the clusters competes with the cluster generation process that also involves Ag atoms. The proposed sequence of elementary steps for the generation of clusters and metal particles is presented in the scheme shown in Figure 5.

Although formation of Ag clusters and metal particles occur with similar rates at short illumination times, formation rates are slower for the polymer crosslinked with GA at longer times. The reason for this difference is the higher extend of crosslinking in the films made with GA. In fact, as shown in Figure 2, formation of clusters is fastest in non-crosslinked PVA films since diffusion of Ag atoms and clusters is faster in polymers without crosslinks than in crosslinked polymers. Although PVA films crosslinked with DMSO yielded faster formation of Ag particles than those prepared with GA, the former suffer from several problems. The first drawback is that the particle formation efficiency decreases by at least a factor of 2 upon aging these films for a few days, and by a factor of 4 after a week of storage even at 190 K. In addition, slow formation of Ag particles occurred in the absence of light when the concentration of  $\text{AgNO}_3$  was close to or above 10 mM. Thus, materials based on PVA crosslinked with DMSO are not well suited to operate as photoadaptive reflectors of IR.

None of these problems are significant in the case of polymer crosslinked with GA. Considering that fast formation of Ag particles at short times is a desired property of the photoadaptive reflector fibers, and that the formation process occurs with similar efficiencies in all polymers during this period, the materials prepared with GA are obviously the best suited for such application. Furthermore, incorporation of hydrogen peroxide into the polymers induced a slow oxidation of the Ag crystallites. However, further photolysis of the bleached films yielded renewed particle formation without altering the rate of this process. These results clearly demonstrate that reversible formation of small Ag crystallites in the crosslinked polymers is feasible.

#### Future Plans:

Although our efforts to characterize the metal particles with powder X-Ray Diffraction (XRD) methods were unsuccessful, we are currently studying the polymer films with transmission techniques, and with a new procedure called Single Particle XRD (in collaboration with researchers from Vanderbilt University). TEM experiments on microtoned samples have also been planned in order to determine particle sizes and size distribution. Reflective IR Spectroscopy characterization is currently in progress, and similar analysis of fibers prepared with GA-crosslinked PVA will be carried out. Emphasis will be placed in optimizing the oxidative decay of the Ag particles by incorporation of oxidants with known redox potentials into the polymeric materials. Systematic variations of oxidants and their concentrations will be attempted, efforts will be made to avoid altering the physical properties of the films or fibers during the incorporation of these chemicals into the polymers.

FIGURE 1. STRUCTURES FOR CROSSLINKS BETWEEN PVA AND GLUTARALDEHYDE

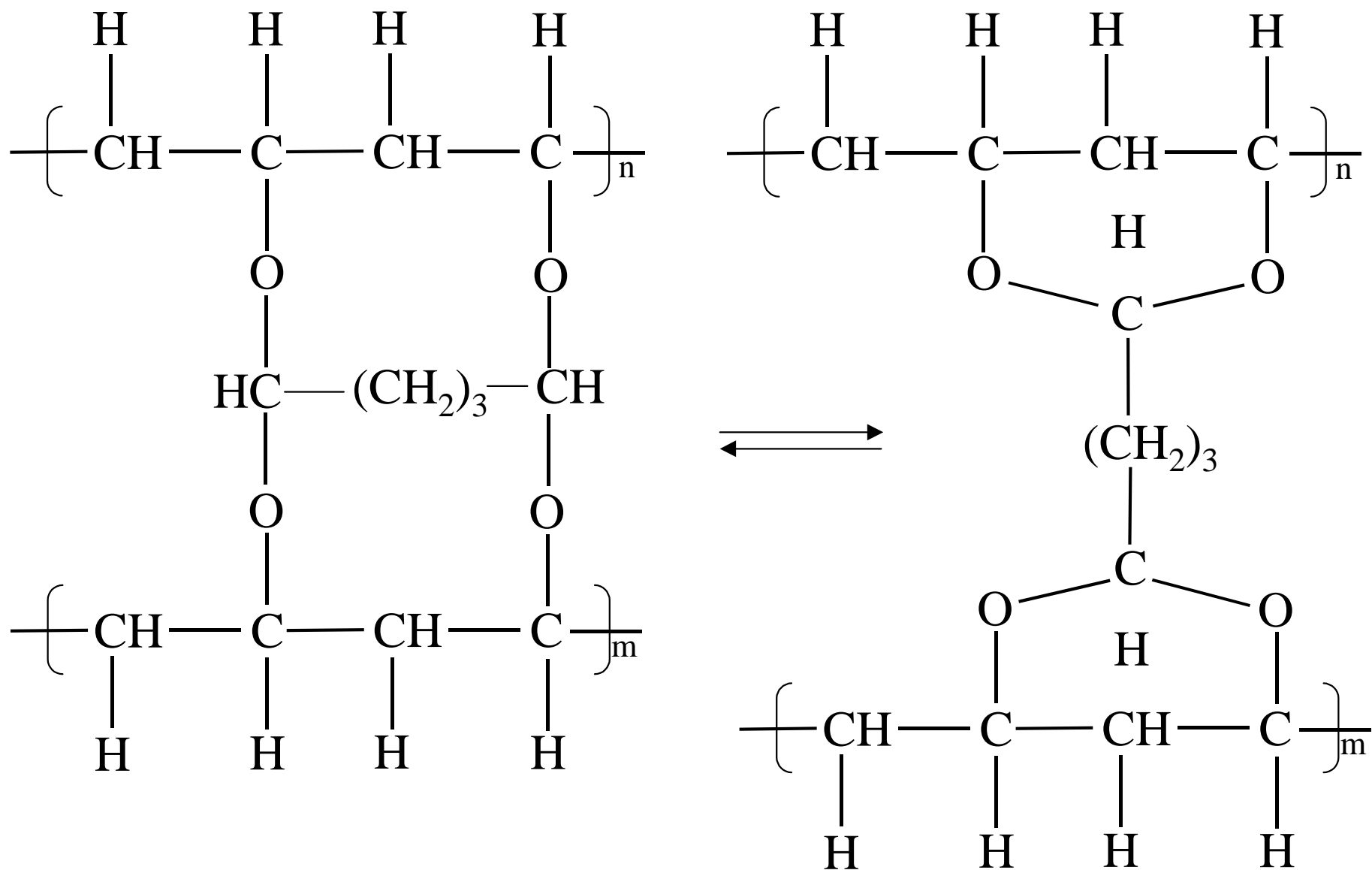


FIGURE 2. CORRECTED OPTICAL SPECTRA OF ILLUMINATED PVA FILMS

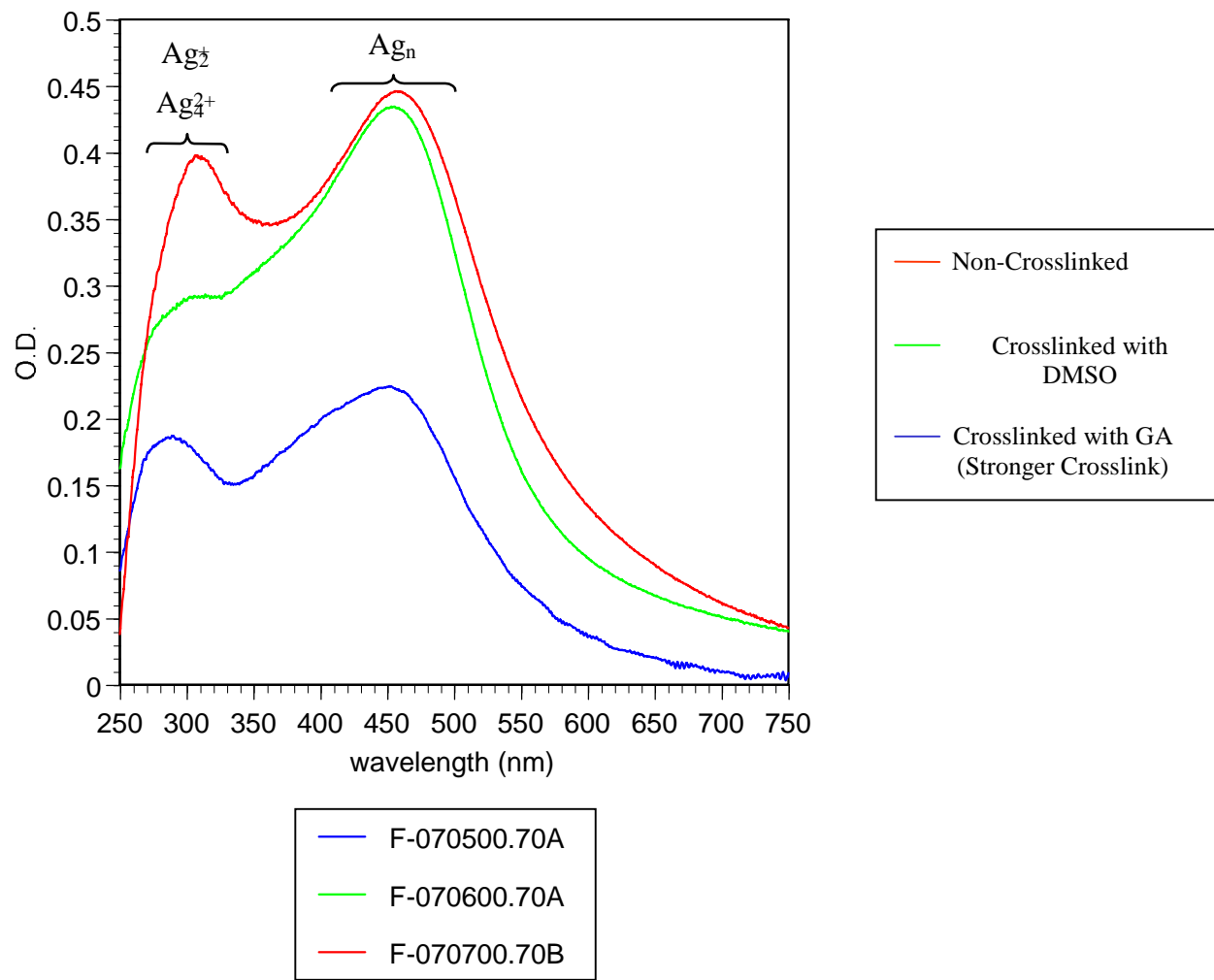


FIGURE 3. KINETIC PLOT OF CLUSTER ABSORPTION AT 280 NM IN PVA FILMS

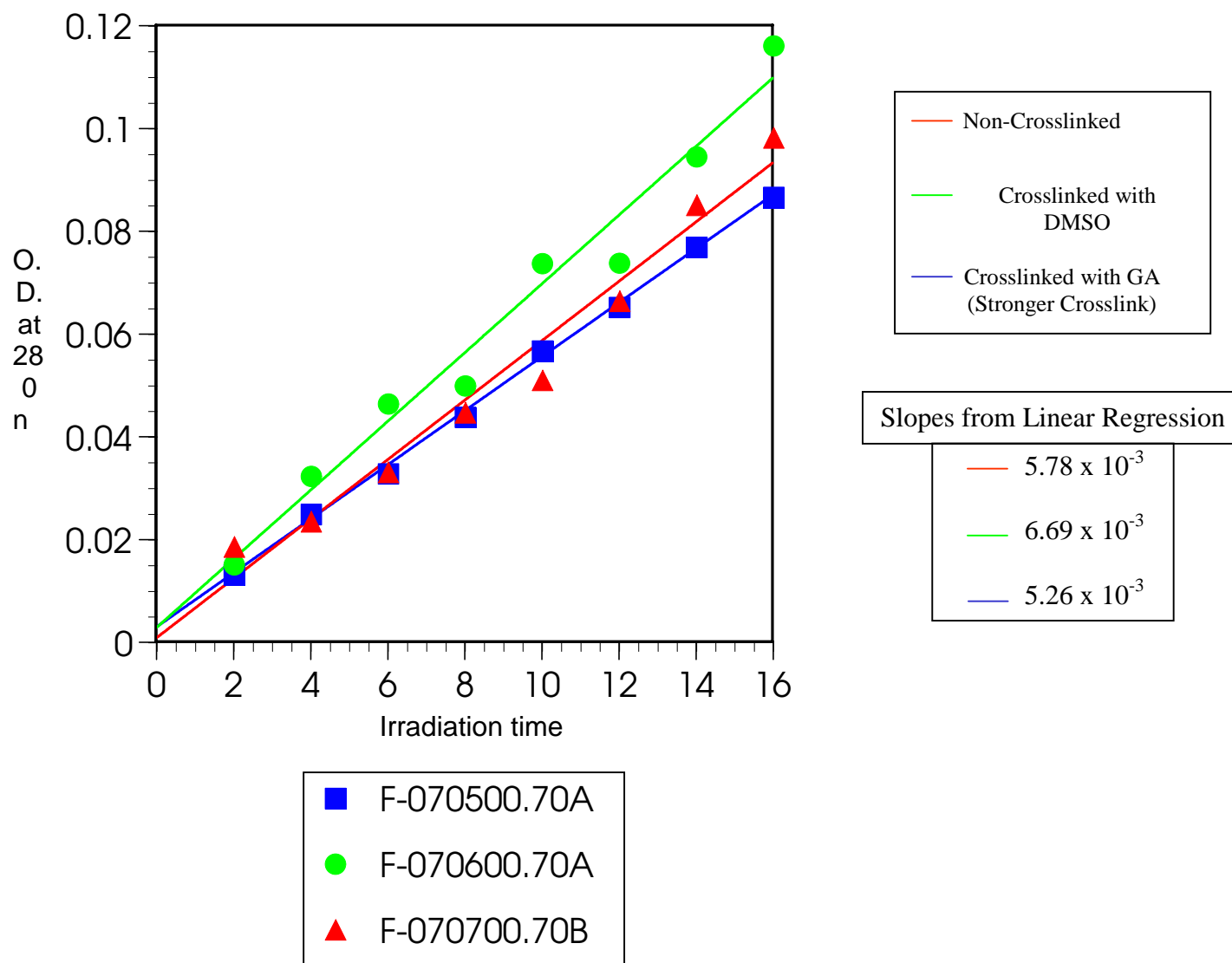


FIGURE 4. EVOLUTION OF THE PLASMON ABSORTION FROM Ag PARTICLES vs TIME

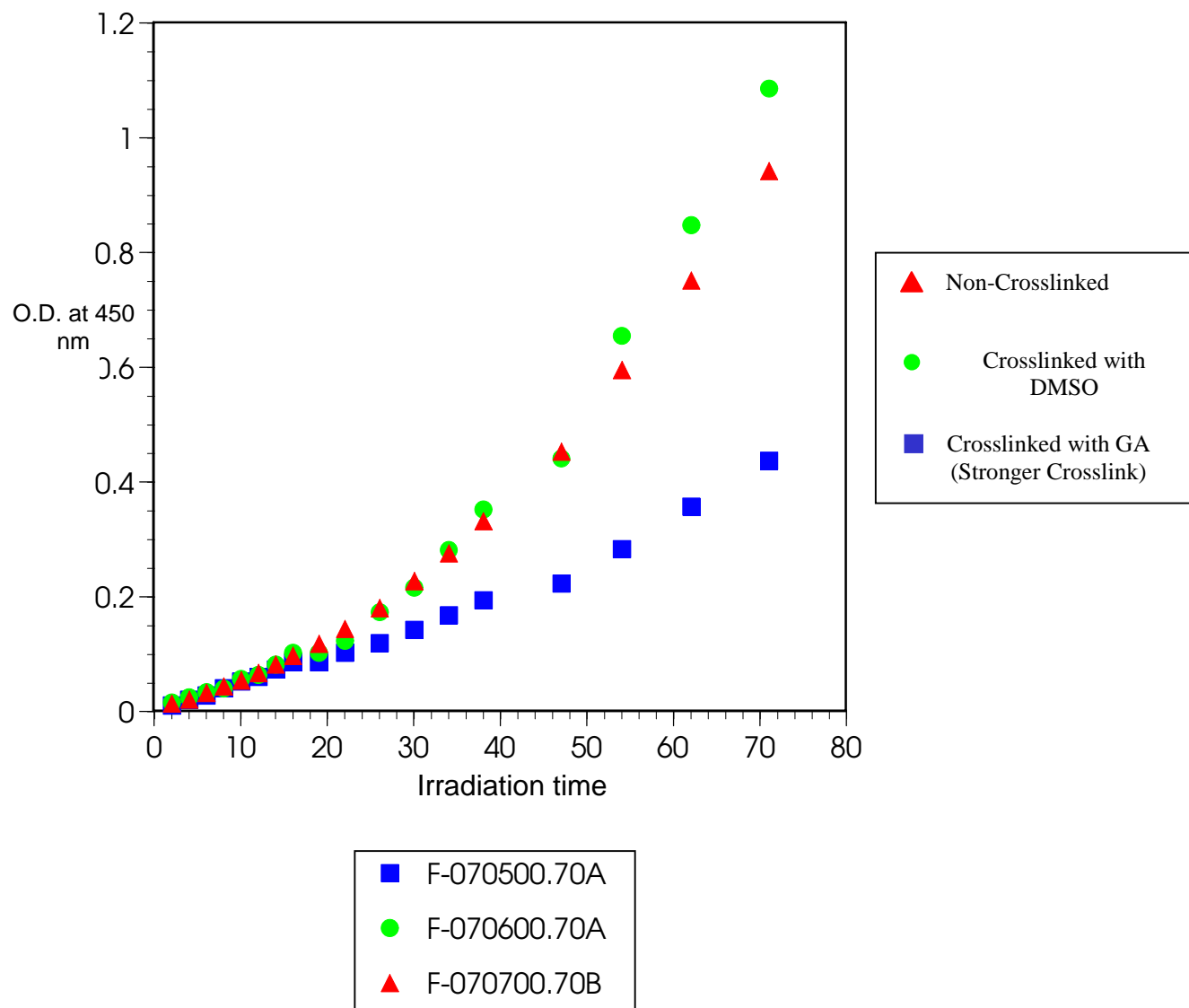
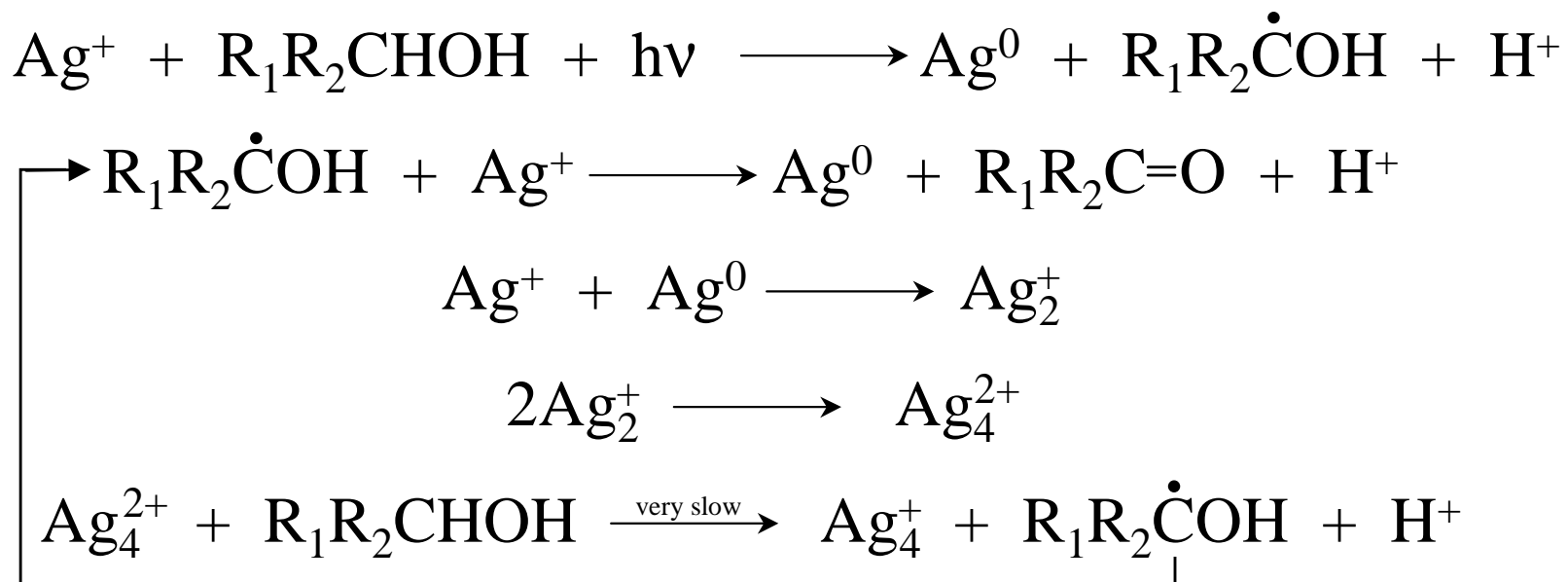
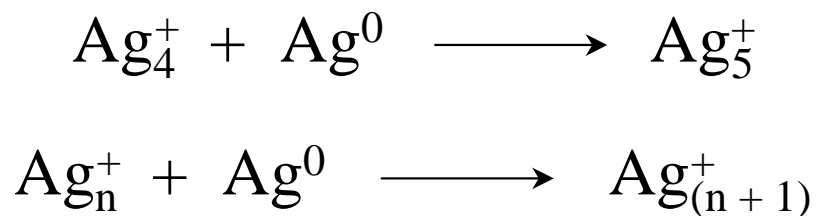


FIGURE 5. PROPOSED PHOTOGENERATION MECHANISM of Ag CLUSTERS and PARTICLES

Reduction of Ag<sup>+</sup> by Chain Reaction



Particle Formation



Bi-radical Termination

