

Mechanisms of Spectral Sensitization of Silver Halides: Role of Sensitizing Dye Complexation*

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We have observed concurrent processes of photoexcited dye deactivation and silver(0) cluster formation in real time under conditions of laser flash photolysis of a merocyanine dye adsorbed to an AgBr nanosol. To our knowledge this is the first time such a comprehensive view of the process of spectral sensitization has been obtained experimentally. Spectral sensitization of AgBr is apparently biphotonic under our conditions; this result, along with observed kinetics of dye ground state repopulation and of silver(0) cluster growth, is consistent with Mitchell's mechanism of spectral sensitization, but not with single-electron transfer or radical pair mechanisms. Control experiments revealed a modicum of photolytic reactivity for undyed nanosol with 2.35 eV photons and suggested operation of an Auger mechanism of photoelectron generation. In this case amplified stimulated emission was observed from photogenerated silver clusters, Ag_n^0 (or a by-product) at photon energies comparable to those that produce the Hirschel effect in conventional photography. We speculatively estimate nuclearity of the silver clusters produced under conditions of our experiments as $n \approx \text{ca. } 12$.

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Introduction

The literature provides a number of mechanistic proposals with respect to the mechanism of spectral sensitization of photolysis of the silver halides for latent image formation in the photographic process. The most commonly cited mechanism¹ involves single-electron injection from a photoexcited, physisorbed dye molecule or aggregate to the conduction band of a silver halide microcrystal; this electron-transfer mechanism has its roots in early proposals of Gurney and Mott² on mechanism of latent image formation. It was later abandoned by one of its initial proponents,³ but then was revived and elaborated in the elegant work of Tani.⁴ Further definitive studies have related electrochemical potentials of dye molecules to sensitizing ability in the context of this model.⁵⁻⁸ In support of this mechanism, Chibisov and coworkers⁹ claim to have ob-

served radical dication products of imida- and oxocarbo-cyanine sensitizing dyes (as would result from single-electron transfer to the conduction band of AgBr from photoexcited dye) under conditions of laser flash photolysis of dyed AgBr photoemulsions. Note that the same radical dication products would have resulted if the adsorbed dye molecules had simply trapped photoholes from the AgBr valence band or surface states.

After an earlier suggestion by one of us,¹⁰ both the Muenter¹¹ and Tani¹² groups have shown that rate constants for electron transfer, k_{et} , presumably the key step in spectral sensitization of silver halide grains with a number of cyanine sensitizing dyes, can be correlated quantitatively with dye reduction potentials, using the Marcus model for single-electron transfer. These experiments, however, obtain k_{et} from fluorescence lifetime ($1/k_f$) measurements, in which it is assumed that intersystem crossing, described by k_{isc} , is unimportant, i.e., $k_{isc} \ll (k_{et} + k_f)$. Recent picosecond- and nanosecond-resolved transient absorption spectroscopic studies on cyanine dyes in solution have shown that this may not necessarily be the case.¹³ It is furthermore equally appropriate to assign the process identified with k_{et} in this analysis to energy transfer.¹⁴

Fassler and colleagues¹⁵ have provided optical and electron spin resonance spectroscopic evidence that photoexcited dye adsorbed to a silver halide grain is reduced by an electron-donating surface state of AgBr (or a donor counterion), so that electron transfer to the silver halide conduction band occurs then from the resulting free radical species. These observations have led to the so-called radical pair mechanism of spectral sensitization.¹⁶ It can be contended, however, that this mechanism operates only in special cases, e.g., with a dye whose HOMO level is uniquely matched to that of the donor state¹¹ or under conditions of supersensitization.^{8,16}

After abandoning the electron-transfer model of spectral sensitization, Mott³ advocated an energy-transfer mechanism that presumed existence of otherwise undefined energy-accepting states located energetically within the forbidden gap of the AgBr host. This approach has been followed by Mitchell¹⁷ in his development of the "coupled electron transfer" model of spectral sensitization. Recent theoretical developments¹⁸ emphasize the continuity between energy transfer and coupled electron-transfer models. Because photon energy in spectrally sensitized photolysis is less than the dissociation energy for AgBr, it has been proposed in these models that spectral sensitization may be a biphotonic process.^{19,20} Mitchell has further proposed in this context that intrinsic, localized donor or acceptor centers within the AgBr crystals are crucial to

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Spectral Sensitization

Monique M. Martin, James T. Hynes



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Spectral Sensitization H. Meier, 1968 Near-Infrared Dyes for High Technology Applications S. Daehne, Ute Resch-Genger, Otto S. Wolfbeis, 2012-12-06 This book summarizes the results of the NATO Advanced Research Workshop on Syntheses Optical Properties and Applications of Near Infrared NIR Dyes in High Technology Fields held at Trest Czech Republic from September 24 to 27 1997 It was attended by 52 scientists from 16 countries among them 18 participants from 8 Eastern Europe The Workshop has been stimulated by the great progress that has been made in utilizing NIR dyes in high technology areas This has been triggered by the availability of reliable vel small and inexpensive laser diodes emitting in the NIR region which raise the analytical detection limits by several orders of magnitude allow time resolved measurements for temporal discrimination between spectrally similar species and make possible miniaturization as well as remote sensing through space and by fiber optical techniques Furthermore NIR dyes proved to be vel important in other high technology fields such as laser physics optical recording techniques nonlinear optics biochemistty and medicine **Photographic**

Sensitivity Tadaaki Tani, 1995-11-30 Notwithstanding the current excitement surrounding cutting edge digital imaging techniques photographic film still provides the highest resolution and most beautiful images of any medium available For the first time in nearly 20 years Photographic Sensitivity Theory and Mechanisms offers a comprehensive systematic description of the subject stressing in particular the characteristics of silver halide photography Topics range from how to prepare silver halide grains and latent image formation to spectral and chemical sensitization to the future of silver halide photography Based on the author s more than 30 years experience in the field Photographic Sensitivity will appeal to a wide range of readers including students chemists and physicists working with silver halide imaging techniques and solid state imaging

Current problems in electrophotography W. F. Berg, K. Hauffe, 2018-12-17 No detailed description available for Current problems in electrophotography *Proceedings of the Symposium on Photoelectrochemistry and Electrosynthesis on Semiconducting Materials* , 1988 **Silver Nanoparticles** Tadaaki Tani, 2015-09-17 Nanoscience and nanotechnology

concern themselves with the research and application of extremely small things and can be used across all scientific fields such as physics chemistry biology material science and engineering Nanoparticles are of great scientific interest as they provide a bridge between bulk materials and atomic or molecular structures Interesting and unexpected properties of nanoparticles are largely due to the large surface area of the material Nanoparticles of noble metals including silver Ag attract the interest of many researchers owing to their high potential for plasmonic devices in future On the other hand nanoparticles of silver Ag and silver halides AgX have played central roles and have been extensively studied for many years in silver halide AgX photography Combining knowledge of nanoparticles of Ag and related materials in plasmonics and AgX photography this book reinforces already existing knowledge but also presents new ideas for metal nanoparticles in plasmonics The first part examines the structure and formation of nanoparticles of Ag and related materials Systematic

descriptions of the structure and preparation of Ag Au and other noble metal nanoparticles for plasmonics are followed by and related to those of nanoparticles of Ag and AgX in AgX photography The exploration of the structure and preparation of Ag and AgX nanoparticles in photography incorporates nanoparticles with widely varied sizes shapes and structures and formation processes from nucleation to growth The second part describes the properties and performances of nanoparticles of Ag and related materials including chapters on light absorption and scattering catalysis photovoltaic effects and stability The accumulated knowledge of many years of research in AgX photography is analysed and explained to deepen the reader s knowledge on metal nanoparticles for plasmonics catalysis and photovoltaics with new ideas arising from the interaction between them

Photochemistry - 6 A. Gilbert, 2016-01-22 Photochemistry 6 is a collection of plenary lectures presented at the Sixth International Symposium on Photochemistry held in Aix en Provence France on July 19 23 1976 Contributors focus on the photochemistry of a variety of compounds and substances including bichromophoric compounds heterocycles and metal carbonyls The results of photochemical studies of visual pigments are also presented This book is comprised of 14 chapters and opens with a review of the state of the art of ab initio quantum mechanical calculations for polyatomic molecules with particular reference to predictions of interest to photochemists The major areas discussed are spectral predictions substituent effects on energy gaps and potential energy surfaces The following chapters explore energy transfer and molecular mobility in polymer photochemistry the photochemistry of polyenes and aromatic N ylides cis trans isomerization in the photochemistry of vision and aromatic aldehyde leuco dye photooxidation The electrochemical boundaries for the photochemistry of spectrally sensitized silver halide emulsions are also examined along with the photochemistry of organic chromophores incorporated into fatty acid monolayers This monograph will be of interest to chemists in general and photochemists in particular

Photochemical Conversion and Storage of Solar Energy E. PELIZZETTI, Mario Schiavello, 2012-12-06 The book collects the lectures and the status reports delivered during the Eighth International Conference on Photochemical Conversion and Storage of Solar Energy IPS 8 held in Palermo Italy from 15th to 20th of July 1990 As usual the main theme of the Conference was that of making the point about the trends and the developments of the studies related to the photochemical exploitation of solar energy and also to report the main lines of potential applications Therefore the contributions reflect this point they vary from those reporting basic and fundamental theories to those reporting cases of possible applications For the sake of following the logical line which links each other the various contributions we report the six areas in which the main theme of the conference was divided a Electron and energy transfer in homogeneous and heterogeneous systems b Photosynthesis organized assemblies and biomimetic systems c Photoelectrochemistry d Photocatalysis homogeneous and heterogeneous regime e Environment photochemical and photocatalytic processes f Solar energy materials and photochemical engineering It remains now to thank persons and institutions which made possible the organization of the Conference The persons to thank are all the members of the

International and National Organizing Committees and in particular Prof A Sclafani and Dr L Palmisano whose efforts were essential for the success of the Conference Journal of Research of the National Bureau of Standards United States. National Bureau of Standards,1932 *Bureau of Standards Journal of Research* United States. Bureau of Standards,1934 Journal of Research of the National Bureau of Standards ,1932 *Confidential Documents* United States. Army Air Forces,1940 *Femtochemistry and Femtobiology* Monique M. Martin,James T. Hynes,2004-04-16 This book reflects the heights of knowledge of ultrafast chemical processes attained in these early years of the 21st century the latest research in femtosecond and picosecond molecular processes in Chemistry and Biology carried out around the world is described here in more than 110 articles The results were presented and discussed at the VIth International Conference on Femtochemistry in Paris France from July 6 to July 10 2003 The articles published here were reviewed by referees selected from specialists in the Femtochemistry community guaranteeing a collective responsibility for the quality of the research reported in the next 564 pages Femtochemistry is an ever growing field where new research areas are constantly opening up and one which both stimulates and accompanies the development of ultrafast technologies The increasing interest in femtobiology and chemistry at the frontier with biology is an obvious indicator of the present impact of life sciences in our society New materials and reactions at surfaces are also some of the relatively new topics that promise rapid developments New methodologies and technologies for probing and following in real time molecular dynamical phenomena have appeared within the last ten years or so These methods based on multidimensional IR spectroscopies ultrafast X ray and electron diffraction techniques are well represented in this book Of ever improving performance they are now applied to the characterization of structural dynamics of an increasing number of chemical and biological systems This book reports the state of research in Femtochemistry and Femtobiology presented at Paris at the Maison de la Chimie in July 2003 representing the tenth anniversary of the conference Overview of the most recent research on ultrafast events Application of new methodologies on chemical and biological systems Contributions by key players in the field **J-aggregates** Takayoshi Kobayashi,1996-10-16 J aggregates have a long history of research but so far no books have been published on this group of very interesting materials The book is on the structures electronic states linear and nonlinear optical properties and spectroscopies of the J aggregates Various properties and processes of J aggregates such as superradiance excitons photon echo geometrical structure electron transfer and femtosecond spectroscopy are also discussed The contributors are those actively working in the field The Lumiere Autochrome Bertrand Lavédrine,Jean-Paul Gandolfo,2013-12-15 Louis Lumi re is perhaps best known in the U S for his seminal role in the invention of cinema but his most important contribution to the history of photography was the autochrome Engagingly written and marvelously illustrated with over 300 images The Lumi re Autochrome History Technology and Preservation tells the fascinating story of the first industrially produced form of color photography Initial chapters present the Lumi re family enterprise set out the challenges posed by early color photography and recount the invention rise and

eventual decline of the autochrome which for the first four decades of the twentieth century was the most widely used form of commercial color photography The book then treats the technology of the autochrome including the technical challenges of plate fabrication described in step by step detail and a thorough account of autochrome manufacture A long final chapter provides in depth recommendations concerning the preservation of these vulnerable objects including proper storage and display guidelines There are also engaging portfolios throughout the book showcasing autochrome photographs from around the world as part of an initiative founded by the French banker Albert Kahn as well as engrossing testimonials by children of men who worked in the Lumi re factories in the early twentieth century The appendix includes transcriptions and facsimile reproductions from the Lumi re notebooks as well as original patent documents

Official Gazette of the United States Patent and Trademark Office, 1996 Manual of Photography Ralph Jacobson, Sidney Ray, Geoffrey G Attridge, Norman

Axford, 2000-08-17 The Manual of Photography is the standard work for anyone who is serious about photography professional photographers and lab technicians or managers as well as students and enthusiastic amateurs who want to become more technically competent The authors provide comprehensive and accessible coverage of the techniques and technologies of photography The Manual has aided many thousands of photographers in their careers The ninth edition now brings this text into a third century as the first edition dates from 1890 Major new updates for the ninth edition include Coverage of digital techniques more emphasis on electronic and hybrid media Greater coverage of colour measurement specification and reproduction illustrated with a new colour plate section Dealing with the fundamental principles as well as the practices of photography and imaging the Manual topics ranging from optics to camera types and features to colour photography and digital image processing and manipulation The authors write in a reader friendly style using many explanatory illustrations and dividing topics into clear sections

Photographer's Mate 3 United States. Bureau of Naval Personnel, 1961 **Official Gazette of the United States Patent Office** United States. Patent Office, 1971 *Thin-Film*

Organic Photonics Tetsuzo Yoshimura, 2017-12-19 Among the many atomic molecular assembling techniques used to develop artificial materials molecular layer deposition MLD continues to receive special attention as the next generation growth technique for organic thin film materials used in photonics and electronics Thin Film Organic Photonics Molecular Layer Deposition and Applications describes how photonic electronic properties of thin films can be improved through MLD which enables precise control of atomic and molecular arrangements to construct a wire network that achieves three dimensional growth MLD facilitates dot by dot or molecule by molecule growth of polymer and molecular wires and that enhanced level of control creates numerous application possibilities Explores the wide range of MLD applications in solar energy and optics as well as proposed uses in biomedical photonics This book addresses the prospects for artificial materials with atomic molecular level tailored structures especially those featuring MLD and conjugated polymers with multiple quantum dots MQDs or polymer MQDs In particular the author focuses on the application of artificial organic thin films to Photonics

electronics particularly in optical interconnects used in computers Optical switching and solar energy conversion systems Bio medical photonics such as photodynamic therapy Organic photonic materials devices and integration processes With its clear and concise presentation this book demonstrates exactly how MLD enables electron wavefunction control thereby improving material performance and generating new photonic electronic phenomena

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