

# Biological nano-ceramic materials for holographic data storage

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## Abstract

New Retinal nano-ceramic materials with pillared hybrid micro-structures are fabricated for potential applications in optical holographic data storage. We observe that the Schiff bases have substantial effect on optical properties of Retinal nano-ceramic films as well as temporal response and diffraction efficiency for holographic storage. These inexpensive synthetic biological nano-ceramic thin films are good candidates for holographic storage and offer a simple procedure to solve the problems of volatility of optical storage in Retinal proteins. In addition, our study indicates feasibility of optimizing optical properties of nano-ceramic clay systems using Schiff bases for a variety of photonic applications.

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## 1. Introduction

Optical holography has been considered as the next generation technique for data storage in view of its extremely high capacity [1–4]. It is capable of processing data in parallel which enables that entire arrays of bits are delivered simultaneously, resulting in exceptional fast data access and transfer rates. Bacteriorhodopsin (bR), a biological Retinal protein has been receiving lot of attention for photonic applications [5–7]. It is among the most promising candidates for holographic memory applications due to its effective photochemistry, high stability and reversibility [8–10]. The bR molecule contains the photo-active chromophore, Retinal, linked covalently in its all-*trans* form by a protonated Schiff base and a lysine residue with the protein. Materials containing the bR possess large optical nonlinearity and unique photonic and electronic properties [5–11]. However, it has some disadvantages for optical data storage applications. For example, a

longer metastate is needed for data storage, but lifetime of the long-lived M state is only in milliseconds or seconds depending on temperature, pH, and chemical optimization [12]. P(Q) state is found to be stable at room temperature, but multi-photon excitation is needed to access this branching state and the efficiency from B to P is low ( $\sim 0.02\%$  in wild type bR). In addition, the bR films are expensive.

We fabricated Retinal nano-ceramic materials with pillared hybrid micro-structures for study of optical properties with applications in holographic data storage. We observed that the Schiff bases have substantial effect on the optical properties of the Retinal ceramic films and these biological/nano-ceramic composite thin films can solve problems of volatility of optical storage in Retinal proteins such as in bR materials. As compared to Retinal proteins, the new nano-ceramic biomaterials with their unique optical properties, low cost, ease of preparation and optimization may have many advantages for photonic applications. In addition, these materials are environmental friendly. A study of optical properties of Retinal chromophores is also important for further understanding of the photochemical process as well as the mechanism of vision.

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## 2. Preparation of biological nano-ceramic films

Laponite XLG structural grade (Southern Clay Products, TX), a synthetic layered aluminosilicate (aluminum and silicon oxides) clay, is used in our study. In order to fabricate ceramic clay films with high optical quality, the particle size of the clays is reduced to order of nanometers by using high energy sonication techniques to minimize light scattering. Aqueous laponite solutions of the clays are sonicated with a 750 W ultrasonic processor. The resulting transparent ceramic clay films cast from these solutions are studied by using atomic force microscopy (AFM). The particle sizes as small as 10 nm are obtained by using the sonication technique. Fig. 1a shows the surface topography of a nano-ceramic film obtained with AFM, indicating the film is formed with nanometer-

sized clay particles. In the sonicated samples some re-aggregation of particles is observed. Surfactants are then added to wrap the clay particles to minimize this effect. To prepare the Retinal ceramic clay films, the biological Retinal molecules are intercalated into the aqueous laponite solutions using the 750 W sonicator for one hour. By using high-energy sonic waves, the molecules can be forced into the galleries of clays to compose a micro-structure that the intercalated molecules are assembled within a pillared metal oxide matrix due to the layered structure of aluminosilicates clays [13]. Fig. 1b shows a schematic of the pillared hybrid organic–inorganic structure wherein the organic chains form discreet regions between metal oxide backbones. The resultant films were uniform and transparent. It is known that the bR molecules have pillared hybrid protein structures around photoactive Retinal molecules and these protein structures play important roles in bR photoisomerization process and its optical properties. In this investigation, we studied the optical properties of Retinal chromophores in inorganic structure of nano-ceramic clays and demonstrated that the optical films of these inexpensive synthetic materials are useful for holographic storage applications. The results also indicate feasibility in solving problems of permanent optical storage in the Retinal proteins.

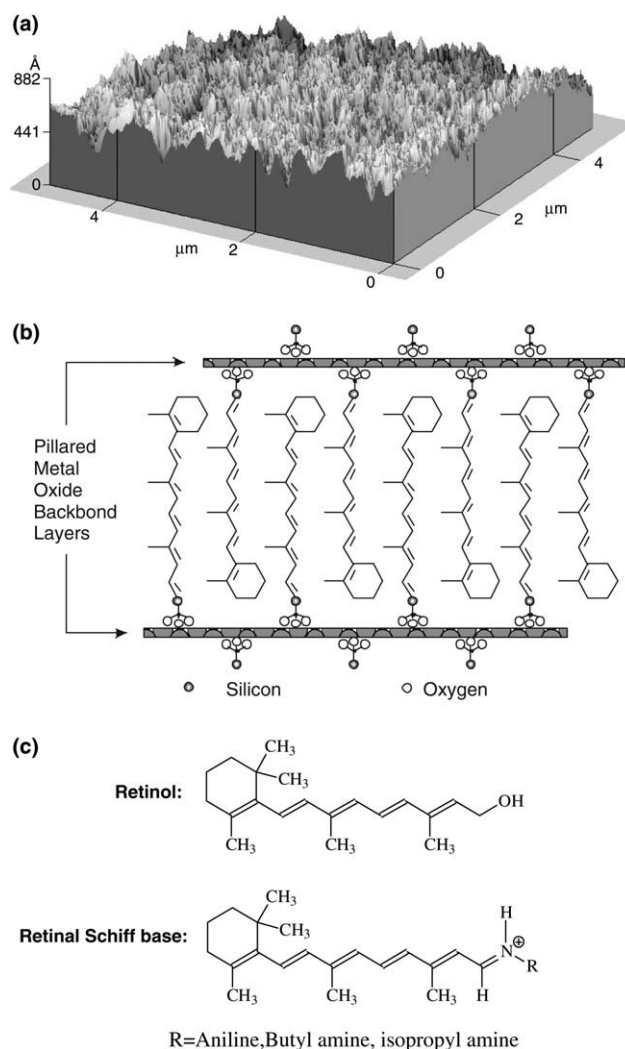


Fig. 1. (a) AFM result of surface topography of nano-ceramic film with 0.5% surfactant. (b) Schematic of Retinal/nano-ceramic composite with the pillared hybrid organic–inorganic structure. (c) Molecular structures for Retinol and Retinal Schiff bases.

## 3. Optically induced anisotropy

As a first step we investigated a simplest Retinal chromophore, Retinol (Vitamin A – a polyene biochemical involved in vision) by using photoinduced anisotropic experiments which reveal changes of refractive index and absorption of the media under irradiation of polarized laser beam. The molecular structure of Retinol is shown in Fig. 1c. The Retinol is intercalated in nano-ceramic clays with ratio of 1:10 by weight. The peak in the absorption spectra occurs at approximately 350 nm with full-width at half-maximum (FWHM) about 120 nm and beyond 500 nm no absorption is observed in the Retinol ceramic thin films. In our experiments, A 45° linearly-polarized 442-nm beam from a He–Cd laser is used to induce photoanisotropic effects in the sample. A vertically-polarized 633-nm beam from a He–Ne laser is used to probe the transient photoanisotropy of the sample. The emerging probe beam then passes through a horizontal polarizer before reaching a photodetector. Fig. 2 shows the transmission results of the probe beam due to photoinduced anisotropy of the Retinol ceramic films. In the absence of 442-nm excitation beam no 633-nm probe light reaches the detector as initially the film is optically isotropic with random distribution of Retinal chromophores. However, the probe signal appears when the film is irradiated by the polarized

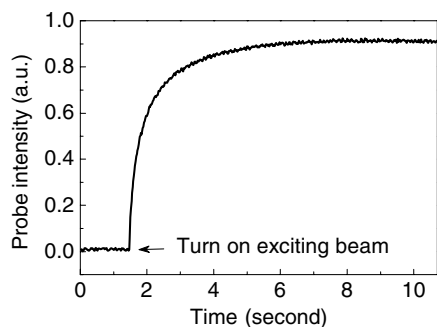


Fig. 2. Photo-induced anisotropic effect of Retinol ceramic film. The intensities for 442-nm excitation and 633-nm probe beams are 300 and 30 mW/cm<sup>2</sup>, respectively.

excitation beam. The photoinduced anisotropy is based on the fact that the photoactive Retinal chromophore has isomeric forms [14]. The stable *trans* form can isomerize to the *cis* isomer by absorption of blue light. As the exciting beam is linearly polarized, the photoisomerization process is orientation-selective in the film, that is, only those molecules oriented with their transition dipole moments for absorption in or near the electric field vector are selectively isomerized. This isomerization process then may result in the change of the pillared organic–inorganic micro-structure of the ceramic film. The spatial difference due to the two isomers of Retinol and the change of nano-ceramic structure results in optical anisotropy in the film which produces a change of polarization of probe beam. The ability of photoinduced anisotropy to convert optical properties like polarization, intensity and wavelength indicates the films may be useful for applications of all-optical devices such as optical switching, spatial light modulation, and optical storage.

#### 4. Results and discussion for holographic data storage

For the application of storage, one requires the data to remain permanently recorded until actively erased. The result of photoinduced anisotropic effect reveals that the biological ceramic films may be used in holographic storage in which data is stored in the film as refractive index grating or absorption index grating. We use two 442-nm laser beams to record holographic grating in the Retinol ceramic films. The recording beams are s-polarized with an intersecting angle of about 10°. A 633-nm beam is aligned at the calculated Bragg angle to read the grating. Fig. 3a shows the experimental results of holographic storage using Retinol ceramic film. The 633-nm reading beam is on all the time and the diffracted signal beam at the same wavelength appears as soon as the two interfering recording beams at 442 nm are turned on. After the

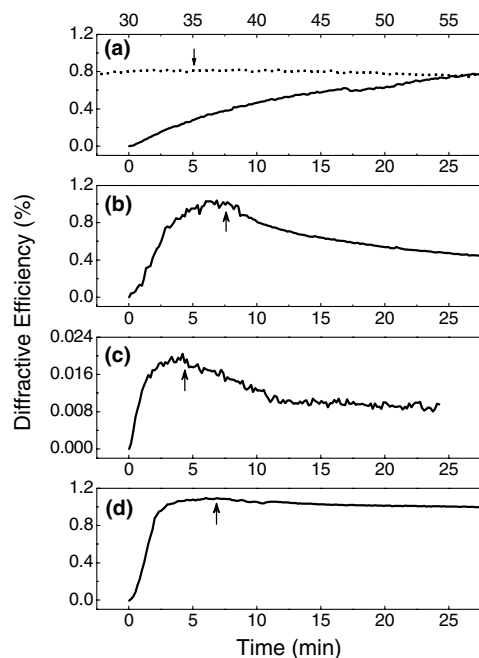


Fig. 3. Experimental results of the first-order diffraction of holographic storage using biological nano-ceramic films. (a) Retinol nano-ceramic film: solid line, signal increases after recording beams are turned on; dot line, the signal process continues with time (top time scale). (b) Retinal Schiff base (aniline) nano-ceramic film; (c) Retinal Schiff base (butylamine) nano-ceramic film. (d) Retinal Schiff base (isopropylamine) nano-ceramic film. Turn on recording beams at  $t = 0$  and turn off recording beams at the arrow. The intensity is about 100 mW/cm<sup>2</sup> for each recording beam.

diffracted signal increases to its maximum, the recording beams are turned off. Our experiments indicate that the new Retinol nano-ceramic films can be used for long-term holographic data storage in contrast to the Retinal proteins. For example, in the bR protein the data can be stored using M state for only seconds and the Retinal protein-Rhodopsin is even worse [15]. As compared to these Retinal proteins which are useful for real-time holographic memory applications [12] where long term storage is not required, the information stored in our Retinol ceramic film is retained for at least one month.

We also fabricated nano-ceramic films using several new Retinal chromophores of Retinal Schiff bases wherein Schiff bases (aniline, butylamine and isopropylamine) are covalently linked to the end of the molecules. The molecular structures of Retinal Schiff bases are shown in Fig. 1c. It is found that all three nano-ceramic films of Retinal Schiff bases have red-shifted absorption peak around 500 nm with broad absorption band from UV to 650 nm. The red shifted spectra indicates that the information can be stored in the Retinal Schiff base films with commercially available small diode lasers emitting green or red light. We use two 568-nm yellow beams from an Ar–Kr ion

laser to record holographic grating in the Retinal Schiff base ceramic films. A diode laser with output at 670 nm is used as reading beam to avoid grating erasure. Fig. 3b–d shows the results of holographic storage by using the new Retinal Schiff bases with aniline, butylamine and isopropylamine, respectively. We found that different Retinal Schiff bases change significantly the temporal features of holographic storage. These Retinal Schiff base ceramic films respond faster to recording beams than the simple Retinol ceramic films. However the diffraction signal for films of Retinal Schiff bases (aniline and butylamine) decreased after turning off the recording beams (Fig. 3b and c). The remaining diffraction signal for these two films continues for more than one week which is shorter than that of the Retinol but significantly long as compared to that of the Retinal proteins. Theoretical calculations indicate that the isomerization (rotation of C=C bond) energy barrier of *cis* conformation of some Retinal Schiff base is only 0.6 kcal/mol which is significantly lower than that of Retinol (14.6 kcal/mol) [16]. We believe the shorter storage time originates from the instability of *cis* isomer of the Retinal Schiff bases. The lower energy barrier can be easily reached at room temperature, which may result in volatility of optical storage in some Retinal Schiff base films. However, by using the films of Retinal isopropylamine Schiff base, the stored information shows no obvious volatility after the recording beams are turned off. The experimental results imply that the different Schiff bases affect the isomerization energy barrier of rotation of C=C bond differently. The isopropylamine base is able to raise the rotation energy barrier of *cis* Retinal conformation so that the photoinduced *cis* isomer becomes stable at room temperature. The experimental results also show that the Retinal Schiff bases affect significantly the diffraction efficiency of holographic storage. A diffraction efficiency of about 1% (for the first order) is obtained by using thin ceramic film of Retinal isopropylamine Schiff base. However, only 0.02% of diffraction efficiency is observed by using thin film of Retinal butylamine Schiff base. The low diffraction efficiency for Retinal butylamine Schiff base films is due to weak holographic grating of *cis* conformation. The relatively fast initial decay of the grating observed for this case indicates a short life-time of the *cis* molecules which is due to its low energy barrier. A similar relationship between energy barrier and *cis* molecular life-times was reported for the Retinal protein bR [17,18]. Since the unstable *cis* molecule can isomerize back to stable *trans* conformation easily, the population of *cis* conformation is low for the Retinal butylamine Schiff base resulting in formation of weak holographic isomerization grating. On the other hand the *cis* conformation is quite stable in the Retinal isopropylamine Schiff

base, which enables the *cis* population to be built up efficiently. As such, the resulting holographic grating is strong as compared to the Retinal butylamine Schiff base. The observation that the Schiff bases significantly alter the optical properties of Retinal ceramic materials for holographic storage application may point the possibilities of molecular design of Retinal chromophores and optimization of nano-ceramic systems for various photonic applications. Since the film thickness is only approximately 10  $\mu\text{m}$ , the observed diffraction efficiency is relatively low. High diffraction efficiency can be easily achieved by using thick films.

## 5. Conclusions

We have fabricated several new biological nano-ceramic thin films. Our study of the transient photoinduced anisotropic effects indicates that the films are useful for photonic applications. Holographic data storage is demonstrated with various Retinal nano-ceramic films. It is found that Schiff bases in the Retinal films alter optical properties like absorption spectra, temporal features and diffraction efficiency of the holographic storage. The films prepared using inexpensive synthetic biological ceramic materials exhibit unique optical properties and are able to solve problems of volatility of optical storage experienced in Retinal proteins like bR materials. It may be possible to enhance optical properties incorporating Schiff bases in new nano-ceramic clay systems for wide applications in photonics.

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