Detuned surface plasmon resonance scattering of gold nanorods for continuous wave multilayered optical recording and readout

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Abstract: In a multilayered structure of absorptive optical recording media, continuous-wave laser operation is highly disadvantageous due to heavy beam extinction. For a gold nanorod based recording medium, the narrow surface plasmon resonance (SPR) profile of gold nanorods enables the variation of extinction through multilayers by a simple detuning of the readout wavelength from the SPR peak. The level of signal extinction through the layers can then be greatly reduced, resulting more efficient readout at deeper layers. The scattering signal strength may be decreased at the detuned wavelength, but balancing these two factors results an optimal scattering peak wavelength that is specific to each layer. In this paper, we propose to use detuned SPR scattering from gold nanorods as a new mechanism for continuous-wave readout scheme on gold nanorod based multilayered optical storage. Using this detuned scattering method, readout using continuous-wave laser is demonstrated on a 16 layer optical recording medium doped with heavily distributed, randomly oriented gold nanorods. Compared to SPR on-resonant readout, this method reduced the required readout power more than one order of magnitude, with only 60 nm detuning from SPR peak. The proposed method will be highly beneficial to multilayered optical storage applications as well as applications using a continuous medium doped heavily with plasmonic nanoparticles.

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References and links

1. Introduction

Interests in plasmonic nanoparticle based optical recording and patterning is gaining momentum [1–18]. In this scheme, surface plasmon resonance (SPR) mediated light absorption facilitate efficient photothermal energy conversion that causes drastic morphological and spectral change [1, 2, 5–9, 13–15]. The exciting aspect of it is the ability to multiplex the recording. Recently five-dimensional optical storage was demonstrated, based on different sizes of gold nanorods (AuNRs) randomly distributed in polymer matrix for spectral and polarization encoding within the same volume of matrix [15]. Multilayering of the recording layer was achieved by sandwiching them with polymer spacers. The readout of the multilayered patterns was performed using two-photon luminescence (TPL) of the
AuNRs, which provides the ability to readout deeper layers without disturbing traversing layers, and much narrower spectral and polarization responses than single photon readout scheme due to the $\sim I^2$ nonlinear character.

The TPL readout, however, necessitates the use of high peak power laser such as femtosecond pulsed lasers, of which the complex, bulky and costly instrumentation prohibits modular integration into a device. For a viable device application, such high peak power pulsed lasers should be replaced with low power continuous-wave (cw) lasers. In this case, the strong scattering at SPR of nanorods can be an alternative readout mechanism. However, the cw techniques in absorptive AuNR-based multilayered recording medium have to endure huge laser power extinction through traversing layers. This issue is exacerbated in readout scheme because the laser beam has to travel the layers twice before it reaches the detector (i.e., signal $\sim$transmittance$^{-n}$, while recording power $\sim$transmittance$^{n}$ where $n$ is the number of layers).

An exemplifying situation for the signal loss in simple multilayer setting can be seen by plotting the ratio of readout signal power (reflected signal) with respect to input power, $\xi(r, n) = P_{\text{signal}}/P_{\text{input}} = (1-e)^{n-1} r$. ($r$ is reflectance, varied from 0.05 to 0.15 in the figure, and $e$ is the extinction. Neglecting absorbance, $e = r$). This is shown in the Fig. 1(A), in which the signal strength is shown to be reduced 2 orders magnitude lower, from first to 20th layer. In order to secure constant signal level, the readout power has to increase exponentially.

![Fig. 1. (A) A schematic for a typical multilayered optical recording medium. (B) Log plot of reflected signal power with respect to layer number with layer reflectance $r$ and extinction $e$ identical throughout 20 layers. The cases $r = 0.05, 0.10, 0.15$ are shown. Exponential decay of the reflected signal power is evident, and best extinction values for readout exist for particular layers. (C) An extinction cross section plot for a single gold nanorod with aspect ratio 3.14, showing sharp SPR peak, which can be useful in varying the extinction if used in multilayered recording medium.](image)

One way to compensate the huge signal loss during beam traversing is to vary the reflectance of each layer, hence to “graphic equalize” the signal level originating from each layer. Optimum reflectance level $r_i$ at $i$th layer in this case can be expressed as $r_i = r_0 / \prod_{j=1}^{i-1} (1-r_j)^2$, which equalizes the signal strength of all the layers to that of the first layer. Recently such reflectance variation method is employed in multilayered optical storage. Ichimura et al [19] demonstrated continuous wave readout on 8 stamped, read-only-memory layers and Mitsumori et al [20] extended such read-only-memory device to 20 layers. This method requires extremely precise control over layer reflectance and spacer layer thicknesses, which can be difficult for mass production. Another type of continuous wave operation is micro-holographic storage [21–23]. In this scheme, two counter-propagating beams are interfered to create micro-gratings at the overlapped focal spot, which in-turn can be readout by reflection from microgratings using a single beam focus. This method, although requires a two beam interference at a tight focus, has demonstrated the capacity to reach tens of layers.

Here in this paper, we show that the detuned scattering readout from sharp SPR condition of AuNRs can provide a unique solution to this problem, reducing the extinction loss orders of magnitude and achieve cw recording and readout up to 16 layers. This method can provide
a viable readout option for multilayered, multidimensional optical storage and patterning, as well as a characterizing method for a thick medium doped with plasmonic nanoparticles. In section 2.1 we start by simulating theoretically optical readout in multilayered recording medium based on single sized, aligned AuNRs. This is extended to the medium based on randomly distributed AuNRs in section 2.2, and in section 3, we experimentally demonstrate 16-layer readout using detuned SPR scattering.

2. Theoretical consideration on cw optical readout in AuNR based multilayered recording medium

2.1. Recording medium based on single sized, aligned AuNRs

For AuNR based optical recording medium, the unique SPR properties are the key in enabling the continuous wave operation in multilayered setting. For cw recording, the threshold photothermal melting at SPR excitation has already shown to be possible [15]. For cw readout, strong scattering signals from NRs, mediated by SPR can successfully replace the TPL. The advantage of SPR is its narrow bandwidth that enables the extinction to be varied drastically by a slight wavelength detuning from the peak. This has an effect that reduces the total layer extinction, meaning that at deeper layers lower extinction can be chosen to reduce the signal loss. However, at detuned wavelengths the strength of scattering signal is decreased. Interestingly, these two signal-strength determining factors compete with each other and results optimal readout wavelength that are specific to each layer – similar effect is illustrated in Fig. 1(B), where up to 4th layer, \( r = 0.15 \) produces strongest signal, but for 5th, \( r = 0.1 \) is the best option, and beyond 8th, \( r = 0.05 \) is the best option. In fact, having a variable extinction is highly beneficial in extracting optical information at deeper layers (or in thick medium) because of the less total extinction during the beam traversing.

The optimal detuning wavelength peak for AuNRs in multilayerd film can be identified by plotting the ratio \( \xi \) of scattering power to the input beam power in 16 layered film, using the equation,

\[
\xi(\lambda, n) = \frac{P_\text{cl}}{P_0} = c l \sigma_s(\lambda) \left[ \exp\left(-2.3 c l \sigma_e(\lambda)\right) \right]^{2(n-1)}. \tag{1}
\]

Here, \( \sigma_s \) and \( \sigma_e \) are scattering and extinction cross sections of gold nanorods, \( c \) is the concentration of the nanorods, \( l \) is the recording layer thickness. The term inside the square bracket represents the transmittance through each layer, which is assumed to be constant. The \( 2(n-1) \) power index represents a number of layers that the readout beam traverses. The \( c l \sigma_s \) term in front of the square bracket represents scattering signal generated from the readout layer in concern. In Fig. 2, ratio \( \xi \) is plotted for gold nanorods of aspect ratio 3.14 and width 14 nm with \( c \sim 40 \text{ nM} \) and \( l \sim 1 \mu\text{m} \). The calculation was based on assumptions that AuNRs have single size, shape, and orientation (Fig. 2(A)), and the impinging light has polarization matching the longitudinal direction of rods. The cross sections can be calculated using Mie-Gans theory [24], with radiation, surface scattering damping corrections [25] and end cap geometry corrections (as cylinders rather than ellipsoids [26]). Its extinction spectrum is shown in the Fig. 2(C). It is clear from the figure that from 4th layer the peak scattering wavelength is detuned from SPR peak position (833 nm) due to reduced extinction. The peak is gradually detuned further to 780 nm (or 877 nm) at layer No. 16. Therefore once recording takes places at SPR wavelength, the readout wavelength can be tuned to match the optimal peak wavelength for maximum scattering signal.

It is important to note that in the recorded region, shape transformed nanorods will have completely bleached their scattering peak and therefore the contrast between recorded region and unrecorded region is simply the scattering peak value, assuming negligible noise. Therefore the Fig. 2(B) can literally be taken as a contrast spectrum, upon recording. The recording powers at deeper layers will also be reduced due to extinction losses, and consequently detuning will occur. However, the equation for a recording power has a power
index of \((n-1)\) rather than \(2(n-1)\) in Eq. (1), reflecting one way extinction. Therefore the loss and detuning will not be as significant as the readout.

**Fig. 2.** (A) Hypothetical 16 layer sample with a single size, aligned AuNRs. (B) Log plot of scattering signal ratio \(\xi(\lambda, n)\) with respect to wavelength and layer number, for a single size, aligned AuNRs with concentration \(-40\) nM, aspect ratio 3.135 and fixed volume. Note the peak evolution at deeper layers, indicating the best readout can be achieved at detuned, off-SPR resonant wavelengths. (C) Extinction spectrum for the single size sample used in the simulation. (D) Readout power comparison between SPR on-resonant (833nm) readout and off-resonant detuned readout, assuming \(1\) \(\mu\)W for first layer power and neglecting collection efficiency. The power reduction reaches \(-1/60\) for detuned readout. (E) 16 layer sample with distributed, randomly oriented AuNRs. (F) Log plot of scattering signal ratio \(\xi(\lambda, n)\) with AuNR concentration \(-40\) nM, mean aspect ratio 3.135, and std. dev. 0.48. The required detuning is more for a distributed sample than a non-distributed sample. (G) Extinction spectrum for the distributed AuNR sample. (H) Readout power comparison between SPR on-resonant (833 nm) readout and off-resonant detuned readout. For distributed rods, the power reduction is only 1/2.4.

The optimal peak wavelength evolution at each layer is overlaid in the Fig. 2(B). Slight asymmetry in the peak shape causes the 780 nm peak being stronger than the 877 nm peak. In Fig. 2(D), we show the required laser power for equalized scattering strength of each layer in the case of on-resonant wavelength and the optimized off-resonant wavelengths, assuming the readout power on 1st layer is \(1\) \(\mu\)W. The on-resonant power is obviously exponentially increased to 1000 \(\mu\)W at 16th layer, while the off-resonant power only increases to 17 \(\mu\)W, reducing the required readout power to 1/60. It should be noted that this difference is specific to a particular nanorod size, shape and concentration, and it can further be increased upon varying these parameters.

### 2.2. Recording medium based on distributed, randomly aligned AuNRs

The situation is more complicated for a real sample, where distribution in aspect ratio, size, and random orientation of nanorods exists (Fig. 2C). In this case the Eq. (1) is modified to,

\[
\xi(\lambda, n) = \frac{P_R}{P_i} = \left[ \frac{1}{2} \int_{R_{min}}^{R_{max}} c(R)\sigma_s(\lambda, R)dR \right]^{-\frac{1}{2}} \left[ \exp \left( -\frac{3}{2} \int_{R_{min}}^{R_{max}} c(R)\sigma_e(\lambda, R)dR \right) \right]^{-\frac{1}{2(n-1)}}
\]

where \(c(R)\) is a concentration distribution function with respect to the aspect ratio \(R\), which can take a normal distribution form with a mean aspect ratio \(R_{mean}\), and its standard deviation \(\sigma_R\).
i.e., $c(R) \sim N(\mu_R, \sigma_R^2)$. $\frac{1}{2}$ factor at the front of concentration is required to take account the contribution from 2D random orientation of nanorods. If an independent relationship between nanorod volume and aspect ratio $R$, i.e., $V(R)$ is known, the $c(R)$ function can be extracted from extinction spectra of a recording sample by fitting the function,

$$\text{Ext}(\lambda) = \frac{1}{2} \int_{R_{c}}^{R_{e}} c(R) \sigma_{\lambda}(\lambda, R) dR$$

(3)

to an experimental extinction spectra. Care must be taken in this procedure, because depending on $V(R)$, the concentration function $c(R)$ and resulting scattering spectrum can take completely different profiles. Examples of different $V(R)$ functional forms, i.e. $V(R) \sim R$ (constant NR width), $V(R) \sim 1/R^2$ (constant NR length), $V(R) = \text{constant}$ (constant NR volume), and the corresponding $c(R)$ distributions are presented in Appendix section (1), where all three different conditions of $V(R)$ are shown to make large difference in the $c(R)$ as well as scattering profile.

The scattering signal spectrum of distributed NR sample in mulilayers is shown in Fig. 2(F), where a Gaussian distribution in aspect ratio ($\mu_R = 3.14$, $\sigma_R = 0.48$) with a fixed volume of 70000 nm$^3$ is introduced as $c(R)$ to the nanorods inside a recording medium. The total concentration of nanorods is kept at 40 nM. The effect of distribution is two-fold. Firstly, scattering peak is broadened for all layers as expected, which result a) increase in amount of detuning from SPR peak (~100 nm of peak evolution illustrated in Fig. 2(F)), and b) the readout signal power enhancement at off-resonant wavelengths at deeper layers being diminished (enhancement only to 2.4 times at 16th layer, compared to single size, aligned case of 60 times). This is illustrated in Fig. 2(H). Secondly, significant scattering background originating from the non-resonant, unmelted nanorods in the focal region can overshadow the benefits of detuning. For a distributed sample, a spectral hole burning effectively takes place during recording, i.e., NRs with matching SPR wavelengths and polarization will be shape-transformed and their scattering peak will be reduced. However the scattering peak will not disappear completely because of the contribution from remaining unmelted NRs that were non-resonant to the recording wavelength, as well as oriented ± 25° away from the polarization direction of recording light [15]. This will constitute as a background in the readout. We have calculated a spectrum of a recorded region (with $\lambda_{\text{record}} = \lambda_{\text{SPR}} = 830$ nm) by negating the spectra of AuNRs in resonant condition, and is shown together with unrecorded spectra in Fig. 3(A). One can expect that the difference between the recorded and unrecorded scattering spectra (background) will constitute a written bit, i.e.

$$\Delta_{\text{scattering}}(\lambda, n) = \xi_{\text{unrecorded}}(\lambda, n) - \xi_{\text{recorded}}(\lambda, n).$$

(4)
Fig. 3. (A) Spectra of recorded and unrecorded region, showing the difference between the two \( \Delta \text{scattering} \). Constituent NR spectra show that the resonant NR spectra are reduced (but not completely, due to contribution from misaligned NRs). Note the maximum \( \Delta \text{scattering} \) is at the recording wavelength. (B) \( \Delta \text{scattering} \) spectrum in multilayer setting, with recording wavelength fixed at SPR. There is no peak detuning at all layers and consequently off-resonant readout provides no real benefits for readout at deeper layers. (C) \( \Delta \text{scattering} \) spectrum in multilayer setting (c ~80 nM), now with recording wavelength also detuned and readout wavelengths being identical to recording wavelength. The graphs show clearly that, at detuned peaks, \( \Delta \text{scattering} \) is much more enhanced compared to that at SPR peak wavelength in deeper layers. (D) Enhancement in \( \Delta \text{scattering} \) and the amount of detuning required for the \( \Delta \text{scattering} \) spectrum, with respect to AuNR concentration. Higher concentration generally makes the higher enhancement in \( \Delta \text{scattering} \), but also increases the amount of detuning. (E) Contrast, i.e., the ratio of \( \Delta \text{scattering} \) (Fig. 3(C)) to the total scattering strength (Fig. 2(F)) reveals that as the detuning increases, the contrast decreases – an expected result, because NR number decreases as the detuning from SPR increase. The contrast spectrum is identical throughout the layers.

If \( \Delta \text{scattering} \) is plotted for each layer (Fig. 3(B)), one can see that the maximum change happens at the SPR wavelength throughout the layers and the peak is no longer detuned from the SPR at deeper layers. This means that detuning readout wavelength from recording wavelength no longer helps improve the readout power, and there is no real benefit in detuned readout when nanorods are distributed. The scattering contributions from non-resonant NRs that are not shape-transformed during laser irradiation are responsible for swamping the advantages of detuning that we have seen in Fig. 2. The constituent NR spectrum of recorded region in Fig. 3(A) show that, similar to the spectral hole-burning examples, non-resonant NRs having their aspect ratios larger or smaller than the resonant NRs are unaffected upon recording, therefore appearing as background noise in detuned readout.

However, this can be rectified if the recording and readout wavelengths both are detuned together at identical wavelengths. Since the \( \Delta \text{scattering} \) is maximized at recording
wavelengths for distributed sample (Fig. 3(A)), this method can reinstate the advantage of the
detuned readout. The plot of $\Delta$scattering for detuned recording-readout for each layer is
shown in Fig. 3(C) illustrating the detuned peak at deeper layers. The benefits of detuning
from the SPR resonant condition is therefore reinstated. In Fig. 3(D), the enhancement in
$\Delta$scattering and the amount of wavelength detuning is plotted against the AuNR
concentration, indicating that the increase in concentration benefits the $\Delta$scattering
enhancement exponentially, while the peak detuning is increased.

At this stage, it is important to recognize the ratio of $\Delta$scattering to the total scattering
strength for each layer, defined as contrast of the bit,

$$\text{Contrast}(\lambda, n) = \frac{\Delta \text{scattering}(\lambda, n)}{\text{scattering}(\lambda, n)} = 1 - \frac{\xi_{\text{recorded}}(\lambda, n)}{\xi_{\text{unrecorded}}(\lambda, n)}. \quad (5)$$

In other words, even if the absolute value of $\Delta$scattering is large, its ratio to the total
scattering strength, i.e., Contrast ($\lambda, n$), can be small. When Contrast ($\lambda, n$) is plotted against
the wavelength and layer number (Fig. 3(E)), all the layers show identical behavior, i.e.,
maximum contrast of 38% at the SPR peak and decreasing contrast as detuning becomes
larger. This behavior is understood from the fact that contrast is primarily determined from
AuNR numbers in the layer. Consequently contrast will be the largest at the SPR peak and
then slowly decreasing as the wavelength detune further away from the SPR peak. Therefore
the increase in peak detuning is not always desirable because of a reduced contrast. This is an
interesting observation, because the absolute $\Delta$scattering is seen to be maximum at the
detuned peak (Fig. 3(D) @ 725 nm), the contrast at that point is rather small at 23% (Fig. 3(E)
@ 725nm). On-resonance is the other extreme case (i.e., @ 833 nm), where despite both
$\Delta$scattering (Fig. 3(C)) and scattering (Fig. 2(F)) signals being low, the contrast ratio is at
maximum (38%). This illustrates that the readout wavelength needs to be carefully selected
with detuning information gained from Fig. 2(F), Fig. 3(C), and Fig. 3(E).

3. Experimental

3.1. Characterization of 16-layer recording medium with distributed, randomly aligned
AuNRs

Based on the theoretical analysis, we have conducted microscopic and optical characterization
of the 16 layer AuNR recording sample to determine the optimal detuned readout wavelength.
The sample was created using the method described previously [15]. Briefly, we produced
near-cylindrical AuNRs with mean aspect ratio 3.14 using the seed-mediated growth method
[27]. The average length and width of rods were 42 and 14.4 nm respectively, with a peak
SPR wavelength occuring at 780 nm in water. We washed the NRs twice, mixed with a 15%
weight solution of polyvinyl alcohol (PVA, 34k MW, Aldrich) at high concentration and the
recording layer was spin-coated. Our previous work with this method has shown this to
produce gold nanorod/pva films of 1 µm thickness [15]. For the 0.9 numerical aperture
objective used in our setup, this corresponds to 25 rods per focal volume. The final SPR
wavelength of the rods is shifted to 833 nm, reflecting the higher refractive index of the PVA
(n = 1.516) compared with water. On top of the spin-coated layer, we placed 10 µm thick
pressure adhesive spacer layer (LINTEC Co. Japan), and then the whole process was repeated
16 times. Total extinction of the sample was 2.3 indicating extinction of 0.14 per layer (~140
nM AuNR concentration per layer). Total thickness of the sample was ~200 µm. Because of
the working distance limit of the objective lens we used (~200 µm), we could not record or
read more than 16 layers.
A transmission electron microscope (TEM) image and aspect ratio histogram of AuNR used in the sample is shown in the Fig. 4(A). From the TEM image and aspect ratio histogram, we analysed the volume of the nanorods with respect to the aspect ratio, i.e., $V(R)$, which is plotted in Fig. 4(B). It is interesting to note that the volume increases as the aspect ratio decreases, hinting that stronger scattering signal is expected from the shorter aspect ratio rods (i.e., scattering $\sim V^2$). A best fit line ($V(R) = 30650 R^{-1.29}$) is plotted on top of Fig. 4(B). This functional form of $V(R)$ is used together with the extinction profile of the 16 layer sample shown in Fig. 4(C) (black line) to extract the concentration function $c(R)$, as described earlier (Eq. (3)). The extracted $c(R)$ overlaid on the histogram of NRs in Fig. 4(A) shows that they are in good agreement, validating the methodology in identifying concentration function $c(R)$. Using $c(R)$ and $V(R)$ functions we have also calculated an expected scattering spectrum (Fig. 4(C), red line), and compared it with an experimental scattering spectrum from a layer (blue line). A reasonable agreement between the two is observed, and importantly, both show a blue shift of 25 nm from the extinction spectrum. This indicates that the stronger scattering component arising from shorter aspect ratio rods is dominating the scattering spectrum. This blue shift causes a mismatch between the scattering signal peak and the layer extinction peak, producing a distorted signal profile. Expected scattering signal ratios $\xi(\lambda, n)$ for 16 layers calculated using $c(R)$ and $V(R)$ functions of this sample are plotted in Fig. 4(D). Slightly
skewed, blue-shifted spectrum in the first few layers are the result of strong scattering from shorter aspect ratio rods, while deeper layers beyond 4th, a dip appears at the extinction peak 833 nm. At 16th layer, the scattering signal ratio enhancement at detuned peak is almost 3 orders of magnitude, compared to that of the SPR peak. However, the overlaid peak evolution shows that the peak detuning at deeper layers is large, reaching below 700 nm. At such large detuning, the \( \text{Contrast}(\lambda, n) \) is reduced to less than 15\% (Fig. 3(E)) and a compromise between maximum contrast and maximum signal had to be reached. We chose the detuning wavelength to be no lower than 765 nm, keeping the contrast above 30\%. The optimized detuning wavelength is overlaid in Fig. 4(D), which reduces the enhancement in scattering signal ratio from 3 orders of magnitude to 1 order of magnitude.

3.2 Demonstration of cw readout on 16-layer recording medium with distributed, randomly aligned AuNRs

Based on the optimal detuned wavelengths determined for this particular sample, optical recording and readout on each layer were conducted using a continuous wave mode Ti:Sapphire laser, tuneable from 700 ~1000 nm. We used a long working distance oil immersion lens with numerical aperture 0.9 for recording and readout. The recording laser irradiation duration was varied between 1 ms and 5 ms. Power and duration of the laser was controlled to avoid photothermal micro-void formation [28]. The sample refractive index was matched with immersion oil, front and back of the sample so that there is no spurious reflection from the sample. Recording beam power was varied from 10 ~115 mW and the readout beam power was also varied from 100 \( \mu \)W to 10 mW depending on the layer number. The sample was attached to a 3D scanning stage and was raster scanned for recording and readout. Scattering signal from the nanorod layer was collected using the same objective and was fed into a photomultiplier tube (PMT) for readout. The PMT voltage was adjusted to reduce the laser power for retrieving patterns at deeper layers.

In Fig. 5, the CW readout of patterned images total 16 layers using detuned wavelengths are shown, where consistent image qualities are observed to the 16th layer. We have only detuned down to 765 nm at 16th layer to keep the contrast of the images at a reasonably constant level (varying between 30\% to 38\% for 16 layers, see Fig. 3(E)). In Fig. 5(B), CW laser readout power at detuned and on-resonant wavelengths used for constant readout signal level is plotted against the layer number. The bias voltage of the PMT was increased at deeper layers to keep the readout power at low level. Therefore the readout power levels shown in Fig. 5(B) are corrected values for the case of constant PMT voltage. Overlaid is the theoretical readout power, extracted from Fig. 4(D). One can see a good agreement between the theory and experiment, with more than one order of magnitude reduction in detuned readout power at layers above 11 compared to on-resonant readout powers. The recordings were checked and confirmed to be due to photothermal reshaping of resonant nanorods – by rotating the readout beam polarization 90 degrees to the recording polarization, we confirmed the image disappearance. This is shown in Fig. 5(C).
Fig. 5. (A) CW readout images (50 x 50 µm$^2$) on 16 layer sample, with readout power and contrast optimised experimentally. (B) CW laser power used for constant readout signal level. The readout was performed with PMT with variable bias voltage, therefore the actual readout power used are much smaller than shown in the figure. The readout of the pattern was conducted using two wavelength, one at detuned (varied between 833 ~765 nm) and one at extinction peak (833 nm). (C) The patterns recorded were all confirmed to be due to photothermal melting of AuNRs, by checking the scattering images with readout beam polarization orthogonal to that of the recording beam. Cases for layer 1 and 16 are shown in the figure, which show little traces of the original recordings.

The benefits of detuned readout are clearly evident in the figures. While the current study has focused on maintaining a reasonable contrast (> 30%) by not detuning fully, it is possible to reduce the readout power up to 3 orders of magnitude as seen in Fig. 4(D). Reduced contrast of images may then be compensated by improving signal-to-noise ratio, which is outside the scope of the current study. Further, similar methodology can be applied for detuning in the polarization domain rather than spectral domain. For this to be possible, the AuNRs in the recording medium need to be all aligned, similar to the hypothetical situation shown in Fig. 2(A). In this case, the readout beam polarization from the NR longitudinal direction is the detuning parameter. This potential scenario is shown theoretically in Appendix section 2. However, polarization detuned readout is impossible with current randomly oriented nanorod sample, because the scattering at SPR peak is omni-directional, i.e., no peak exists in polarization domain. Producing perfectly aligned nanorods in large scale and in multilayers is also challenging, but perhaps with modern fabrication technologies such as electron beam and focused ion beam lithography techniques, detuning in polarization may be possible.

4. Conclusions

In conclusions, we have proposed the detuned continuous wave recording and readout on gold nanorod based multilayered optical storage, and demonstrated the 16 layer readout with more than one order of magnitude reduction in laser power by detuning only 60 nm from SPR peak. We have demonstrated that the detuned readout can operate in heavily distributed and randomly oriented nanorod sample, but with a single size, aligned nanorods the benefits can be maximised. This work will be obviously highly beneficial to future high-density optical storage applications based on gold nanorods, where complicated pulsed laser operation can be replaced with cost and space effective continuous wave lasers. This technique can easily be extended to one hundred layers in multilayered in optical storage with longer working
distance objective lens, and will help the data capacity of optical storage systems to ready beyond Terabytes per disk. This work can also be beneficial to many other areas of gold nanorod applications, where nanorods are embedded inside of a thick continuous medium. For example in bio-labelling applications [29, 30], where nanorods are penetrated deeply into a tissue, the SPR scattering peak will be detuned and therefore off-resonant readout shall produce stronger signals at a fraction of power. Many photonic device applications [31, 32], where heavy nanoparticle doping is required will also benefit from the proposed technique.

Appendix 1: The effect of volume variation in AuNR scattering and concentration profiles

In this section, we demonstrate the effect of AuNR volume function \( V(R) \) for determining concentration function, \( c(R) \), by fitting Eq. (3) in the main text to the experimental extinction spectra.

As can be seen in Fig. 6, it is vital that the \( V(R) \) function is determined before the correct \( c(R) \) can be extracted. Previous methods by Eustis & Elsayed [33] simply assumes a constant volume for varying aspect ratio for seeded growth method of AuNRs, but as seen in Fig. 4(B), this can vary sample by sample. Further, as shown in Fig. 6(C), the scattering profiles of the samples can be completely different to extinction profile. This can cause an asymmetry in detuning profiles, as seen in Fig. 4(D).

Fig. 6. The effect of varying \( V(R) \) on determining \( c(R) \) and scattering spectrum. (A) Legends for different \( V(R) \) functional form on different conditions, i.e., constant length, constant volume and constant width. (B) Fits to experimental extinction profile of AuNRs, demonstrating that all three conditions can easily fit to experimental results. (C) Resulting scattering profiles plotted using parameters obtained by fitting experimental extinction profile in (B). It clearly shows the large differences in the scattering profile for each \( V(R) \) condition, even though their extinction profiles are identical. (D) Resulting concentration function \( c(R) \) profiles plotted using the parameters obtained by fitting experimental extinction profile in (B). Again, it shows large differences in concentration profiles, even though their extinction profiles are identical.
Appendix 2: Detuned polarization readout

While it is challenging to demonstrate experimentally, the detuning methodology can be extended to polarization domain. In this case, the readout beam polarization from the peak alignment to the NR longitudinal direction is the detuning parameter, as shown in Fig. 7(A). As shown in the diagram, it should be assumed that the NRs in the recording medium are all perfectly aligned to one direction. The Eq. (1) now takes the form,

\[ \xi^{SPR} (\theta, n) = \frac{P}{P_0} = c \sigma^{SPR}_e (\theta) \left[ \exp(-2.3c\sigma^{SPR}_e (\theta)) \right]^{\frac{1}{n}} \]  

(A1)

where the superscript SPR represents that the readout wavelength is at the SPR peak. If the NRs are all aligned to the 90° (arbitrary direction) in the layers, as the layer number increases, it is more efficient to readout using detuned polarization than at the peak 90°. This is shown in Fig. 7(B) where the best polarization angle to readout for each layer is slowly detuned away from 90°. Experimental demonstration of this method is impossible with current randomly oriented nanorod sample, because the polarizational SPR peak disappears. Producing perfectly aligned nanorods in large is also challenging, but perhaps with modern fabrication technologies such as E-beam and Focused ion beam techniques, detuning in polarization could be possible.

Fig. 7. (A) In the case of polarization detuned readout scheme on perfectly aligned and single sized AuNR array, the laser polarization direction relative to the longitudinal direction of AuNRs (θ) becomes the detuning parameter. (B) Log plot of scattering signal ratio ξ with respect to readout polarization direction and layer number.

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