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Magnetic Tuning of Plasmonic Excitation of Gold Nanorods

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Ⓢ *Supporting Information*

ABSTRACT: By using gold nanorods as an example, we report the dynamic and reversible tuning of the plasmonic property of anisotropically shaped colloidal metal nanostructures by controlling their orientation using external magnetic fields. The magnetic orientational control enables instant and selective excitation of the plasmon modes of AuNRs through the manipulation of the field direction relative to the directions of incidence and polarization of light.

Localized surface plasmon resonance (LSPR) of noble metal nanostructures has been intensively studied for a wide range of applications, such as chemical sensing, optoelectronics, catalysis, and photothermal therapy.[1−5] As the oscillation of electrons is sensitive to the size, shape, and surrounding of the particles, many efforts have been devoted to tuning the plasmonic property by controlling these parameters during chemical synthesis of the metal nanostructures[6−14] or by assembling them into defined secondary structures to take advantage of the near-field plasmonic coupling between neighboring particles[15−19] or controlling their alignment if the nanostructures are anisotropic in shape.[20−26] In spite of these prior studies, instantaneous and reversible tuning of the plasmonic property of metal nanostructures remains a challenge, which however holds great promise for developing novel optoelectronic devices and more effective chemical and biomedical sensors by allowing instant selective excitation or quenching of specific plasmon modes.[27−29] For the first time, we report the dynamic and reversible tuning of the plasmonic property of colloidal anisotropic metal nanostructures by controlling their orientation using external magnetic fields. By using gold nanorods (AuNRs) as an example, we demonstrate that magnetic orientational control of the nanostructures can be achieved by binding them to superparamagnetic iron oxide nanorods in a parallel manner so that the resulting hybrid nanostructures tend to align along the external magnetic field in order to minimize the magnetic potential energy, thus enabling selective excitation of the plasmon modes of AuNRs through the manipulation of the field direction relative to the directions of incidence and polarization of light.

AuNRs usually display two resonance modes: transverse and longitudinal modes, which correspond to two bands of different wavelengths in extinction spectrum.[30] The band at a shorter wavelength is attributed to the excitation of transverse plasmon, in which electrons oscillate along the short axes, whereas the band at a longer wavelength results from the excitation of longitudinal plasmon, in which electrons oscillate along the longer axis. The excitation of transverse and longitudinal modes is determined by the orientation of the nanorods relative to the direction of oscillating electric field of incident light, in other words, the polarization of light.[31] When the polarization of light is parallel to the long axis of the nanorods, only the longitudinal plasmon is excited. Similarly, only the transverse mode will be excited if the polarization of light is parallel to the short axes of AuNRs. Figure 1 schematically illustrates the excitation of plasmon modes of AuNRs upon the incidence of ordinary light. For the simplicity in discussion, the direction of light is fixed in *y* axis, and then the electric field of light oscillates in *xz* plane as it is always perpendicular to the propagation direction of light. If AuNRs are aligned along *z* axis, both the transverse and the longitudinal plasmon along the *x* and *z* axes will be excited, displaying two typically observed bands in the extinction spectrum. Aligning AuNRs along the *x* axis leads to a similar result as both longitudinal and transverse modes can be excited. However, a dramatic difference occurs when AuNRs are aligned

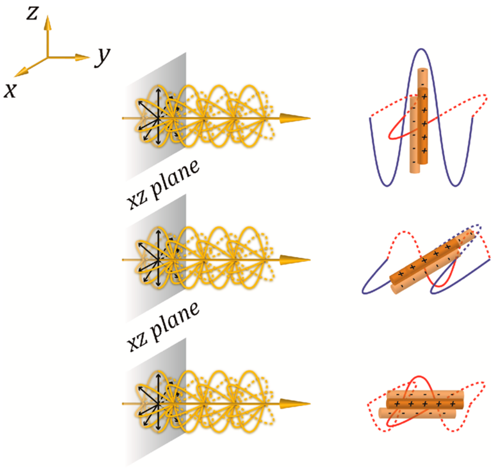

Figure 1. Plasmon excitation of AuNRs under ordinary light. The black arrows indicate the polarization of light, and blue curves represent longitudinal plasmon resonance, while red curves represent transverse plasmon resonance.

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along the *y* axis. In this case, electron oscillation only occurs along the short axes, therefore results in the excitation of transverse plasmon only.

The above analysis suggests a new mechanism that allows dynamic tuning of the optical property of AuNRs even under normal light illumination. A critical question is then how to enable instant and reversible alignment of AuNRs in three dimensions. Magnetic field is an ideal tool for this purpose because it can be applied instantly and remotely.[32−34] Another important advantage of magnetic control is the anisotropic nature of magnetic interactions, which allow effective alignment of magnetic dipoles along the external fields. However, as Au is nonmagnetic, additional magnetically active material needs to be incorporated to enable the desired magnetic orientational control of AuNRs. This challenge can be overcome by attaching AuNRs to the surface of magnetic nanorods in a parallel manner so that orientational control of AuNRs can be simply achieved by aligning the magnetic nanorods. As magnetic nanorods tend to orient themselves parallel to the direction of the external magnetic field to minimize their magnetic potential energy and dipole−dipole interaction,[35] the AuNRs attached to the magnetic nanorods will be aligned along the same direction, thus enabling magnetic control of their plasmonic excitation.

In order for the designed scheme to work, there are a few requirements on the magnetic nanorods. The most important requirement is that their net magnetization should be small enough to avoid magnetically induced aggregation, but their magnetic response should be strong enough to guarantee an effective reorientation under normal magnetic fields. The diameter of the magnetic nanorods should be kept close to that of the AuNRs so that a parallel attachment is highly preferred when the two types of nanorods are brought together through coordination covalent bonds. In order to produce magnetic nanorods with the required features, we have developed a unique solution phase synthesis which involves first preparation of nonmagnetic iron oxyhydroxide (FeOOH) nanorods,[36,37] coating with a thin layer of silica through a sol−gel process and then dehydration and reduction in diethylene glycol to produce magnetite (Fe_3O_4) nanostructures of a similar morphology. The silica layer on the surface plays important roles: it helps maintaining the rod-like morphology during reduction, prevents the as-reduced magnetic Fe_3O_4 from aggregation, and also facilitates the surface functionalization of magnetic nanorods with amino-groups for linking to AuNRs. AuNRs stabilized by polyvinylpyrrolidone (PVP) were synthesized[38] and then allowed to bind to magnetic nanorods through the amino groups grafted to the Fe_3O_4 surface. Due to the high affinity between gold surface and amino groups, AuNRs tend to attach to the magnetic nanorods by maximizing the contact area, as confirmed by the TEM observation shown in Figure 2a.

Magnetic tuning of the optical property of the AuNRs under ordinary light is then investigated. In accordance with the above discussion, the perceived color of AuNRs changes with the direction of magnetic field (see Supporting video). When the field is parallel to the incident light, AuNRs are aligned along the same direction so that only transverse plasmon can be excited, resulting in a red color of the dispersion; when the field is tuned perpendicular to the direction of incidence, the color turns to green, owing to the dominant excitation of the longitudinal plasmon mode. The plasmon response is very sensitive to the external magnetic field, including both its direction and strength. As the angle between the directions of incident light and the magnetic field changes from 90° to 0°, the excitation of longitudinal mode decreases in magnitude, leading to an attenuated band at the wavelength of around 700 nm, as shown in Figure 2b. Meanwhile, only a slight change over the plasmon band at 520 nm can be observed as transverse plasmonic mode is excited all the time. Importantly, only a relatively weak magnetic field is required to drive the rotation of nanorods. As shown in Figure 2c, when a magnet moves along the incident direction toward the sample, the resonance band at 700 nm becomes significantly suppressed. A change in the extinction spectrum can be observed when the magnet is 20 cm away from the sample, which corresponds to a field strength of 8 G, indicating an acute response of the sample to magnetic fields. The band at 700 nm reaches a minimum at a sample-magnet distance of 4 cm, corresponding to a field strength of 50 G.

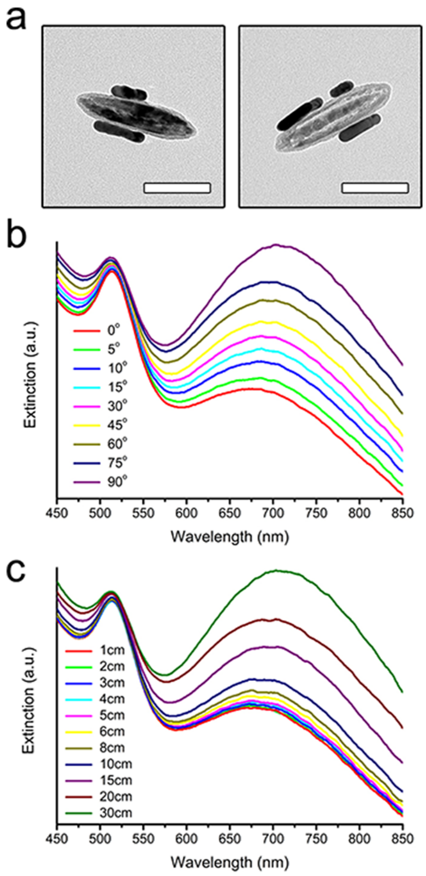

Figure 2. (a) TEM images of the as-assembled structures; scale bar: 100 nm. (b) Spectra of a dispersion of the hybrid nanostructures under magnetic fields with different directions relative to that of the incident light (from perpendicular (90°) to parallel (0°)). (c) Spectra of the dispersion under magnetic fields with varying strengths controlled by the sample-magnet distance. The field direction is parallel to the incident direction of light.

Magnetic orientational control of AuNRs under the illumination of linearly polarized light provides more opportunity in tuning their plasmon resonance, e.g., by completely suppressing either the transverse or longitudinal modes. As schematically illustrated in Figure 3a, under the illumination of *z*-polarized light incident along *y* axis, the plasmon excitation of AuNRs changes differently when they are rotated in the *yz* and *xy* planes. When AuNRs are aligned along the *z* axis, the transverse mode resonance is completely

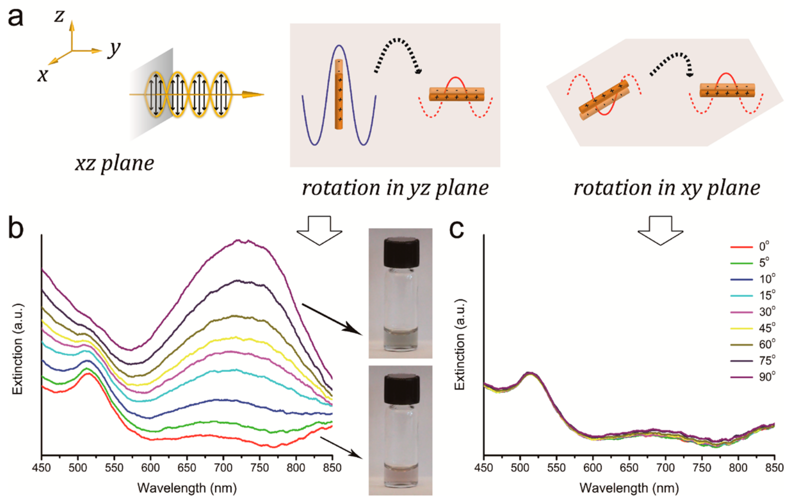

Figure 3. (a) Scheme showing the plasmon excitation of AuNRs under polarized light. (b) Spectra of a dispersion of the hybrid nanostructures under a magnetic field with its direction varying from perpendicular to parallel within the *yz* plane relative to the incident light. The incident light is polarized along the *z* axis. The inset shows digital images of the dispersion under a magnetic field with its direction parallel (bottom) and perpendicular (up) to the incident beam. (c) Spectra of the dispersion under a magnetic field with its direction varying within the *xy* plane from perpendicular to parallel relative to the incident light.

suppressed, and only a strong band for longitudinal mode can be observed (Figure 3b). Rotating the nanorod orientation from *z* toward *y* axis gradually enhances the transverse plasmon excitation while at the same time suppressing the longitudinal mode, as evidenced by the gradual decrease of the band at 700 nm and rise of the one at 520 nm. In the end, the band at 700 nm disappears almost completely, indicating very good alignment of AuNRs along the *y* direction. The color of nanorod dispersion changes accordingly, from green to red, as shown in the inset in Figure 3b. When the orientation of AuNRs is tuned within the *xy* plane, the longitudinal mode cannot be excited so that only the band at 520 nm dominates the absorption spectra (Figure 3c) and the AuNRs dispersion remains in a red color.

In order to obtain a quantitative understanding of the rate of optical response, we illuminated the system with laser beams under alternating magnetic fields.[39,40] Upon the application of an alternating field parallel to the incident direction, the AuNRs oscillates, leading to alternating changes in their orientation and consequently extinction spectra. As indicated in Figure 4, in a ~200 Hz magnetic field, AuNRs showed a 6% modulation to the intensity of a laser beam at 650 nm (red curve), which is close to the excitation wavelength of longitudinal mode. To confirm that this effect resulted from AuNRs, another laser beam at 532 nm (corresponding to the resonant wavelength of the transverse mode) was chosen, and only a 0.15% modulation was achieved. The modulation percentage shows no changes after many cycles, indicating good reversibility of the magnetic tuning. The optical response of the system to a rotating magnetic field has also been tested by placing the colloidal dispersion on top of a magnetic stirrer and illuminating it with light. The nanorods self-rotate just like a stir bar, displaying alternating green and red colors under ordinary light with an incident direction parallel to the rotating plane of stirrer. Interestingly, no color change can be observed when the sample is illuminated under lights polarized perpendicular to the rotating plane, in great accordance with the above discussions.

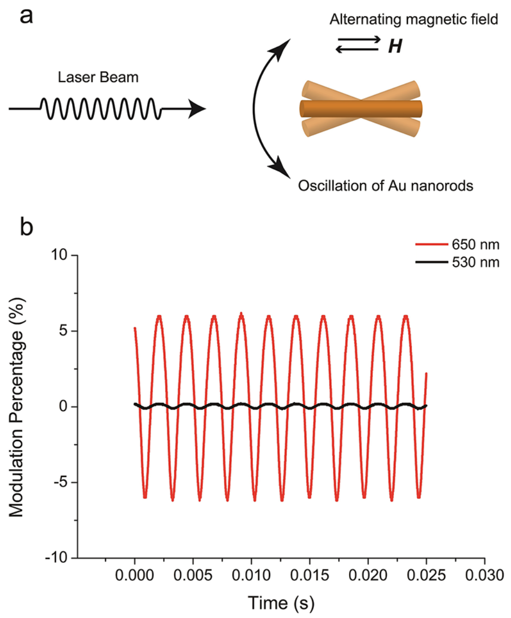

Figure 4. (a) Scheme showing optical modulation using AuNRs oscillating under an alternating magnetic field with field direction parallel to the incident laser beam. Longitudinal plasmon can only be excited when AuNRs are displaced from the parallel position and illuminated by light with comparable wavelength. The resulting change in extinction thus leads to intensity modulation of the laser beam. (b) Optical modulation of AuNRs to laser beams with different wavelengths under a ~200 Hz alternating magnetic field: 650 nm (red) and 532 nm (black).

In summary, we have successfully demonstrated the magnetic manipulation of plasmonic excitation of AuNRs by controlling their orientation relative to the incident lights. Such tuning is enabled by attaching AuNRs to Fe_3O_4 nanorods whose orientation can be magnetically controlled. By tuning the direction of magnetic field, we are then able to control the excitation of plasmonic modes of AuNRs under the incidence of both ordinary and polarized light. The colloidal dispersion of AuNRs shows instant color switching in response to the changes in the orientation or strength of external magnetic fields. The optical switching is extremely sensitive and can operate under considerably weak magnetic fields or alternating magnetic fields with high frequency. The same strategy can be extended to dynamic tuning of the optical property of other anisotropic plasmonic nanostructures by using magnetic fields. These tunable plasmonic hybrid nanostructures not only enhance our understanding of plasmonic tuning but also provide a new platform for building novel active optical components, color presentation and display devices, and highly sensitive and selective chemical and biomedical sensors.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and setups, TEM images, UV−vis spectra, and captions for videos. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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