Plasmon-Enhanced Light Harvesting of Chlorophylls on Near-Percolating Silver Films via One-Photon Anti-Stokes Upconversion

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There exists a wealth of means of efficient utilization of solar energy in nature, with photosynthesis of chlorophylls as a prime example. Separately, artificially structured plasmonic materials are versatile in light harvesting and energy conversion. Using a simple and scalable design of near-percolating silver nanostructures, we demonstrate that the light-harvesting efficiency of chlorophylls can be drastically enhanced by tuning the plasmon frequency of the constituent silver nanoparticles to coincide with the maximal photon flux of sunlight. In particular, we show that the photon upconversion efficiency can be readily enhanced by over 20 folds, with the room-temperature fluorescence quantum yield increased by a factor of 2.63. The underlying mechanism for the upconversion enhancement is attributed to a one-electron-per-photon anti-Stokes process, involving absorption of a characteristic phonon mode of the chlorophylls. These findings suggest that chlorophylls can serve as molecular building blocks for high-efficiency light harvesting and solar energy conversion.
significance because this band coincides with the region of the maximal photon flux of sunlight. We also introduce a theoretical mode, based on the measured fluorescence intensity and decay rate, to calculate and analyze the quantum yield of the plasmon-enhanced fluorescence and excitation energy transfer in the nanosystem. We find that the upconversion efficiency can be readily enhanced by over 20 folds, and the fluorescence quantum yield increased by a factor of 2.63 at room temperature. These findings demonstrate that the chlorophyll molecules assisted by plasmons can be even better light harvesters around the red/infrared region than those unassisted by plasmons. Our study serves as another example of how solar energy can be utilized more efficiently when a man-made nanomaterial system works together with a natural material system.

**Results**

**Structural design and tunable plasmon resonance.** Two types of chlorophyll samples were used in our study: natural chlorophyll mixtures (Chl-mix) and pure Chl-\(\alpha\). The red absorption bands of Chl-mix and Chl-\(\alpha\) are near 665 nm and 662 nm, respectively. The chlorophyll samples and polyvinylpyrrolidone (PVP) were dissolved in ethanol and the prepared solution was spin-coated onto the nanostructured silver films grown on SiO\(_2\) substrates. The thickness of the Chl:PVP films was approximately 40 nm, and the average gap distance between the silver nanoparticles is about 4 nm. The Chl:PVP coating layer on the silver film leads to a red shift in the LSPR. Quantitatively, the near-percolating film has smaller red-shift induced by the coating dielectric layer due to smaller gap distances between the silver nanoparticles. Figure 1c is a scanning electron microscopy (SEM) image of the near-percolating films with normalized deposition time \(t_d/t_c = 0.94\). It shows fractal-nanostructured silver clusters with inhomogeneous size and shape distributions of the constituent nanoparticles, and the average size of the silver nanoparticles is about 40 nm, with an average gap separation of 4 nm. The LSPR of the silver film is significantly broadened by the near-percolating fractal nanostructure, as shown in Figure 1d, and it spans from the visible region to the near infrared region with a central peak, \(\lambda_{SP}\), which is around both the region of maximal photon flux of sunlight and the red-absorption band of chlorophylls. The nanostructured films strongly enhance the local fields in a large spectral range, including the chlorophyll emission wavelength (\(\lambda_{emi} = 675\) nm) and the laser excitation wavelength (\(\lambda_{exc} = 735\) nm).
One-photon anti-Stokes upconversion of the chlorophyll molecules. Figure 2a shows the upconversion fluorescence spectra of the Chl-mix suspensions in ethanol, which is excited by a continuous wave (CW) laser with an excitation wavelength \( \lambda_{exc} = 735 \) nm. As shown in Fig. 2a, the peak intensity \( (I_{FL}) \) of the upconversion fluorescence at \( \lambda = 673 \) nm is increased by \( \sim 160\% \) as the sample temperature is increased from 279.7 K to 334.9 K. This intensity increase is attributed to the phonon-assisted processes during anti-Stokes upconversion\(^{56,57}\). We found that \( \ln I_{FL} \) is linearly dependent on \( -1/kT \), as shown in Fig. 2b, where \( k \) is the Boltzmann constant. The proportionality constant, \( \omega_0 = \ln I_{FL}/(\epsilon(-1/kT)) \), which is a measure of the average phonon energy involved in the anti-Stokes upconversion of the Chl-mix and Chl-a is found to be 139 and 136 meV, respectively. These values are in good agreement with the measured Raman shift of the corresponding phonon mode; the latter is \( \sim 133 \) meV\(^{4}\).

Figure 2c shows the excitation-power dependence of the fluorescence peak intensity \( (I_{FL}) \) of the Chl-mix and Chl-a with CW excitation, and the reference sample rhodamine \( b \) (RDM-\( b \)) with ps-pulse excitation. The emission power index \( \nu = \ln I_{FL}/\ln p_{exc} \) of the Chl-mix and Chl-a is measured to be \( \sim 0.97 \) and 0.98, respectively, even when the time-averaged excitation power density \( p_{exc} \) is decreased to as low as 0.5 mW/cm\(^2\). This linear scaling is distinctly different from those for upconversion via two-photon absorption, such as for the reference sample RDM-\( b \), where \( \nu \sim 2 \) in the weak excitation region\(^{11,12}\). This linear scaling indicates that the upconversion fluorescence of chlorophylls is induced by one-photon absorption. The dependencies of chlorophyll upconversion on the temperature and excitation power indicate that one electron in chlorophylls can be pumped to a high energy level by simultaneously absorbing a single low-energy photon in the near infrared region and a phonon of the sample.

Plasmon-enhanced light harvesting of the chlorophyll molecules. Next, we used the nanostructured silver films to enhance the light-harvesting efficiency of the Chl-mix:PVP. Figure 3a shows the upconversion fluorescence spectra of Chl-mix:PVP-coated silver films excited by a CW laser with \( \lambda_{exc} = 735 \) nm. Upconverted fluorescence spectra of the Chl-mix:PVP on the silver films with normalized deposition time of \( t_d/t_c = 0, 0.26, 0.43, 0.60, 0.77, 0.94, 1.06, 1.11 \), and 1.28. The upconversion fluorescence of the Chl-mix:PVP film was strongly enhanced by the use of discontinuous Ag island films \( (0.26 < t_d/t_c < 0.94, 600 \text{ nm} < \lambda_{SP} < 740 \text{ nm}) \), as shown in Fig. 3a, but weakly...
enhanced by the use of continuous Ag films \((t_d/t_c > 1.06)\), as shown in Fig. 3b. The strongest fluorescence occurs at \(t_d/t_c = 0.94\) and the corresponding emission peak is slightly shifted from 675 nm to 690 nm, where the enhancement factor \(R_{FL} = I_{FL}/I_{FL}^{(0)}\) reaches the maximum value of 21.5. This enhanced fluorescence of chlorophyll molecules in the vicinity of silver film is mainly attributed to the efficient excitation of excitons to the higher levels via plasmon-induced enhancements of local excitation field and exciton-phonon coupling in the anti-Stokes processes.

**Plasmon-enhanced fluorescence decay rate.** The fluorescence decay rate of chlorophylls is also enhanced by the silver films. The total decay rate, \(\Gamma\), is the sum of the radiative rate, \(\gamma_{rad}\), and the nonradiative rate, \(k_{nr}\). We use \(\Gamma^{(nr)}\), \(\Gamma^{(0)}\), and \(\Gamma\) to denote the total decay rates of chlorophylls suspended in ethanol, and that of Chl-mix:PVP in the absence and presence of the silver films, respectively. From the recorded fluorescence decay traces of the three samples shown in Fig. 4, we obtained the values of the three decay rates: \(\Gamma^{(nr)} = 0.160 \text{ ns}^{-1}\), \(\Gamma^{(0)} = 0.323 \text{ ns}^{-1}\), and \(\Gamma = 0.980 \text{ ns}^{-1}\) \((t_d/t_c = 0.94)\). \(\Gamma^{(nr)}\) is about twice as large as \(\Gamma^{(0)}\) due to increased nonradiative energy relaxation between the chlorophyll molecules in the solid PVP films. \(\Gamma\) is much larger than \(\Gamma^{(0)}\), and the decay rate enhancement factor \(R_\Gamma = \Gamma/\Gamma^{(0)}\) reaches 3.04 due to interaction between the chlorophylls and silver films.

The radiative rate is increased by the plasmon-exciton interaction with the relationship \(\gamma_{rad}/\gamma_{rad}^{(0)} = [f(\lambda_{emi})]^2\), where \(f(\lambda_{emi})\) is the local field enhancement factor at the emission wavelength. The increase of nonradiative rate is described by \(k_{nr} = k_{nr}^{(0)} + \Delta k_{nr}\), where \(\Delta k_{nr}\) is the nonradiation energy transfer rate from the chlorophylls to the metal film. We found that the total decay rate enhancement factor \(R_\Gamma\) reaches the maximum 3.44 when \(\lambda_{SP}\) of the silver film grown at \(t_d/t_c = 0.77\) near the chlorophyll emission wavelength. As \(t_d/t_c\) increases from 0.77 to 1.28 (Fig. 5), even though the morphology of the films varies from being discontinuous to semi-continuous, the decay rate enhancement factor \(R_\Gamma\) decreases monotonically from 3.44 to about 1. This observation indicates that the enhanced decay rate can be mainly attributed to the radiative rate increase by the local field enhancement of the silver films. This increased radiative emission is the origin of the observed red-shifting (from 675 nm to 690 nm) of the fluorescence peak of the chlorophyll molecules on the silver films.

**Discussion.** The fluorescence quantum yield defined as \(Q_{FL} = \gamma_{rad}/(\gamma_{rad} + k_{nr})\) represents the fraction of the excitons relaxed by radiative decay relative to the total decay, and quantitatively describes the emission efficiency. The plasmon resonances enhance the fluorescence intensity, the decay rate, as well as the quantum yield. The quantum yield enhancement, \(R_{QY}\), the fluorescence enhancement factor, \(R_{FL}\), and the decay rate enhancement factor, \(R_\Gamma\), are related through the following equations

\[
R_{FL} = R_{QY}[f(\lambda_{emi})]^2,
\]

\[
R_{QY} = (R_\Gamma)^{-1}[f(\lambda_{emi})]^2,
\]

where \([f(\lambda_{emi})]\) is the local field enhancement factor at the excitation wavelength. Combining equations (1) and (2), the quantum yield enhancement is obtained as,

\[
R_{QY} = \frac{[f(\lambda_{emi})]}{[f(\lambda_{emi})]} \left( \frac{R_{FL}}{R_\Gamma} \right)^{1/2}.
\]

If the separation of the excitation and emission wavelength is small and the plasmon resonance of the metal nanostructure is broadened, then the differences of both absorption coefficients \(\alpha\) and field enhancements at the two wavelengths are very small \(> 10\%\). This leads to a good approximation, \([f(\lambda_{emi})]/[f(\lambda_{emi})]^2 \approx \alpha(\lambda_{emi})/\alpha(\lambda_{exc})\). In this case, \(R_{QY}\) can be directly calculated from the measured \(R_{FL}\) and \(R_\Gamma\) with a very simple relationship,

\[
R_{QY} \approx \left( \frac{\alpha(\lambda_{emi})}{\alpha(\lambda_{exc})} \right)^{1/2} \left( \frac{R_{FL}}{R_\Gamma} \right)^{1/2}.
\]

For the anti-Stokes upconversion of the chlorophyll molecules, the difference in the wavelengths, \(\Delta\lambda = \lambda_{emi} - \lambda_{exc}\), is only 60 nm resulting in a very small difference in the absorptions \(\alpha(\lambda_{emi})\) and \(\alpha(\lambda_{exc})\). Meanwhile, for the near-percolating nanostructured silver films used in our studies, the inhomogeneous size and shape distributions of the constituent silver nanoparticles led to significantly-broadened plasmon resonances as shown in Fig. 1b. The quantum yield enhancement \(R_{QY}\) of Chl-mix:PVP is calculated accordingly to be 2.63 based on the experimentally measured results of \(R_{FL} = 21.5\) and \(R_\Gamma = 3.04\) for the silver films with \(t_d/t_c = 0.94\).

**Figure 4** Time-resolved fluorescence decay traces of chlorophylls and Chl-mix:PVP films excited by a picosecond pulse laser and recorded at the emission wavelength \(\lambda_{emi} = 675 \text{ nm}\). Normalized fluorescence decay traces of the Chlorophylls suspended in ethanol (decay rate \(\Gamma^{(nr)} = 0.160 \text{ ns}^{-1}\)), the Chl-mix:PVP film on blank fused quartz substrate (\(\Gamma^{(0)} = 0.323 \text{ ns}^{-1}\)), and the Chl-mix:PVP film on a near-percolating silver film with \(t_d/t_c = 0.94\) (\(\Gamma = 0.980 \text{ ns}^{-1}\)).

**Figure 5** Time-resolved fluorescence decay traces of Chl-mix:PVP films excited by using a picosecond pulse laser and recorded at the emission wavelength \(\lambda_{emi} = 675 \text{ nm}\). Normalized fluorescence decay traces of Chl-mix:PVP on the silver films with \(t_d/t_c = 0.77, 0.94, 1.11,\) and \(1.28\), respectively. The decay rate \(\Gamma\) reaches the maximum when \(\lambda_{SP}\) of silver film is around \(\lambda_{emi} = 675 \text{ nm}\) \((t_d/t_c = 0.77)\).
Figure 6 synoptically presents plasmon resonance absorption and three enhancement factors ($R_{FL}$, $R_F$, and $R_{QY}$) of fluorescence, decay rate and quantum yield of Chl-mix:PVP/Ag as a function of normalized deposition time $t_d/t_c$ of the silver films. The absorption ratio $\alpha(\lambda_{emi})/\alpha(\lambda_{exc})$ is very close to 1 when the plasmon resonance wavelength $\lambda_{SP}$ is around $\lambda_{emi}$ and $\lambda_{exc}$ (Fig. 6a and 6b). $R_F$ reaches the maximum value of 3.44 when $t_d/t_c = 0.77$ (Fig. 6c), and $R_{FL}$ and $R_{QY}$ reaches the maximum 21.5 and 2.63 when $\lambda_{SP}$ is tuned to around $\lambda_{exc} = 735$ nm for the near-percolating silver film ($t_d/t_c = 0.94$) (Figs. 6d and 6e). When $t_d/t_c > 1$, the silver films become semi-continuous (conductive), the plasmonic resonance absorption vanishes, and both $R_{FL}$ and $R_{QY}$ dramatically decrease. Based on these observations, we conclude that the dominant mechanism of the maximal anti-Stokes fluorescence is plasmon-enhanced excitation, and this excitation enhancement is commonly reported in the Stokes processes. We also notice that the silver film with $t_d/t_c = 0.94$ is close to the percolating regime, so the percolating effect could be partially involved in fluorescence enhancement, which remains to be further studied.

For comparison, the upconversion parameters of pure Chl-$a$ have also been measured, as listed in Table 1 along with the corresponding values of Chl-mix. These results confirm that the fluorescence of the Chl-mix can be attributed to Chl-$a$. The enhancement factors of the fluorescence intensity and the decay rate of the Chl-$a$:PVP samples are measured to be $R_{FL} = 14.6$ and $R_F = 3.71$, respectively. Compared with the Chl-mix, the Chl-$a$ samples have a larger $R_F$, owing to a smaller $\Gamma^{\text{em}}$, and smaller $R_{QY}$ and $R_{FL}$ due to the higher $Q_{FL}$. Our results suggest that natural Chl-mix should be preferred over pure Chl-$a$ as the material of choice for practical solar energy conversion, due to their much lower cost and higher plasmon enhancement factor.

So far we have shown that (i) the near-percolating silver films have broadened LSPR around the red-absorption band of chlorophylls, where the maximal photon flux of sunlight is located; (ii) both the light-harvesting efficiency of chlorophylls and the fluorescence quantum yield are significantly improved by the near-percolating silver films, and the underlying mechanism for the plasmon-enhanced upconversion is identified to be via a one-photon anti-Stokes process, involving the absorption of a characteristic phonon mode of the chlorophylls, which effectively generates one higher-level electron per lower-energy photon; and (iii) the theoretical model proposed here for the calculation of quantum yield enhancement offers a useful tool to study energy transfer and fluorescence enhanced by metallic nanostructures with broadened LSPR.

Finally, we would like to point out that the photon-excited carriers assisted by plasmon resonances could in principle be efficiently transferred to other proper contacts/leads with much faster transfer rates than the radiative rate when the chlorophylls are used in potential photoelectronic and photocatalytic devices. Therefore, plasmon-enhanced efficient generation of photoelectrons via one-photon anti-Stokes processes as demonstrated here may offer new opportunities in developing novel photovoltaic and photocatalytic devices. Taken together, the present study suggests that chlorophylls, assisted by near-percolating metal films through their enhancement of the local fields in a broadened spectral region, can serve as a molecular building block in artificial photosynthetic systems for high-efficiency sunlight harvesting and solar energy conversion.

| Sample       | $v$    | $\omega_0$ [meV] | $\Gamma^{\text{em}}$ [ns$^{-1}$] | $\Gamma^{\text{exc}}$ [ns$^{-1}$] | $R_F$ | $R_{FL}$ | $R_{QY}$ |
|--------------|--------|------------------|---------------------------------|----------------------------------|-------|----------|----------|
| Chl-mix      | 0.97   | 139              | 0.323                           | 0.980                            | 3.04  | 21.5     | 2.63     |
| Chl-$a$      | 0.98   | 136              | 0.200                           | 0.742                            | 3.71  | 14.6     | 1.94     |

Table 1 | Anti-Stokes fluorescence parameters of Chl-mix and Chl-$a$
Methods
Preparation of nanostructured silver films and Chl-PVP coating films. The silver films were deposited by sputtering in an argon atmosphere with a sputtering pressure of 5 Pa and a power of 1.5 kW × 7 mA. The average deposition rate was about 4.0 nm/min. The nanoparticle size and LSPR of the films were adjusted by controlling the sputtering deposition time \( t_d \), whose range was from 15 to 150 s. The nanostructured films were analyzed using SEM on a FEG SEM Sirion 200 operated at an accelerating voltage of 25.0 kV. The Chl-mix used in our studies were purchased from Shanghai Tianzhu Pharmaceutical Co. Ltd (China). The purified Chl-a (purity \( \geq 85\% \)) which was made from spinach, was purchased from Sigma-Aldrich (USA). The content of the Chl-mix was determined by measuring the absorption spectra of the samples. The calculated Chl-a, Ch-b and carotenoid content was approximately 2.73%, 0.61% and 0.82%, respectively. As expected, Chl-a contributed the most to the upconversion fluorescence. The chlorophylls (0.5 mg/ml) and PVP (33 mg/ml) were separately dissolved in ethanol. The prepared chlorophylls and PVP solutions were mixed with a volume ratio of 1.0: 1.0, and the mixture was spin-coated onto the nanostructured silver films on a fused quartz substrate. The thickness of the Chl-PVP film, measured using a profilometer (TalySurf Profiler-54C, Taylor Hobson), was approximately 50 nm when the spin-rotation rate was 1500 r/min.

Optical measurements. The absorption spectra of the silver films and the Chl-PVP coating films were recorded at room temperature on a Varian Cary 5000 spectrophotometer. To measure fluorescence, a wavelength-tunable Ti:sapphire laser (Mira 900, Coherent) was used as the excitation source; the laser can run in CW mode and mode-locked pulse mode. The pulse width was \( \approx 2.5 \) ps, and the repetition rate was 76 MHz. The incident angle of the excitation source was \( \approx 80^\circ \). The upconversion fluorescence of the chlorophylls was excited by the CW laser with wavelengths from 725 nm to 775 nm. The down-conversion fluorescence of the chlorophylls was excited by a 415 nm laser, generated by focusing a 830 nm mode-locked pulse laser into a second harmonic generation (SHG) system (HarmoniXX, APE GmbH). The chlorophyll fluorescence was measured in reflection mode and recorded via spectrometry (Spectropro 2500i, Acton) with a liquid-nitrogen-cooled CCD (SPEC-10, Princeton). A long-wave pass filter or a short-wave pass filter was used to filter the excitation laser. The time-resolved fluorescence decay traces were recorded using a time-correlated single-photon counting system (PicoQuant GmbH).

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**Author contributions**

The samples of Ag films and Chl:PVP films were prepared by Y.L.W., L.Z. and Y.Y.; The experimental measurements and data collection were carried out by F.N., X.N.P., Y.Y. and Q.Q.W. with assistance of Y.L.W., Z.K.Z., X.L.L. and Z.H.H.; Data analysis and theoretical modeling were performed by Y.L.W., W.Z., Q.Q.W. and Y.W. The manuscript was written by Z.Z. and Q.Q.W. with assistance of Y.L.W. and L.Z.; The project was supervised by Z.Z. and Q.Q.W.

**Additional information**

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

**Competing financial interests:** The authors declare no competing financial interests.

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