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Ultrafast carrier dynamics of Cu_2O thin film induced by two-photon excitation*

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Cuprous oxide (Cu_2O) has attracted plenty of attention for potential nonlinear photonic applications due to its superior third-order nonlinear optical property such as two-photon absorption. In this paper, we investigated the two-photon excitation induced carrier dynamics of a Cu_2O thin film prepared by radio-frequency magnetron sputtering, using the femtosecond transient absorption experiments. Biexponential dynamics including an ultrafast carrier scattering (< 1 ps) followed by a carrier recombination (> 50 ps) were observed. The time constant of carrier scattering under two-photon excitation is larger than that under one-photon excitation, due to the different transition selection rules and smaller absorption coefficient of the two-photon excitation.

Keywords: carrier dynamics, cuprous oxide, transient absorption, two-photon absorption

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1. Introduction

Cuprous oxide, as a p-type semiconductor, has been regarded as a promising material for applications in the fields of solar cells, photocatalysis, photoelectrode, photovoltaics and sensors,[1–7] owing to its high optical absorbance, nontoxicity and low cost. Recently, the optical nonlinearity of Cu_2O has attracted much interest, and indicated potential nonlinear photonic applications.[8–10] Since the valence bands and conduction bands of Cu_2O have the same parity, direct optical transition is parity forbidden but the two-photon transition is allowed. This initiates studies that focused on the two-photon absorption properties of Cu_2O, demonstrating considerable applications in optical limiting, ultrafast all-optical modulation, and so on.[11–13]

As is known, understanding the carrier dynamics is essential for semiconductor optoelectronic devices. It has been proved that the carrier distribution generated by two-photon excitation is more uniform than that by one-photon excitation, due to the former has relatively weaker absorption coefficient.[14] As a result, carrier diffusion and surface recombination effects could be effectively avoided in the two-photon excitation scheme. However, the two-photon absorption generated carrier dynamics of Cu_2O has not been investigated to the best of our knowledge. Therefore, it deserves deep insight into the carrier dynamics induced by two-photon excitation for future applications in the nonlinear photonics.

In this work, we prepared a Cu_2O thin film using the radio-frequency magnetron sputtering. X-ray diffraction (XRD), scanning electron microscopy (SEM) and linear transmission spectra were applied to define the crystal structure, morphology and particle size. Using typical non-collinear ultrafast transient absorption experiments, carrier dynamics induced by the two-photon excitation were investigated, revealing an ultrafast carrier scattering process in hundreds femtoseconds and a slow carrier recombination in more than tens of picoseconds. Meanwhile, the carrier dynamics induced by the corresponding one-photon excitation were also studied for contrast. The time constant of carrier scattering process is found larger for two-photon excitation, since two-photon excitation generates carriers with less concentration for analogous laser peak power density.

2. Experimental details

Generally, several techniques such as electrochemical deposition,[7] molecular beam epitaxy,[15] thermal evaporation[16] and magnetron sputtering[17] have been employed to prepare the Cu_2O film. Among these methods, radio-frequency magnetron sputtering is the best adopted one due to its high deposition rate, low resistivity and effective control of the chemical composition. Here, we prepared the Cu_2O thin film deposited on a glass slide by a radio-frequency magnetron sputtering system (CS-300, Yuhua), using a Cu_2O target with a purity of 99.99%, diameter of 60 mm and thickness of 5 mm. Before deposition, the glass slide was ultrasonically cleaned in deionized water, acetone and ethanol successively. Presputtering was performed for 10 min to remove the impurities on the surface of the target. During deposition, high-purity argon was used as the sputtering gas for 2 hours at 200 °C, with a 46 sccm flow rate, 1.3 Pa vacuum chamber pressure and 70 W power.

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XRD (PANalytical Empyrean) was carried out to determine the crystal structure of the Cu_2O thin film. The surface morphology was characterized by a FIB field emission scanning electron microscope (FESEM, Carl Zeiss Auriga-BU). The linear transmission spectrum was measured using a UV-Vis-NIR spectrophotometer (Hitachi UH-4150) to obtain the optical bandgap.

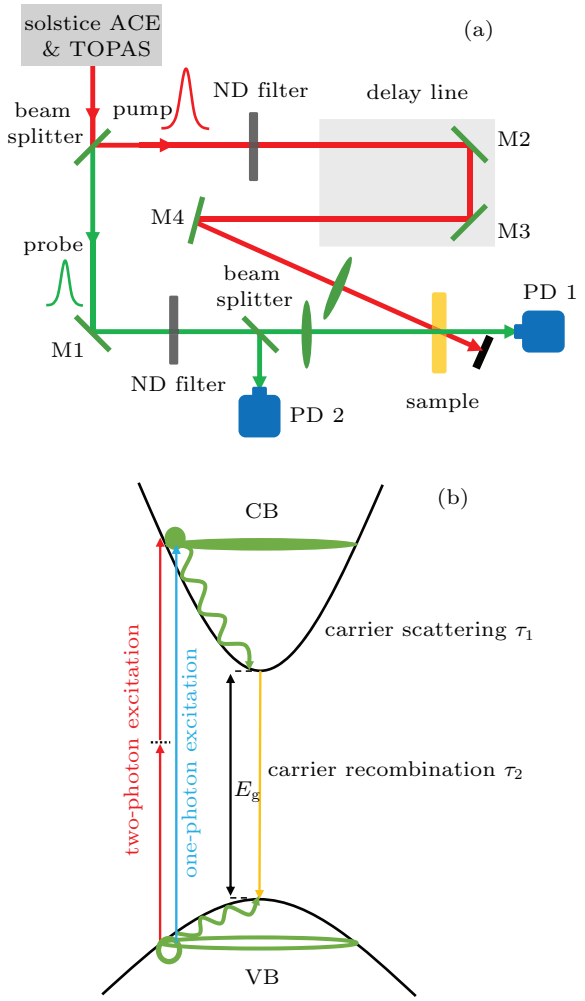


Fig. 1. (a) Non-collinear ultrafast pump-probe setup. M1–M4 are reflection mirrors. PD 1 and PD 2 are photodiodes. For one-photon excitation, a BBO crystal in inserted in the pump beam (not shown). (b) Schematic energy-level diagram of the processes during two- or one-photon excitation on Cu_2O thin film.

The carrier dynamic measurements of the Cu_2O thin film were carried out via typical non-collinear ultrafast pump-probe setup, as shown in Fig. 1(a). An amplified Ti:sapphire laser source (Solstice ACE, Spectra-Physics) with 800 nm wavelength, 120 fs pulse width, 1 kHz repetition rate passes through an optical parametric amplifier system (OPA, TOPAS-Prime, Light Conversion) and generates wavelength tunable femtosecond pulses (240 nm–2600 nm). The residual 800 nm pulse served as the pump beam for the two-photon excitation, while the output pulse from OPA served as the probe. The differential transmission of the probe beam was recorded by a couple of synchronized photodiodes (918D-UV-OD3R, Newport). The delay time between the pump and probe pulses was controlled through a retroreflector mounted on a linear motor stage (M-ILS200CC, Newport) in the pump arm. Two neutral density filters (ND filter) were placed in the two arms to adjust the laser powers. In addition, a BBO crystal was inserted in the 800 nm arm to generate the 400 nm pulses to implement one-photon excitation for comparison. Both the pump and probe laser in our experiments were horizontal polarized.

3. Results and discussion

The XRD pattern of the obtained Cu_2O thin film is shown in Fig. 2(a), showing obvious diffraction peaks. Each diffraction peak matches with that in JCPDS file No. 01-078-2076, indicating that the pure polycrystalline Cu_2O film is obtained. The average particle size is evaluated to be about 25 nm according to the Scherrer's equation.[18]

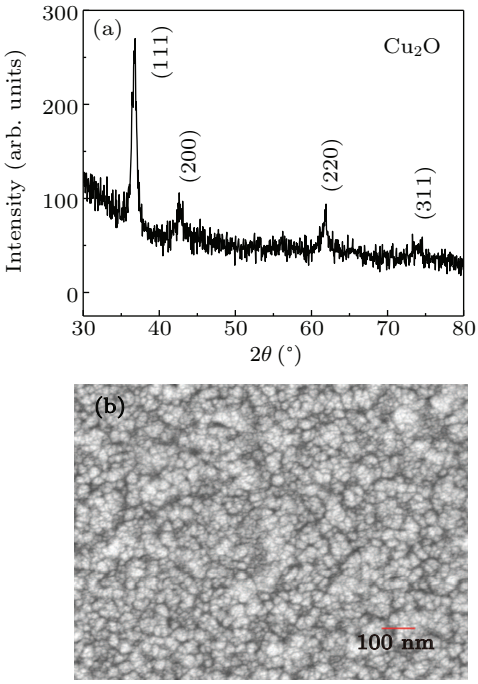


Fig. 2. (a) XRD pattern and (b) SEM image of the Cu_2O thin film.

The SEM image in Fig. 2(b) indicates that the surface is compact and uniform. The linear transmission spectrum and the corresponding relationship between $\alpha h\nu^2$ and $h\nu$ were plotted in Fig. 3. According to the Tauc's equation,[19] the optical bandgap E_g is obtained to be 2.54 eV by using linear extrapolation method

$$(\alpha h\nu)^2 = C(h\nu - E_g), \tag{1}$$

where α is the linear absorption coefficient and can be calculated from the linear transmission spectrum, $h\nu$ is the photon energy of the incident light, and C is a constant. The obtained E_g of the present Cu_2O thin film is larger than the calculated value of bulk Cu_2O, which is due to the nanoscale particle size.[20,21]

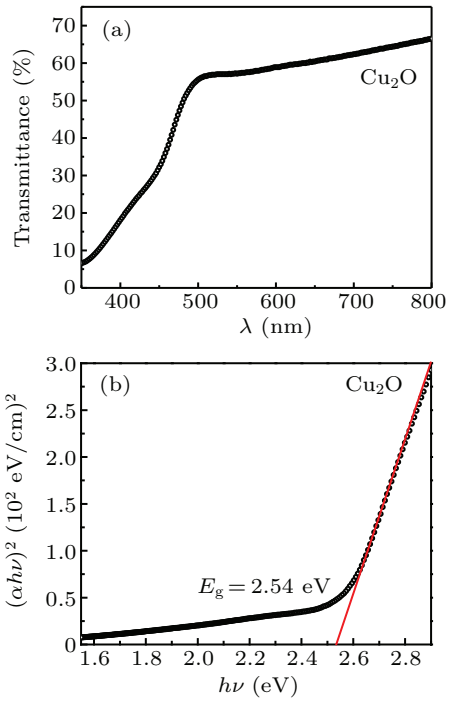


Fig. 3. (a) Linear transmission spectrum of the Cu_2O thin film. (b) Tauc's plot of $(\alpha h\nu)^2$ versus $h\nu$ and the obtained bandgap.

In order to investigate the carrier dynamics of Cu_2O thin film under the two-photon excitation, transient absorption measurement was performed with 800 nm pump pulse and 600 nm probe pulse. It is worth mentioning that the photon energy of the pump pulse (1.55 eV) is less than E_g but more than $E_g/2$. This leads to an interband transition from the valence band to the conduction band via the two-photon absorption. While the photon energy of the probe pulse $E_{probe} = 2.07$ eV is less than E_g, implying that no linear absorption of the probe pulse would happen. Figure 4(a) illustrates the temporal evolution of differential transmission $\Delta T/T$ under different focal peak power densities of the pump pulse I_{800}. $\Delta T/T$ is defined as the differential transmission of probe beam with pump beam on and off, $\left(T_{pump_on} - T_{pump_off}\right)/T_{pump_off}$. The focal peak power density of the probe pulse is set to 1.17 GW/cm^2. The $\Delta T/T$ firstly dropped to a negative maxima at the delay time $t = 0$ and then exhibited a short period of rapid recovery, and followed by a long period of slow recovery during $t > 0$. The inset in Fig. 4(a) shows that the maxima $\Delta T/T$ at $t = 0$ depends linearly on I_{800}. This indicates that the negative peak of $\Delta T/T$ at $t = 0$ was caused by a transient effect, i.e., the interband two-photon absorption induced by the pump light. Besides, no other nonlinear effects such as two-photon absorption saturation occurred under the experimental condition.

Biexponential function $A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$ was applied to fit the normalized $(-\Delta T/T)$ as plotted in Fig. 4(b), where τ_1 and τ_2 are time constants for the fast and slow processes, respectively, and A_1 and A_2 are weights. The extracted τ_1 and τ_2 for different I_{800} are listed in Table 1. As I_{800} increases, τ_1 exhibits a decreasing trend, which denotes that the generated carriers undergo an ultrafast carrier scattering process and then relax to the bottom of the conduction band, as illustrated in Fig. 1(b). The time constant τ_2 is more than 30 ps, indicating a carrier recombination process.

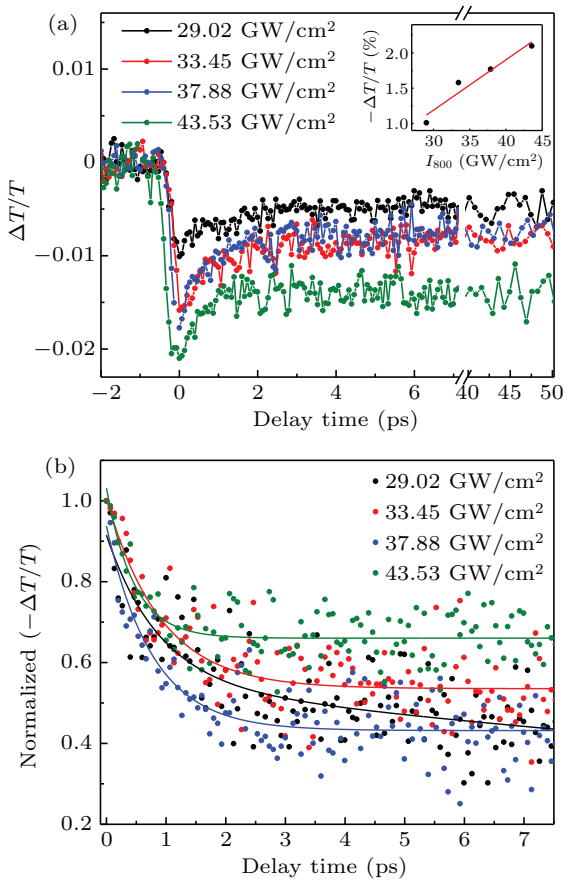


Fig. 4. (a) Time resolved differential transmission $\Delta T/T$ under different I_{800} for two-photon excitation. The inset shows the dependence of the maxima $\Delta T/T$ at $t = 0$ on I_{800} and linear fitting. (b) Biexponential fitting for time resolved normalized $(-\Delta T/T)$ under different I_{800}.

Table 1. Time constants of carrier scattering and recombination under different pump intensities for two- and one-photon excitation.

Two-photon excitation				
I_{800} (GW/cm^2)	29.02	33.45	37.88	43.53
τ_1 (ps)	0.88 ± 0.28	0.91 ± 0.13	0.77 ± 0.10	0.46 ± 0.07
τ_2 (ps)	> 30	> 50	> 50	> 50
One-photon excitation				
I_{400} (GW/cm^2)	19.86	28.72	31.77	37.88
τ_1 (ps)	0.28 ± 0.03	0.29 ± 0.06	0.20 ± 0.02	0.14 ± 0.02
τ_2 (ps)	> 50	> 50	> 50	> 50

We further investigated the transient absorption pumped by 400 nm pulse (photon energy 3.1 eV) through one-photon excitation and probed by 600 nm pulse. The focal peak power density of the probe pulse is 1.14 GW/cm^2. At the first glance of Fig. 5(a), the differential transmission $\Delta T/T$ appears similar evolution trend with the two-photon excitation case, that is a fast drop followed by a slow recovery. The maxima $\Delta T/T$ is also linearly dependent on the focal peak power density of the pump pulse I_{400} without saturation.

Figure 5(b) illustrates the fitting curves with the biexponential function. The extracted time constant τ_1 for carrier scattering also shows a decreasing trend with the increase of I_{400}, and the time constant τ_2 for carrier recombination is more than 50 ps. It is noticed that τ_1 is smaller than that in the two-photon excitation case. We attribute it to the different transition selection rules as well as the much smaller absorption coefficient of two-photon absorption than one-photon absorption. Consequently, the carrier concentration generated by the two-photon excitation is less than that by the one-photon excitation for analogous I_{800} and I_{400}, leading to slower carrier scattering time τ_1 under the two-photon excitation. This would make the Cu_2O great potential in the nonlinear optical applications.

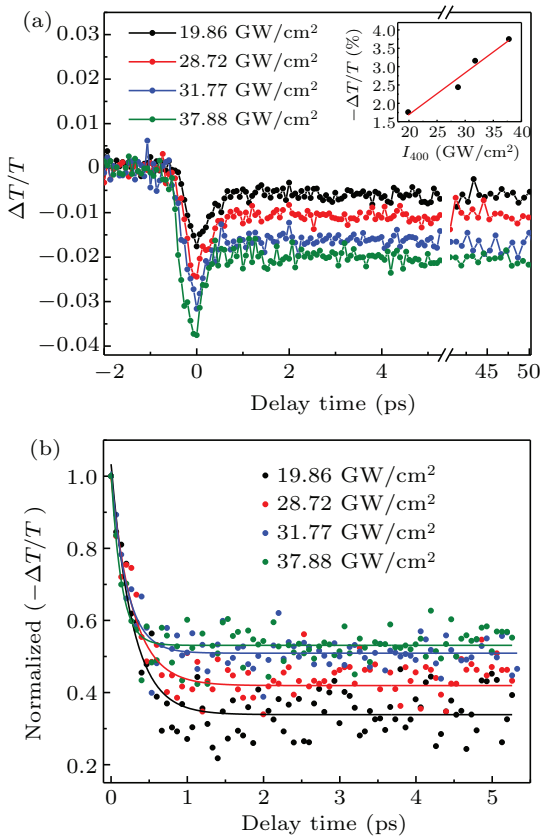


Fig. 5. (a) Time resolved differential transmission $\Delta T/T$ under different I_{400} for one-photon excitation. The inset shows the dependence of the maxima $\Delta T/T$ at $t = 0$ on I_{400} and linear fitting. (b) Biexponential fitting for time resolved normalized $(-\Delta T/T)$ under different I_{400}.

4. Conclusion

In summary, pure Cu_2O thin film has been prepared by radio-frequency magnetron sputtering. Using transient absorption experiments, the carrier dynamics have been investigated under the two- and one-photon excitation. It revealed an ultrafast carrier scattering in hundreds femtoseconds and carrier recombination in more than tens of picoseconds. Owing to the smaller absorption coefficient for the two-photon absorption, the carrier scattering time constant for the two-photon excitation is slower than that for the one-photon excitation. This study has provided essentical understanding of the carrier dynamic processes following the two-photon excitation, thus paves the way for further nonlinear optical applications of Cu_2O based on the two-photon absorption, such as optical limiting, ultrafast all-optical switching and femtosecond laser reductive sintering.

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