Research article

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Enhanced broadband nonlinear optical response of TiO_2/CuO nanosheets via oxygen vacancy engineering

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Abstract: Cupric oxide (CuO), as a transition metal oxide (TMO) semiconductor, has attracted tremendous attention for various applications. In the present work, we synthesize the CuO nanosheets modified by TiO_2 nanoparticles via a facile, non-toxic two-step method. Subsequently, the morphology and the structures of CuO and TiO_2/CuO nanocomposites are investigated. By utilizing the common Z-scan technology, broadband nonlinear optical (NLO) properties of the as-prepared CuO nanosheets and TiO_2/CuO nanocomposites are demonstrated, elucidating the enhancement on the NLO response via the TiO_2 dopant, which is attributed to the more oxygen vacancies and the formed p-n junctions. Furthermore, CuO nanosheets and TiO_2/CuO nanocomposites are implemented to the passively Q-switched bulk lasers operating in the near-infrared (NIR) region, generating broadband ultrastable pulses. Ultimately, TiO_2/CuO nanocomposites were integrated in a passive mode-locking bulk laser for the first time, achieving stable mode-locked pulses and verifying its ultrafast optical response potential. Our results illustrate the tremendous prospects of the CuO nanosheets modified by oxygen vacancy engineering as a broadband NLO material in ultrafast photonics field.

1 Introduction

Two-dimensional (2D) nanomaterials have aroused unprecedented research enthusiasm on accounts of their eminent mechanical, electrical and optical properties [1, 2]. 2D materials have been extensively applied in the fields of electrodes, photovoltaics, catalysis and nonlinear optics including photonic coupling, plasmonics, optical modulators and switches [3–12]. Besides, these nanomaterials have also successfully acted as saturable absorbers (SAs) for the generation of ultrafast pulses laser [13–15], benefiting from their distinguished third order optical nonlinearity, ultrafast carrier dynamics, and prominent broadband response characteristics [16, 17]. Lately, transition metal oxides (TMOs) have launched a new upsurge of research on nanomaterials owing to their strong phonon–electron coupling and electron–electron correlation, diverse optical and electrical properties [18]. Especially in the nonlinear optics, TMOs present itself by the high thermal and chemical stability, wide absorption bandwidth and strong optical nonlinearity [19, 20]. Among the multitudinous TMOs, cupric oxide (CuO) attracts numerous attentions owing to its remarkable superconductivity, high temperature stability, non-toxicity, fast recovery time of picosecond order and high third order nonlinearity coefficient [21–23]. Moreover, CuO has a monoclinic crystal structure with a narrower bandgap (E_g) of 1.2–1.4 eV [24], making it more appropriate in the near-infrared (NIR) region. Despite CuO nanomaterials possess strong NLO properties, the research on the optical modulation and nonlinear saturation absorption is rare [25], remaining blank in the broadband nonlinear photoresponse nature of CuO nanomaterials yet. In addition, no efforts are made to optimize the CuO nanomaterials in order to obtain a more stable and excellent modulation effect.

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In a perfect CuO structure, the Cu atom is embraced by four coplanar O atoms, forming an approximately rectangular parallelogram structure [26]. However, during the preparation of TMOs, there will be oxygen vacancy (OV) defects and other point defects, disturbing the original physical structures and electronic states essentially. The OV defects commonly capture electrons by acting as the shallow donors to increase the density of carriers, thus improving the electrical conductivity, gas sensing performance and optical properties [27–30]. Even more amazing is that the crystal structure is still extremely stable with these OV defects [27]. Based on these, some endeavors have been put to enhance the properties of the TMOs by manipulating and optimizing their defect structures and density artificially [30, 31]. Owing to the induced OV defects, the bandgap of the semiconducting TMOs would decrease, because the OV defects act as donors which can generate new energy levels in the band gap. Thus, much smaller photon energies are required to realize the electron transition from the valence band to the conduction band [31]. This provides an inspiration for us to reduce the band gap and improve the broad spectral band response performances in the CuO nanomaterials and other TMOs. Titanium (IV) oxide (TiO_2) as a multifunctional material of TMOs, has been extensively extended to the photocatalyst, photovoltaic devices, and biosensors [32–34]. More importantly, studies have demonstrated that the Ti^{3+} in TiO_2 can bring more OV defects [35], leading to the decrease of the bandgap [36, 37]. Hence, it is rational to anticipate that the composite of TiO_2 nanoparticles on CuO hierarchical substrates can introduce more OV defects, reduce the E_g effectively, and improve the broadband response characteristics. In addition, TiO_2 is a typical n-type semiconductor while CuO is a p-type semiconducting material. During the compositing process, the formation of p-n heterojunction would lead to electron–hole pairs separation effectively and increase the density of photogenerated carriers resulting to the variation of nonlinear absorption [38]. What's more, TiO_2 nanomaterials possess ultrafast carrier recovery time [36], high damage threshold [39], and giant third-order nonlinearity [40]. Accordingly, the formation of TiO_2/CuO nanocomposites was expected to improve the ultrafast response and enhance the nonlinear characteristics of CuO nanosheets thanks to the stronger quantum local effect of TiO_2 nanoparticles [41].

In this work, CuO nanosheets were fabricated by a facile water bath strategy and then TiO_2/CuO nanocomposites were synthesized with CuO nanosheets as the precursor via the titanium tetrafluoride (TiF_4) solution etching process. The uniformity of the dispersions and effectiveness of the composites were characterized. Then

the broadband nonlinear optical absorption properties were elucidated via the open-aperture Z-scan technique at different operating wavelengths in NIR region. The results confirmed that the NLO properties were improved by TiO_2 dopant in CuO nanosheets. Based on the large NLO responses, we implemented the CuO and TiO_2/CuO nanocomposites as SAs in passively Q-switched (PQS) lasers operating at 1064, 1342 and 1878 nm to ulteriorly investigate the broadband nonlinear optical response characteristics. Finally, we utilized TiO_2/CuO nanocomposites as a passive modulator in a mode-locked bulk laser for the first time, obtaining stable mode-locked pulses with a signal-to-noise (SNR) of ~55 dB. Our results might open the gate to investigate the boosting effects of the oxygen vacancy defects in TMOs on NLO properties and broaden its application in nonlinear and ultrafast photonics.

2 Fabrication and characterization

In our experiment, we fabricated the CuO nanosheets by the method of a simple water bath under an alkaline atmosphere. First, 1.52 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 0.443 g hexamethylene tetramine (HMTA) were independently dissolved into 60 mL pure deionized (DI) water, respectively, and the mixtures were vigorously stirred. Then we quickly poured the HMTA solution into the $\text{Cu}(\text{NO}_3)_2$ solution with the magnetic stirring at 50 °C for 1 h to make them mix uniformly. Subsequently, 12 mL 2.5 M sodium hydroxide (NaOH) solution was added dropwise into the above homogeneous mixed solution with vigorous magnetic stirring for 2 h at 80 °C, alone with the formation of black precipitates. Afterward, collecting the formed precipitates after several times centrifugation and washing in the DI water and ethanol, then drying it in a vacuum oven for 48 h at 60 °C. In this step, owing to the reducing HMTA, Cu^{2+} was produced as well as Cu^+ , leading to the OV defects in the prepared CuO powder.

After that, we took the prepared CuO powder (0.025 g) and dissolved the powder into 60 mL DI water. Then the mixture was ultrasonicated for 1 h and subsequently magnetically stirred for 0.5 h in order to get the well-distributed dispersion. Thereafter, 0.4 mL 0.02 M titanium tetrafluoride (TiF_4) aqueous solution was dropped into the above solution with vigorous magnetic stirring for 2 h. Here, TiF_4 not only worked as the precursors to hydrolyze the TiO_2 , but also served as the corrodent to etch the CuO nanosheets forming a rough surface, facilitating the attachment of the TiO_2 nanoparticles. During the hydrolysis of TiF_4 , reducing H atom will change tetravalent Ti^{4+} to trivalent Ti^{3+} [42], generating abundant OV defects.

Subsequently, we transferred the above mixture into a 150 mL sealed Teflon-lined autoclave under the atmosphere of 200 °C for 2 h. The ending products were collected, centrifuged and washed with DI water and ethanol for several times. Then the powder was dried in a vacuum oven for 48 h at 60 °C. By then, the pure CuO and the TiO₂/CuO powders were successfully synthesized.

To fabricate the CuO nanosheets and the TiO₂/CuO nanocomposites as SAs, the as-prepared powders were dissolved into alcohol and then the mixtures were ultrasonically shaken for 2 h at a speed of 5000 rpm. After that, decanting the supernatants before the centrifugation for 30 min at 10,000 rpm. Finally, 10 mL supernatant dispersions were spin coated onto 150 µm thick quartz glass substrate, and then dried in a vacuum oven for 24 h at 60 °C. It is worth noting that the operation consistencies of the CuO and the TiO₂/CuO nanocomposites processing have been strictly guaranteed throughout all the process.

The crystalline structure of CuO is shown in Figure 1a, in which the Cu atom is neighbored with four O atoms. The scanning electron microscope (SEM) image indicated the as-prepared CuO nanosheets exhibited a shape of willow leaves with a length of ~2 µm, as shown in Figure 1b. After the introduction of TiF₄, the surface of the composites showed the morphology of “snowflakes falling on the

leaves” (Figure 1c), which would generate massive nanoscale p-n junctions and change the characteristics of the carrier migration [42]. Moreover, the energy dispersive spectra (EDS) patterns (Figure 1d) were employed to determine the accurate chemical composition and the high purity of our above-prepared CuO and TiO₂/CuO. Figure 1e showed the transmission electron microscopy (TEM) image of the pristine CuO, further verifying the elongated nanosheets morphology with a smooth surface, exactly coinciding with the SEM results. On the contrary, from Figure 1f, we could see that the surface of the composites TiO₂/CuO had been roughened, which was conducive to the attachment of TiO₂ nanoparticles with the average size of ~10 nm. As well as the evidence of TiO₂/CuO p-n heterojunction in TEM image, the resistances of CuO and TiO₂/CuO were measured as 1.3 and 14.8 MΩ, respectively. The increased resistance of TiO₂/CuO was attributed to the depletion layer during the formation of the p-n junction.

The crystal structures and phases of the pristine CuO and the composites TiO₂/CuO were characterized by the X-ray diffraction (XRD), as illustrated in Figure 2. The XRD patterns of the as-synthesized pure CuO of the red line presented the strong diffraction peaks of ($\bar{1}11$), (111), ($\bar{2}02$), ($\bar{1}13$), ($\bar{3}11$), (113) planes, located at about 35.5°, 38.7°, 48.7°,

Figure 1: Microstructure and morphology characterization of cupric oxide (CuO) and TiO₂/CuO nanocomposites.

(a) Crystal structure of monoclinic CuO. (b) Scanning electron microscope (SEM) image of CuO. (c) SEM of TiO₂/CuO. (d) Energy dispersive spectra (EDS) images of CuO and TiO₂/CuO nanocomposites. (e) Transmission electron microscopy (TEM) of CuO. (f) TEM of TiO₂/CuO nanocomposites.

Figure 2: X-ray diffraction (XRD) patterns of the prepared (a) CuO and (b) TiO₂/CuO nanomaterials.

61.5°, 66.2° and 67.9°, respectively, agreeing well with the monoclinic CuO (JPCDS: 72-0629). For the composites of the purple line, in addition to the above-mentioned XRD patterns of CuO, there was a small diffraction peak of (101) located at 24.8°, which could be indexed to JPCDS No. 21-1272 of the anatase TiO₂. The absence of other TiO₂ diffraction peaks in nanocomposites could be ascribed to the low TiO₂ concentration. There were no other peaks in the XRD spectra, revealing the high purity of the crystal phases.

To further characterize the difference between the OV defects contained in the prepared CuO nanosheets and TiO₂/CuO nanocomposites, the electron paramagnetic resonance (EPR) spectroscopy measurements were performed. As shown in Figure 3a, for both nanomaterials, the room-temperature EPR spectrums were centered at the magnetic field strength of 3516 Gs with $g = 2.002$, which could be ascribed to the surface unpaired electrons trapped on oxygen vacancies [43]. Moreover, the TiO₂/CuO nanocomposites exhibited stronger EPR intensity than pure CuO nanosheets, confirming the more existence of OV defects [44]. To further elaborate the influence of the OV defects on the bandgap of CuO nanosheets, the UV-Vis-NIR spectrophotometer tests were performed. As depicted in Figure 3b, the bandgap could be reckoned by the horizontal intercepts of the tangents to the $(\alpha h\nu)^{1/2}$ versus the incident photon energy ($h\nu$). By extrapolating the linear part of the

curve to the $h\nu$ axis (vertical axis equal to zero), the E_g of CuO nanosheets was calculated to be 1.36 eV. Compared with CuO nanosheets, the bandgap of TiO₂/CuO nanocomposites was exactly red-shifted to 1.24 eV due to the induced more OV defects.

3 Experimental results and discussion

3.1 Broadband NLO responses

To scrutinize the broadband nonlinear optical properties of the CuO nanosheets and TiO₂/CuO nanocomposites, the open-aperture (OA) Z-scan technique was performed at 1.06, 1.34 and 1.87 μm , respectively (see the details of the measurements in the Supporting Information). As shown in Figure 4, all normalized transmittances gradually increased to the maximum as the sample closed to the focus point ($Z = 0$) symmetrically, exhibiting the prominent saturable absorption properties of both CuO and TiO₂/CuO nanocomposites. Notably, under the same experimental conditions, the empty substrates did not show any nonlinear response. For a two-level energy system, the experimental data can be theoretically fitted with the following equation [45]:

Figure 3: (a) Electron paramagnetic resonance (EPR) spectrum. (b) Optical absorption spectrum of cupric oxide (CuO) nanosheets and TiO₂/CuO nanomaterials.

Figure 4: The nonlinear transmission curves and saturable absorption curves (the insets) of cupric oxide (CuO) and TiO_2/CuO nanocomposites at (a) $1.06 \mu\text{m}$, (b) $1.34 \mu\text{m}$ and (c) $1.87 \mu\text{m}$.

$$T = \sum_{m=0}^{\infty} \frac{[-q_0(z, 0)]^m}{(m+1)^{1.5}}, m \in \mathbb{N} \quad (1)$$

$$q_0(z, 0) = \frac{\beta_{\text{eff}} L_{\text{eff}} I_0}{(1 + Z^2 / (Z_0^2))}$$

In which $L_{\text{eff}} = (1 - e^{-L/\alpha_0})/\alpha_0$ was the effective length while L was the actual length of the samples, I_0 was the on-axis peak intensity. Moreover, α_0 and β_{eff} were the linear absorption and the nonlinear absorption coefficient, constituting the absorption model: $\alpha(I) = \alpha_0 + \beta_{\text{eff}} I$. In addition, employing the prevalent single photon absorption model of SAs, we fitted the nonlinear transmittance evolutions curves as shown in the insets of Figure 4. It intuitively presented that the transmittance increased as the incident laser intensity increased until saturation, which was examined a typical feature of saturable absorbers. During the fitting, we assumed that the nanomaterials possessed instantaneous response with the following relationship [45]:

$$T = 1 - \Delta T \exp(-I/I_s) - T_{\text{ns}} \quad (2)$$

where, ΔT was the modulation depth, I_s was the saturation intensity, and T_{ns} was the nonsaturable losses, which could be fitted by the experimental data as summarized in Table 1. The deviations of the measured I_s and β_{eff} of the prepared

CuO nanosheets from the previous reports [46], could be ascribed to the different thickness, size, layers and quality of the nanosheets determined by different synthetic techniques, which has also been elaborated in MoS_2 samples [47]. Compared with the pure CuO nanosheets, the synthesized TiO_2/CuO nanocomposites exhibited larger ΔT and β_{eff} under the same experimental techniques and conditions. The enhancement of the nonlinearity would be ascribed to the strong quantum confinement and local field effects from dielectric confinement and saturable excitonic resonance [48] of the introduced TiO_2 nanoparticles. Furthermore, the formed p-n junctions in TiO_2/CuO nanocomposites would cause more separations of electron-hole pairs, leading to the increase of the carrier concentration [38]. Therefore, under laser irradiation, the nanomaterials needed to absorb more photons to reach the bleached state, which increased the nonlinear absorption coefficient and enhanced the nonlinearity. Moreover, by comparing with the NLO properties of several typical nanomaterials at ~ 1 , ~ 1.3 and $2 \mu\text{m}$, TiO_2/CuO nanocomposites exhibited strong nonlinear absorption coefficient and lower saturation intensity. In summary, the above-mentioned results definitely manifested the potential of the CuO and TiO_2/CuO nanocomposites for constructing broadband modulated pulsed lasers in NIR wavebands.

Table 1: Nonlinear absorption characteristics of CuO and TiO_2/CuO nanocomposites and the comparison with different nanomaterials.

Material	λ (nm)	ΔT (%)	T_{ns} (%)	I_s (MW/cm ²)	β_{eff} (cm/MW)	Ref
CuO	1064	9.3 ± 0.8	17.7 ± 1.2	0.56 ± 0.02	-0.32 ± 0.01	This work
	1342	10.8 ± 1.0	10.1 ± 0.9	0.55 ± 0.01	-0.41 ± 0.03	
	1878	11.4 ± 1.1	7.7 ± 0.8	0.76 ± 0.05	-0.71 ± 0.09	
TiO_2/CuO	1064	21.7 ± 1.5	18.4 ± 1.3	0.68 ± 0.04	-0.35 ± 0.02	This work
	1342	11.8 ± 1.1	9.4 ± 0.7	0.4 ± 0.03	-0.45 ± 0.05	
	1878	15.3 ± 1.3	10.3 ± 0.9	0.92 ± 0.07	-0.83 ± 0.04	
Tellurene	1064	24	—	40.29	-0.058	[49]
InSe	1340	3.78	26.06	1.21	-0.28	[50]
InSe	1985	7.94	6.23	0.31	-0.88	[50]

3.2 Broadband modulation characteristics in all-solid PQS state laser

The marvelous broadband saturable absorption properties endowed CuO and TiO₂/CuO nanocomposites with the potential application in passively Q-switched lasers. In this section, the Nd:GdVO₄ ($^4F_{3/2} \rightarrow ^2I_{11/2}$), Nd:GdVO₄ ($^4F_{3/2} \rightarrow ^2I_{13/2}$) and Tm:YLF crystals were utilized as the gain mediums to evaluate the capabilities for pulsed lasers at 1.06, 1.34, 1.87 μm , respectively. The detailed information of the schematic setups was illustrated in Figure S2 of the Supporting Information. In our case, all experimental conditions ensured strict consistency of CuO and TiO₂/CuO nanomaterials.

3.2.1 Q-switching at 1.06 μm

For the Q-switching at 1.06 μm , stable operations were achieved with either CuO-SA or TiO₂/CuO-SA integrated into the cavity. By removing the SAs from the resonator, only continuous wave (CW) operation was generated, and the threshold pump power was 0.49 W. On inserting the CuO and TiO₂/CuO nanomaterials, the Q-switching thresholds were optimized to be 1.08 and 0.98 W, respectively. The PQS lasers characteristics for both cases were sketched in Figure 5. The output power of the CW laser and PQS lasers of CuO-SA or TiO₂/CuO-SA increased quasi-linearly with the incident pump power, corresponding to the slope efficiencies of 51.8, 21.4 and 21.6%, respectively. Besides, the stabilities of these two PQS lasers were detected for 40 min at the maximum pump power of 1.96 W

and both instabilities were <2% in root mean-squared error (RMSE). In addition, the TiO₂/CuO-SA PQS laser exhibited a marginally higher stability. Higher slope efficiency and modulation stability can be foreseen by further cooling the SA and crystal with nitrogen and optimizing the mirror coating process.

Figure 5b depicted the pulse duration and repetition rate versus the incident pump power in detail. The pulse width decreased with the enhancement of the pump power, while the repetition rate displayed a contradictory tendency, which was typical of SAs in modulation characteristics and agreed well with the PQS theory. At the identical maximal pump power of 1.96 W, the TiO₂/CuO-SA yielded shorter pulses of 120 ns at a higher repetition rate of 243 kHz, which demonstrated that the CuO doped with a small amount of TiO₂ could compress the pulse duration more effectively and generate higher repetition rate at the same pump power level. Previous studies have shown that the carrier recovery time in CuO is about ~50 ps [24], while TiO₂ has an ultrafast saturation recovery time of 1.5 ps [36], which is more conducive to achieving high repetition rate output as an optical modulator. Compared with pure CuO (Figure 5c), the introduction of TiO₂ accelerates the carrier recombination process and plays an important role on the faster Q-switching. Shorter Q-switching pulse duration could be anticipated with a larger modulation depth of TiO₂/CuO-SA, by synthesizing felicitous number of layers and thickness [51]. Then we calculated the single pulse energy and the peak power, as depicted in Figure S3a and both of them presented the upward trends with increasing of the pump power. The temporal pulse trains of about

Figure 5: Experimental performances of the passively Q-switched (PQS) lasers with cupric oxide (CuO) and TiO₂/CuO nanocomposites at 1.06 μm .

(a) Continuous wave (CW) and Q-switched average output power. (b) Pulse width and repetition rate versus the incident pump power. (c), (d) Typical Q-switched temporal pulse profile and trains of CuO and TiO₂/CuO lasers, respectively.

500 μs and single pulses were displayed in Figure 5d. No satellite pulses were observed and the pulse-to-pulse instability was calculated to be less than 3% RMSE, demonstrating the high stable modulation characteristics in 1 μm . In addition, the transverse movement of the saturable absorber could hardly impact the output performance, demonstrating that the spin-coating CuO nanosheets and TiO_2/CuO nanocomposites on the substrates were rather homogeneous.

3.2.2 Q-switched laser at 1.34 μm

For the ${}^4\text{F}_{3/2} \rightarrow {}^2\text{I}_{13/2}$ transition of the $\text{Nd}:\text{GdVO}_4$ operating at 1.34 μm , the Q-switched performances of pure CuO and TiO_2/CuO nanocomposites as SAs were shown in Figure 6. Compared to 1.06 μm , the threshold pump power of the CW laser increased to 0.59 W at 1.3 μm , which due to the weaker emission cross section of $\text{Nd}:\text{GdVO}_4$ at 1.3 μm . As shown in Figure 6a, at the highest incident pump power of 2.74 W, the maximum PQS average output power was 225 mW by utilizing TiO_2/CuO -SA, corresponding to a higher slope efficiency of 22.6%. Under this pump power level, the minimum pulse duration of 158 ns and the highest repetition rate of 270.8 kHz was obtained with TiO_2/CuO as SA (Figure 6b), corresponding to the single pulse energy of 830 nJ and the peak power of 5.25 W, as shown in Figure S3b in the Supporting information. Moreover, the transient pulse profiles were depicted in Figure 6c and d, clearly demonstrating that both CuO and TiO_2/CuO nanocomposites could realize ultra-high stability modulation in 1.34 μm .

3.2.3 Q-switching at 1.9 μm

Subsequently, to further testify the capabilities of pulse response characteristics of CuO and TiO_2/CuO nanocomposites at longer wavelengths in the mid-infrared region, we studied the CW and Q-switching regimes at $\sim 2 \mu\text{m}$. The measured CW output spectrum was shown in Figure S4 with a central wavelength of 1878 nm. Under the incident pump power of 3.03 W, the obtained maximum PQS output powers were 155.9 and 166.8 mW with CuO and TiO_2/CuO as SAs, respectively, illustrated in Figure 7a. Compared with that in the above-mentioned NIR laser, the reason for the lower output power here was that the water vapor has a strong absorption peak in the 2 μm band, causing the great losses in the laser resonator. Moreover, the gain of the $\text{Tm}:\text{YLF}$ crystal is much lower owing to the smaller emission cross section. By increasing the incident pump power from 1.23 to 3.03 W, the pulse duration was compressed from 1286 to 210 ns with CuO-SA, while from 1321 to 179 ns with TiO_2/CuO nanocomposites as the SA (Figure 7b), indicating that the composites CuO doped with little TiO_2 had better pulse performance. The temporal pulses trains were displayed in Figure 7c and d, demonstrating the good amplitude stability. However, compared with that at 1.06 μm , the pulse stability was worse. Because the absorption of the $\text{Tm}:\text{YLF}$ crystal was lower, the residual pump laser in the cavity resulted in a stronger thermal effect, affecting the stability of the modulation.

The results clearly showed that the PQS lasers based on TiO_2/CuO nanocomposites exhibited more prominent modulation performance compared with the pristine CuO

Figure 6: Experimental performances of the passively Q-switched (PQS) lasers with cupric oxide (CuO) and TiO_2/CuO nanocomposites at 1.34 μm .

(a) Continuous wave (CW) and Q-switched average output power. (b) Pulse width and repetition rate versus the incident pump power. (c), (d) Typical Q-switched temporal pulse profile and trains of CuO and TiO_2/CuO lasers, respectively.

Figure 7: Experimental performances of the passively Q-switched (PQS) lasers with cupric oxide (CuO) and TiO₂/CuO nanocomposites at 1.87 μm .

(a) Continuous wave (CW) and Q-switched average output power. (b) Pulse width and repetition rate versus the incident pump power. (c), (d) Typical Q-switched temporal pulse profile and trains of CuO and TiO₂/CuO lasers, respectively.

nanomaterials. The enhancement of the optical saturable absorption properties was attributed not only to the formed p-n junctions with the introduction of TiO₂ nanoparticles, but also to the increased massive OV defects. Indeed, p-n heterojunctions in TiO₂/CuO nanocomposites would cause electron-hole pairs separation, and increase the carrier concentration. While the massive OVs would modify the band gap, leading to the red shift of the absorption spectrum. The OV defects involved energy transitions were definitely beneficial to the NIR or even MIR optical absorption [52]. The synergy of the two effects effectively enhanced the nonlinear optical properties of TiO₂/CuO nanocomposite in the near-infrared band. Therefore, the nonlinear optical absorption and modulation characteristics at 1.34 and 1.88 μm might come from the massive intermediate trap states.

Table 2 summarized the PQS bulk lasers performances with different NLO materials as SAs. Exactly as presented, compared with other nanomaterials, the synthesized

TiO₂/CuO nanocomposites featured better optical modulated properties and more potential to generate shorter pulse width and higher repetition rate. More importantly, the higher stability of the output pulses further evinced its remarkable manifestation in nonlinear photonics.

4 Ultrafast photonics application

Sparked by the abovementioned prominent nonlinearity and laser performances of the TiO₂/CuO nanocomposites, an ultrafast mode-locked laser established on a TiO₂/CuO nanocomposites became a fascinating proposition and constituted the major spotlight of this section. As shown in Figure 8a, the construction of the mode-locked Nd:GdVO₄ laser was a 1.44 m long Z-type resonator and the details were illustrated in the Supplementary materials.

Without TiO₂/CuO nanocomposites in the cavity, only continuous wave (CW) laser could be obtained and the

Table 2: Broadband performance comparison of PQS bulk lasers with different NLO materials.

Material	Laser crystal	SA properties			Pulse output properties			Ref
		ΔT (%)	I_s	λ (nm)	Width (ns)	Rate (kHz)	Power (mW)	
InSe	Nd:YVO ₄	3.78	1.21 MW/cm ²	1340	520	150	420	[50]
MoS ₂	Tm,Ho:YAP	21	0.8 MW/cm ²	2129	435	55	275	[53]
BP	Nd:GdVO ₄	35.48	6.14 GW/cm ²	1064	495	312	22	[54]
Bi ₂ Se ₃	Nd:YAG	14.7	4.6 kW/cm ²	1064	576	28.57	150	[55]
Bi ₂ Se ₃ /G	Tm:YAP	6.6	0.44 MW/cm ²	2000	238	108	2340	[56]
TiO ₂ /CuO	Nd:GdVO ₄	21.7	0.68 MW/cm ²	1064	120	243	213	This work
	Nd:GdVO ₄	11.8	0.4 MW/cm ²	1342	158	270	225	
	Tm:YLF	15.3	0.92 MW/cm ²	1878	215	100	156

Figure 8: (a) Experimental setup of the continuous wave mode-locking (CWML) laser based on TiO_2/CuO nanocomposites at $1.06 \mu\text{m}$. (b) Output power of CW and CWML regime versus the incident pump power.

threshold pump power of 0.59 W. When inserting the TiO_2/CuO nanocomposites and adjusting the mirrors carefully, the stable CW mode-locking (CWML) operation was achieved. Figure 8b depicted the relationships of the CW and CWML output power versus the incident pump power. As shown in Figure 8b, when the incident pump power is larger than 4.8 W, the CWML operation can be self-started. Under the incident pump power of 6.7 W, the maximum CWML output power was 0.44 W. When increasing the pump power, the accumulated heat inside the sample would lead to the instability of mode-locking. Thereby, we did not further enhance the pump power during the experiments. Importantly, when reducing the pump power to the original level, stable mode-locked operation could be restored to the origin state, revealing the good thermal and chemical stability of the TiO_2/CuO nanocomposites.

The detailed CWML output characteristics were illustrated in Figure 9. The interval between two adjacent pulses was 9.6 ns and the repetition rate was 103 MHz (Figure 9a), coinciding well with the total cavity length of 1.44 m. Assuming a Gauss intensity profile, the pulse duration of a single pulse was fitted to be 541 ps (Figure 9b). The spectrum of the CWML was centered at 1063.2 nm with

the FWHM of 0.14 nm (Figure 9c). The time-bandwidth product (TBP) was calculated to be 20.1, great than the typical value of Gauss pulse profile ($\text{TBP} = 0.44$), manifesting the large frequency chirping in the cavity. Accordingly, shorter mode-locked pulse could be anticipated by adding prism pairs to compensate the group delay dispersion (GDD) in the cavity and fabricating the materials with larger modulation depth. For the radio frequency (RF) spectrum, the fundamental peak was located at 103 MHz with a signal-to-noise ratio (SNR) of ~ 55 dB (Figure 9d), matching well with the cavity length, demonstrating the great potential of the ultrafast optical modulation properties of the fabricated TiO_2/CuO nanocomposites.

5 Conclusion

In conclusion, the pure CuO nanosheets and TiO_2/CuO nanocomposites were synthesized based on a facile hydrothermal method and a TiF_4 solution etching process, respectively. Subsequently, the Z-scan experimental results demonstrated that both CuO and TiO_2/CuO nanomaterials possessed outstanding saturable absorption

Figure 9: Experimental performances of the continuous wave mode-locking (CWML) lasers with TiO_2/CuO nanocomposites at $1.06 \mu\text{m}$. (a) Pulse train. (b) Single pulse profile. (c) Spectrum. (d) RF spectrum with a span of 800 MHz.

performances in NIR spectra range, but ensuring the consistency of the experimental conditions, the TiO_2/CuO nanocomposites had the larger nonlinear absorption coefficient and modulation depth. In virtue of these, the broadband PQS lasers and ultrafast mode-locking laser utilizing CuO and TiO_2/CuO nanocomposites as SAs were constructed for the first time, which output results once again confirmed the prominent characteristics of the TiO_2/CuO nanocomposites. The promoted modulation performances could be assigned to massive OV defects and the formed p-n junctions, resulting to the decreased band gap, the red shift of absorption wavelength and strong broadband NLO response characteristics. Our work is likely to trigger more thinking about the effects of the OV defects on the bandgap or the modulation characteristics of the nanomaterials, especially the TMOs.

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