Invited Paper

Emergent progress in the interaction of terahertz wave and functional materials

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Abstract: Terahertz (THz) technology has attracted great attention for its application potential in next-generation communications, medical imaging, security, etc. The investigation on the interaction of THz wave and functional materials is the fundamental issues for exploring new physics in condensed matter and then developing advanced THz devices. This review elucidates some emergent work focusing on this point, including ultrafast phenomena studied using time-resolved THz spectroscopy, nanoparticles as contrast agents for THz medical imaging, and spintronics in THz range. The technical problems and research difficulties for present and future work are also presented. This review aims to afford researchers a better understanding of the different THz function materials and their applications.

Keywords: THz, Material, Spin dynamics, Biomedical imaging, Spectroscopy

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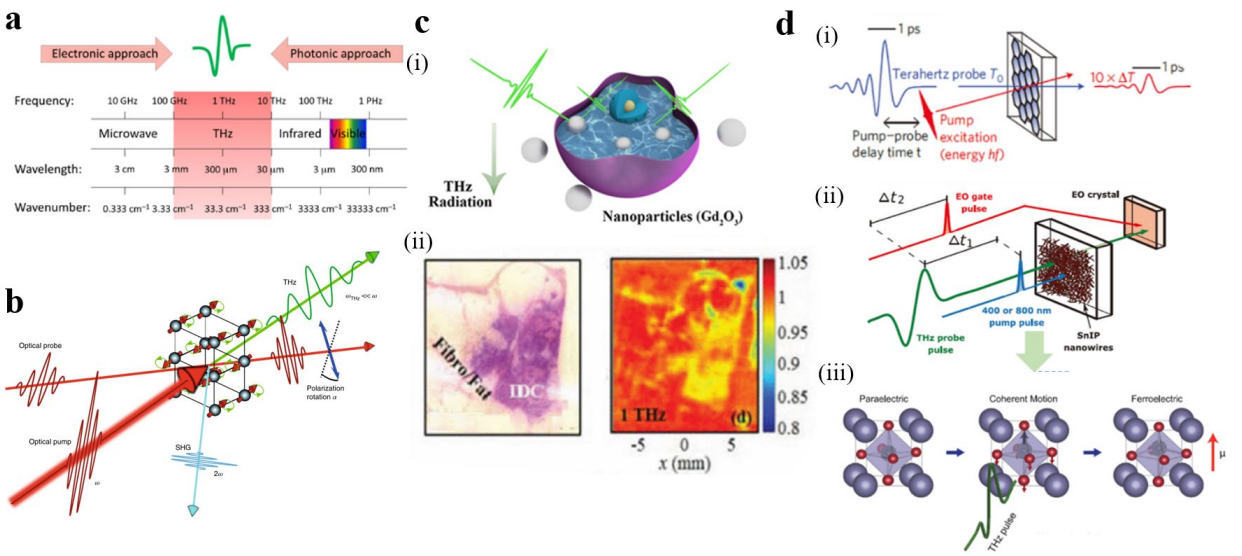

Fig. 1 (a) The THz Region[1]. (b) Schematics of investigation of spin dynamics in antiferromagnets by THz radiation [63]. (c) Application of nanoparticle contrast agent for THz medical imaging. (i) Schematic of gadolinium oxide (Gd_2O_3)-enhanced THz imaging[43]; (ii) Terahertz images of AGS cells containing GONPs[58].(d) Schematic of Time-resolved ultrafast spectroscopy studies on the interaction between THz and materials. (i)Time-resolved carrier dynamics of graphene for two different photon energies using optical pump–terahertz probe measurements; (ii) Photoinduced differential THz transmission as a function of pump-probe time delay on a drop-cast SnIP thin film studied using time-resolved terahertz (THz) spectroscopy[21]; (iii) The ultrafast phase transition in $SrTiO_3$ between the paraelectric phase and ferroelectric phase by using intense terahertz electric field excitation[34].

1. Introduction

Electromagnetic waves with frequencies between 0.1 and 10 *THz* (3000-30 μm) are described as THz radiation (Figure 1a). They are assigned in the electromagnetic spectrum between the microwave and the far-infrared regions. Many molecular rotations in the gas phase, crystalline phonon vibrations, low-frequency vibrations, and intermolecular vibrations in the solid state have been proven by spectroscopic procedures in the THz range. Numerous biological and chemical compounds exhibit characteristic absorptions and dispersions in this range, providing fingerprint information for THz detection and identification. These characteristics make THz technology a promising research field [1].

Following the development of laser-based THz time-domain spectroscopy in the 1980s and 1990s, the field of THz science and technology expanded rapidly. Non-destructive imaging [2], wireless communication [3], and biochemical sensing [4] are conventional research directions.

With the deepening of research, THz materials show unexpectedly excellent performance in dynamic devices [5], such as convertible photonic devices and functional devices [6]. In addition, the discovery that the strong THz field can modulate all electromagnetic waves [7] and the in-depth study of the process interface and magnetic interface of coherent THz waves [8] have brought more possibilities to information dissemination. The research on THz metamaterials has placed unprecedentedly excellent solid devices for our science [9]. Metamaterials also have possible applications in modulating THz phenomena and even camouflage layers [10]. In the study of conductors, the THz spectrum can help to study the photoinduced suppression and recovery of superconducting gaps in certain conductors [11]. It has been reported that THz has a strong coupling effect on exciton-polarized excitons [12, 13], which can be applied to the current hot semiconductor research. Overall, the interaction of THz waves and functional materials opens up plenty of new phenomena in physics, presents enormously possible applications in advanced THz devices, but still has a lot of potential to be explored.

2. Time-resolved ultrafast spectroscopy studies on the interaction between THz and materials

Based on the progress of generation and detection technology of THz waves, researchers have developed a series of THz spectroscopy techniques [14-16], including the THz time-domain spectroscopy system, time-resolved ultrafast optical-pump THz-probe spectroscopy (OPTP), and ultrafast THz-pump optical-probe system. The ultrafast technique is of great significance for understanding the photoinduced dynamical processes in materials and unveiling the interaction between light and matter [17], such as the optoelectronic properties of semiconductors, ultrafast carrier dynamics, charge transport properties, lattice vibrations, etc. Due to its special electromagnetic band, the THz spectrum belongs to both electronic and optical categories. Ultrafast THz technique is sensitive to the response of charge quasiparticles [18], e.g., free carriers, polarons, and excitons. In general, the interaction between THz spectra and materials is mainly related to two types of physical phenomena. The first is the movement of electrons in materials [19] (free carriers, excitons, etc.), and another is crystal lattice molecular vibration [20]. Time-resolved ultrafast optical-pump THz-probe spectroscopy is a powerful tool to detect the dynamic response processes of new materials under optical excitation, including transient THz photoconductivity changes [21], carrier recombination processes [22], charge transport properties [23], mobility measurements [24], hot electron cooling [25], the photoinduced metal-insulator transition process in phase change materials [26, 27], etc. The ultrafast THz-pump optical-probe system is mainly used to observe the new behavior when strong-field THz provided extremely versatile stimuli for controlling the matter.

The intense THz transients as a means of material manipulation enable driving the new dynamic states of matter, including lattice collective vibrational modes (phonons) [28], electric field tunnel breakdown [29], and nonlinear carrier behavior [30], etc. Next, we will mainly introduce the application of these two ultrafast terahertz spectroscopies in materials research.

In the OPTP system, a laser with photon energy higher than the bandgap of material is used to photoexcite the interband transition of charge carriers. The photogenerated charge carriers lead to the attenuation of the THz electric field. After the THz saturable absorption, the recombination of excited carriers results in increasing the transmission of the THz wave [18]. The time-resolved ultrafast carrier recombination processes based on THz transient are achieved by scanning the time delay between pump beam and THz pulse. Based on the OPTP system, the ultrafast temporal evolution of charge-carrier dynamics and charge-carrier mobilities were investigated in the photovoltaic semiconductor, such as Si nanowires [22], lead mixed-halide perovskites [31], and so on. Tang et al. [22] demonstrated relative high values in the carrier lifetime and mobility of the nanowires by measuring the dynamics and transport properties of photogenerated carriers in nanowires derived from an intrinsic silicon wafer. Based on THz photoconductivity transients, Rehman et al. [31] analyzed the charge-carrier dynamics including recombination rate constants and mobilities across the range of compositions in the mixed-halide lead perovskite system $FAPb(Br_yI_{1-y})_3$. Time-resolved terahertz spectroscopy was employed to study the charge-transfer process and the relaxation of hot electrons on 2D Van der Waals materials. Lee et al. [23] observed the efficient charge transfer induced sub-picosecond carrier dynamics in $MoTe_2/WTe_2$ van der Waals heterostructures by using the ultrafast THz photoconductivity spectroscopy, as shown in Figure 2a. Tielrooij et al. [25] used optical-pump terahertz-probe measurements to investigate the energy relaxation process of the primary photoexcited electron-hole pair in doped single-layer graphene, as shown in Figure 2a. Han et al. [32] summarized the physical properties of two-dimensional heterojunction materials based on ultrafast terahertz spectroscopy methods, including exciton formation and relaxation processes, the relaxation of hot electrons in graphene layers, and the conductivity modulated by femtosecond laser pulses, and their related physical properties. Compared to conventional conductometric measurements, THz spectroscopy enables non-contact measurements of the photoconductive properties of materials. THz spectroscopy is used to probe charge transport. Time-resolved THz spectroscopy is a powerful tool for studying ultrafast carrier dynamics and transport properties in various homogeneous and heterogeneous new materials. Dong et al. [24] found the high-mobility band-like charge transport in semiconducting two-dimensional Metal-organic frameworks (MOFs) and measured room-temperature mobility up to ~ 220 $cm^2\ V^{-1}\ s^{-1}$ by using high-frequency terahertz photoconductivity. Purschke et al. [21] used time-resolved THz spectroscopy to study picosecond charge carrier dynamics in a new material that double-helix

Nanowires SnIP films, as shown in Figure 2b. Based on the photoconductive spectroscopy analysis, they found electron mobility as high as 280 $cm^2\ V^{-1}\ s^{-1}$ along with the double-helix axis and hole mobility as 238 $cm^2\ V^{-1}\ s^{-1}$ perpendicular to the double-helix axis. On the other hand, the time-resolved THz spectroscopy is used to probe photoinduced insulator-to-metal transition of phase change materials at picoseconds time scale, such as VO_2, $Ge_2Sb_2Te_5$, and so on. Xiao et al. [33] investigated the ultrafast photoinduced phase transition dynamic processes of VO_2 film and W-doping VO_2 film. Their result suggests that W-doping slows down the dynamic processes including the fast non-thermal process and the slow metallic phase propagation process in VO_2 film and also reduces the photoexcited fluence threshold. Zhu et al. [26] used the time-resolved THz spectroscopy to display the volatile and nonvolatile switching of phase change material $Ge_2Sb_2Te_5$, as shown in Figure 2c.

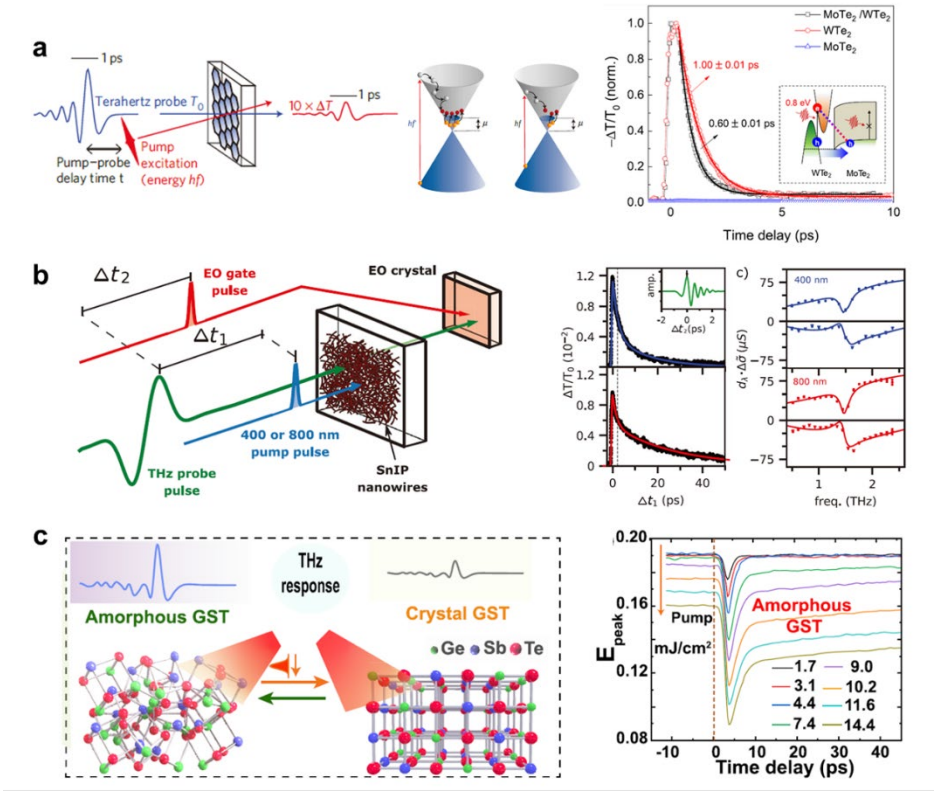

Fig. 2 (a) Time-resolved ultrafast dynamics of two-dimensional materials, including the carrier dynamics of graphene for two different photon energies and the charge transfer across the interface and the subsequent interlayer exciton formation in $MoTe_2/WTe_2$ van der Waals Heterostructures[23, 25]. (b) Photoinduced differential THz transmission as a function of pump-probe time delay on a drop-cast SnIP thin film studied using time-resolved terahertz (THz) spectroscopy[21]. (c) Laser pumped transient change of the THz electric field peak transmitted on phase change materials amorphous GST sample[26].

THz wave can also control the collective excitations in solids, to drive phase transitions and associated changes in material properties. The ultrafast THz-pump optical-probe technology is an important tool to study the emergence of new states of materials under strong-field terahertz excitation and manipulation. Although the photon energy of THz is very low (photon energy of ~4 *meV* at 1 *THz*), some materials have coherent lattice vibrations frequency located in the THz band. For these materials, the strong field THz enables direct excitation of collective lattice oscillations to drive new states of matter or discover some hidden phase transition processes.

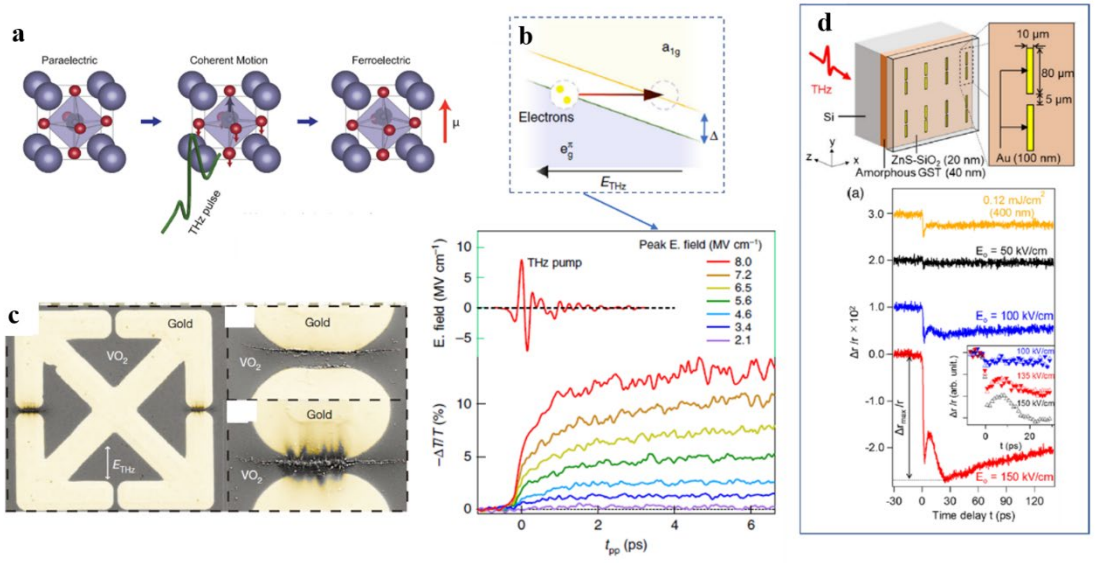

Fig. 3 (a) The ultrafast phase transition in $SrTiO_3$ between the paraelectric phase and ferroelectric phase revealed using intense terahertz electric field excitation[34]. (b) Terahertz-driven ultrafast electronic Mott transition in V_2O_3 based on the non-resonant THz field induces energy band distortion[36]. (c) THz field-induced insulator-metal transition in VO_2 by using metamaterial-enhanced THz pulses[37]. (d) Strong field THz pulses induced crystallization process in the phase-change material $Ge_2Sb_2Te_5$ [29].

Li et al. [34] found a hidden ferroelectric phase in quantum paraelectric strontium titanate ($SrTiO_3$) and they observed the ultrafast phase transition between the paraelectric phase and ferroelectric phase by using intense terahertz electric field excitation, as shown in figure 3a. Yoshikawa et al. [35] demonstrated that the amplitude mode of the charge density wave is directly excited by a strong field THz pulse, which resulted in an ultrafast switching to an insulating-like metastable state in the layered transition metal dichalcogenide compound 3R-$Ta_{1+x}Se_2$. A strong THz pulse can be used to control not only the structural phase transition but also a sub-picosecond electronic switching like the Mott transition. Giorgianni et al. [36] demonstrated that intense THz

pulses electric-field can drive a Mott transition in vanadium sesquioxide (V_2O_3). And the results shown the emergence of an instantaneous purely-electronic insulator-to-metal transition overcoming the thermal regime. Besides, the strong THz electric field concentrating in a small area can cause a temperature increase in the materials via Joule heating, which in turn leads to nanometer-scale crystal growth or temperature triggered insulator-to-metal phase transitions. For example, Liu et al. [37] used metamaterial-enhanced picosecond, high-field THz pulses to achieve a THz field-induced insulator-metal transition in VO_2, as shown in figure 3c. Sanari et al. [29] investigated the strong field THz pulses induced crystallization process in the phase-change material $Ge_2Sb_2Te_5$. As shown in figure 3d, the Au antenna can enhance THz electric field of 150 *kV*/*cm* and then trigger the phase change.

3. Nano-contrast agents for THz biomedical imaging

THz medical imaging has attracted great attention due to its unique characteristics different from the previous medical imaging technologies. It's well known that THz wave is non-ionizing and a large number of biomolecules have characteristic fingerprints in THz regime [38-40]. So THz wave is quite suitable for medical imaging and would be a good complementary tool for the present medical imaging methods [41-48]. Nevertheless, most tissues and organs contain too much water or exist in an aqueous environment. The water will strongly absorb THz wave and lead to deteriorate imaging contrast [49]. There have been some effective solutions for *in vitro* imaging, using freezing, dehydration, and paraffin embedding [50, 51] to obtain waterless samples. By contrast, the *in vivo* imaging has been largely blocked by the problem of low contrast in THz imaging. Recently, the concept of terahertz imaging contrast agent has been proposed. The most studied mechanism of THz imaging contrast agent is based on the photothermal effect. Here a laser excitation causes the material to heat up and thus leading to increased temperature. Subsequently, it would result in increased THz reflection amplitude, which corresponds to enhanced THz imaging contrast [43].

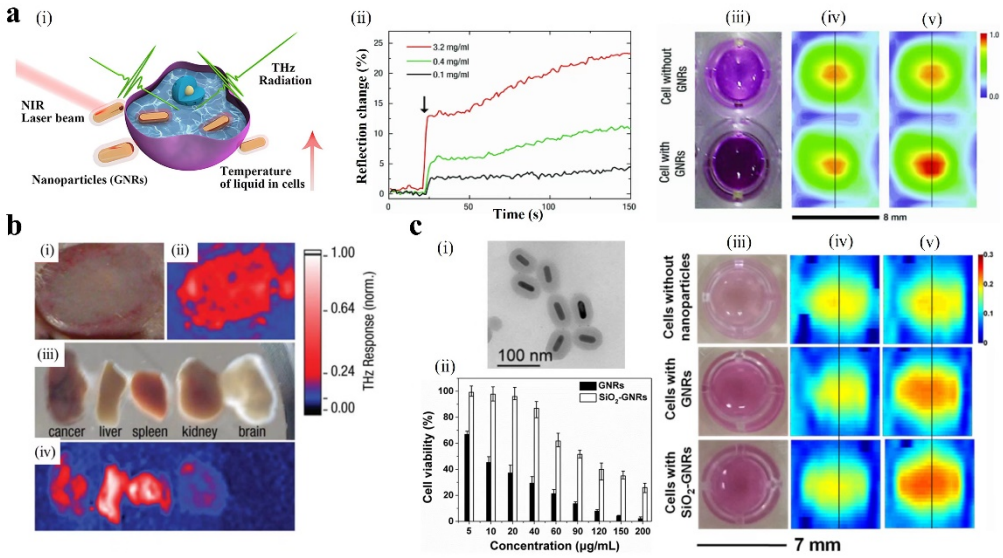

Fig. 4 Gold nanorods as a terahertz imaging contrast agent. (a) (ⅰ) Schematic of GNR-enhanced THz imaging[43]; (ⅱ) Peak reflection changes in THz signals from live cancer cells with GNRs[53]; (ⅲ) optical image[53]; (ⅳ) THz image without infrared (IR) irradiation[53]; (ⅴ) THz image with IR irradiation[53]. (b) (i) Optical image of an A431 tumor in a mouse[42]; (ⅱ) THz image of (ⅰ); (ⅲ) Optical images of cancer, liver, spleen, kidney, and brain samples; (ⅳ) THz image of (iv). (c) (i) Transmission electron microscope (TEM) images of GNRs coated with silica; (ii) dose-dependent cytotoxicity of L929 cells determined by MTT assay after exposure to uncoated and silica-coated GNRs for 24 h. Prostate cancer cells with and without nanoparticles; (iii) optical image; (iv) THz image obtained without near-infrared (NIR) laser irradiation; (v) THz image obtained after NIR laser irradiation[54].

The first developed contrast agent material is gold nanorods (GNRs), which was proposed by Oh's team in 2009 [53]. When GNRs are excited by a near-infrared (NIR) laser, the resonance frequency of the laser is similar to that of GNR. It then generates a local surface plasmon resonance effect (LSPR). The strong absorption of laser can cause an increase in the temperature of the surrounding environment. In Oh's work, GNRs were injected into human epidermoid carcinoma cells (A431) and imaged using a terahertz reflectance imaging system. The experimental results showed that the reflected signal of cells containing GNRs was enhanced by 20% (Figure 4a(ⅱ)) under the irradiation of NIR light [53]. Figure 4a(ⅴ) shows that the terahertz imaging contrast of the cells containing the contrast agent has been improved largely.

Researchers then modified the surface of GNRs with specific receptors to make it a targeting contrast agent and experimented on a live cancer-stricken mouse [42]. Imaging experiments were performed on this mouse 24 hours after intravenous injection of a contrast agent. The results showed that terahertz imaging with the aid of a contrast agent could clearly distinguish the location

and size of the tumor (Figure 4b(i)(ii)). After dissecting this mouse and imaging its organs (Figure 4b(iii)(iv)), a certain amount of contrast agent was also found in the liver and spleen, indicating its gradual enrichment to the tumor area through its circulatory system and finally metabolized by the kidneys.

However, it's found that the residual surfactants (such as CTAB) in the preparation of GNRs were cytotoxic, which led to a low survival rate in cell experiment. Huang et al. [54] used SiO_2 to modify the surface of GNRs, which greatly improved their cell stability and attenuated cytotoxicity without affecting their imaging effect. The experimental results are shown in Figure 4c, which would promote the application of GNRs as terahertz contrast agents further.

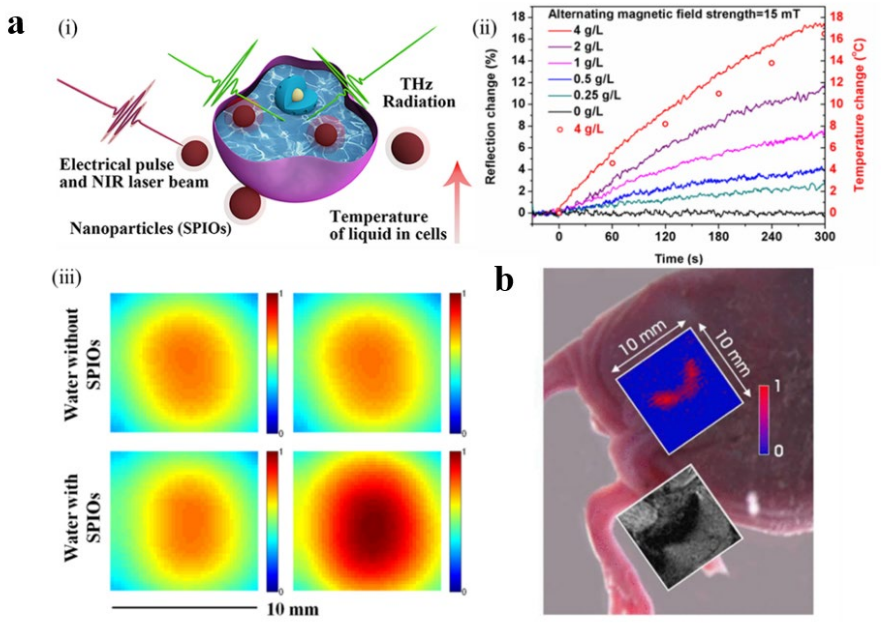

Fig. 5 (a) (ⅰ) Schematic of the responses of an SPIO to a THz pulse and a near-field pulse[43]; (ⅱ) SPIO solution concentration dependence of reflected THz signal under alternating magnetic fields and temperature changes of the SPIO solution at a concentration of 4 g/l [55]; (ⅲ) THz images of water before and after 15 min of exposure to an alternating magnetic field: images before (i) and after (ii) alternating magnetic field exposure. (b) In vivo THz (upper) and magnetic resonance imaging (MRI) (lower) images 24 h after SPIO transfection of mouse ovarian cancer [56].

The other contrast agents based on thermal effect for THz imaging have also been investigated. For example, Zhang [55] used superparamagnetic iron oxide nanoparticles (SPIO), a magneto-

thermal material, to improve THz imaging contrast. Excited by magnetic field, SPIO could be used to warm up the surrounding water environment due to the magneto-thermal effect. Then it can enhance the THz wave reflection signal (Figure 5a(ⅱ)) and improve the contrast of imaging. As shown in Figure 5b, THz imaging was performed on aqueous solutions of water and SPIO, and the contrast of the samples containing SPIO increased dramatically when the excitation of magnetic field was applied.

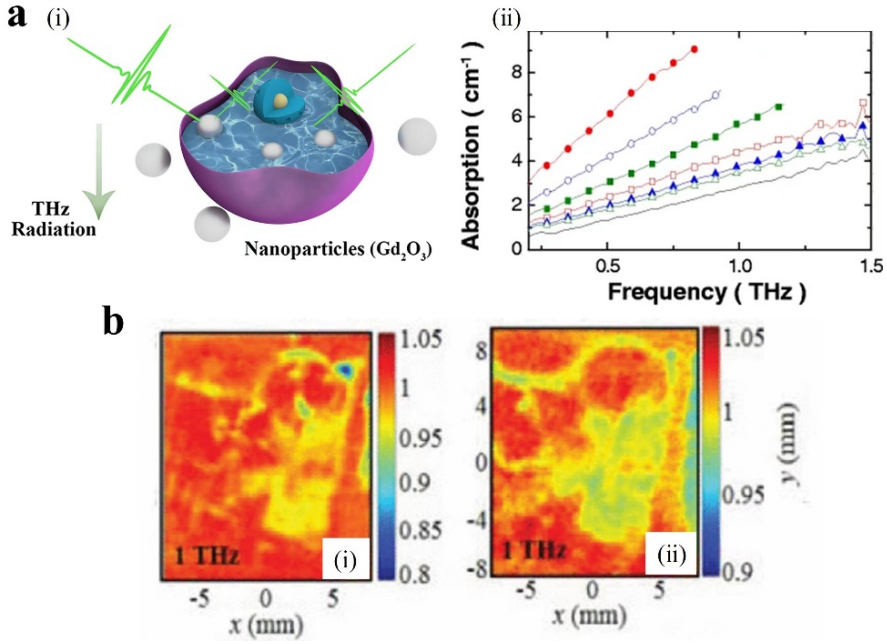

Fig. 6 (a) (ⅰ)Schematic of GONPs -enhanced THz imaging[43]; (ⅱ) THz absorption at various concentrations of GONPs [57]. (b) THz images of AGS cells containing different concentrations of GONPs [58].

Furthermore, new materials and mechanisms for THz imaging contrast agents are still been explored. Lee et al. [57] used gadolinium oxide nanoparticles (GONPs) as a contrast agent for THz imaging, because it was found that their THz absorption intensity was about three orders of magnitude higher than that of water. The huge absorption difference made it perfectly suitable as a contrast agent for THz imaging (Figure 6a). Figure 6b indicates an enhanced THz imaging contrast for human gastric cancer cells (AGS) in culture assisted by the use of GONPs [58]. Bowman's group [59] proposed carbon-based nanoparticles as contrast agents. They performed an imaging experiment using micron diamonds, nanodiamonds (NDs), and nanoscale onion-like carbon (OLC) in simulated tissues. It showed that OLC can interact with THz waves, resulting in signal alteration and enhanced imaging contrast.

4. Monitoring and control of spin dynamics by THz technology

Advances in THz and electric-dipole coupling [60, 61] have made it possible to observe and even control low-energy fundamental excitations including spin dynamics on the femtosecond timescales [62]. In recent years, the interaction between THz and magnetic-dipole has gradually entered the field of researchers' vision, inspiring a new approach to the study of THz and spin interaction. The frequency of collective spin modes of many multiferroic materials, antiferromagnetic (AFM) materials and ferromagnetic (FM) materials are in the THz band, which allows THz to detect the spin dynamics of materials. On the other hand, the strong THz pump has the possibility to control the spin state. Thus, the interaction of spin and THz wave can be carried out in two ways: i) the use of THz technology in understanding the complexities of materials and ii) the exploration of new THz functionalities of emerging materials for further advancement of THz technology. Here we will summarize the work of researchers in recent years from these two perspectives.

Multiferroics have attracted great attention in research of spintronics because of the promising applications in coupling between magnetic and electric degrees of freedom. Among them, multiferroic rare-earth manganites $RMnO_3$ (R=rare earth) have pronounced coupling between magnetization and ferroelectric polarization (magnetoelectric effect), which can be traced back to the specific couplings between spins and the deformable lattice [63]. Such materials could be used in future electronic devices including nonvolatile memories and spin filters. In order to further understand the mechanism of ferroelectric effect of multiferroic $RMnO_3$, THz spectroscopy has been used to study the complex properties of multiferroic $RMnO_3$ [63-67].

In 2010, Goian et al. [63] reported the infrared and THz spectroscopies of $Y_{1-X}Eu_XMnO_3$. Figure 7b shows the THz absorption spectrum. Two significant absorption peaks correspond to AFM resonance and an impurity mode or multi-phonon absorption peak respectively, demonstrating hadronic lattice coupling. In 2014, Chaix et al. [64] first carried out research on magnetic electrons in $ErMnO_3$. Their experimental results (Figure. 7d) showed that the magnetic loss of the magneton in $ErMnO_3$ was completely transformed into an electrically activated excitation, and this magnetoelectric dynamic phenomenon was explained by the hybridization between the CF level transition of Er magnetic rare earth and Mn magneton. Fabreges [66] investigated the spin waves as sociated with the Mn order together with Ho crystal field excitations in the multiferroic hexagonal manganite $HoMnO_3$. They found that the THz absorption spectrum of $HoMnO_3$ was different from the other hexagonal manganese compounds such as $YMnO_3$ or $ErMnO_3$ (Figure 7e). It indicated the effect of Ho on the THz spectrum. The complex ho-Mn coupling phenomenon in $HoMnO_3$ extends the researchers' understanding of the structural properties of multi-iron materials,

and also provides a new understanding of the dynamic coupling phenomenon of rare earth transition metals in the THz range.

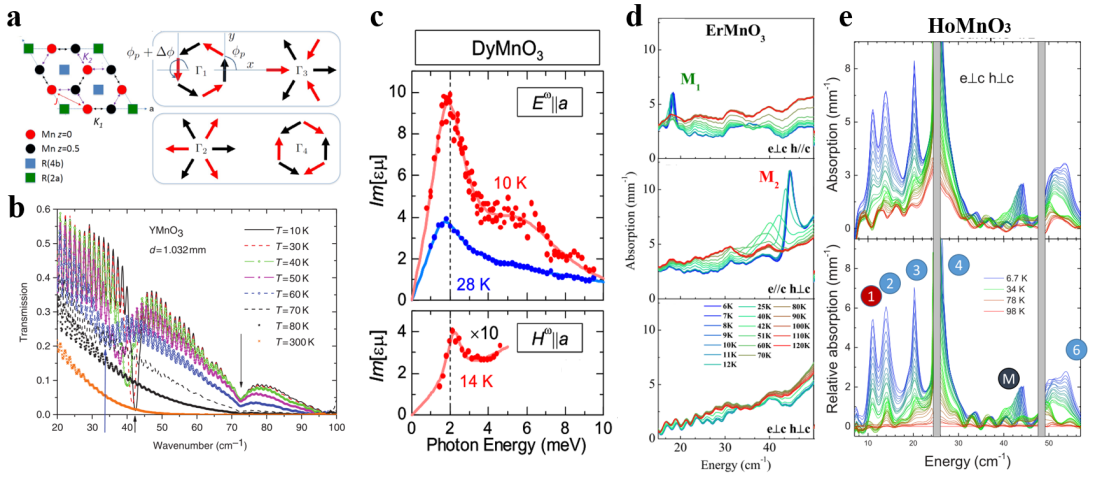

Fig. 7 (a) Sketch of $RMnO_3$ crystallographic and magnetic structures[66]. (b) THz transmission spectra of $YMnO_3$ at various temperatures[63]. (c) Low-energy electrodynamics of spin excitations in ferroelectric *bc* (at 10 *K*) and *ab* (17 *K*) spiral spin phases of $DyMnO_3$[67]. (d) THz absorption spectra of $ErMnO_3$ for three different orientations of the electromagnetic wave *e*, *h* fields with respect to the crystal *c* axis[65]. (e) THz absorption spectra of $HoMnO_3$ for the three different orientations of the electromagnetic wave *e*, *h* fields with respect to the crystal *c* axis[66].

In addition to multiferroic $RMnO_3$, we review the THz and spin system interactions in AFM. The AFMs lattice contains a finite number of magnetons, but these magnetizations compensate each other, resulting in the total magnetization being zero in the ground state [68]. Taking a double sublattice AFM, NiO [62], as an example. In its ground state, the magnetization intensity of the two opposite sub-lattice is exactly the same, resulting in a net magnetic moment of zero [69,70]. The symmetry constraint leads to the possibility of non-zero mean spin magnetization being strictly zero, making AFM insensitive to magnetic field disturbances and multilayer stability [62]. To realize THz control and monitor the spin dynamics of NiO crystals, Kampfrath T. et al. [62] created a hybrid laser system. Figure 8a shows that a single THz transient triggers an exponentially decaying spin precession. Their work not only proves the THz coherent control of AFM spin dynamics, but also describes the possibility of THz pumps performing Boolean operations on AFM spin states. By virtue of the excellent interaction characteristics of THz waves and NiO materials, Khymyn et al. [71] established an AFM THz-frequency Josephson-like oscillator driven by spin current (Figure 8b(i)). In the case of a NiO (5 *nm*)- Pt (20 *nm*) bi-layer, it is possible to achieve the generation of 0.1–2.0 *THz* signals with reasonable current densities that were previously achieved

in FM spin-torque nano-oscillator of a similar geometry.

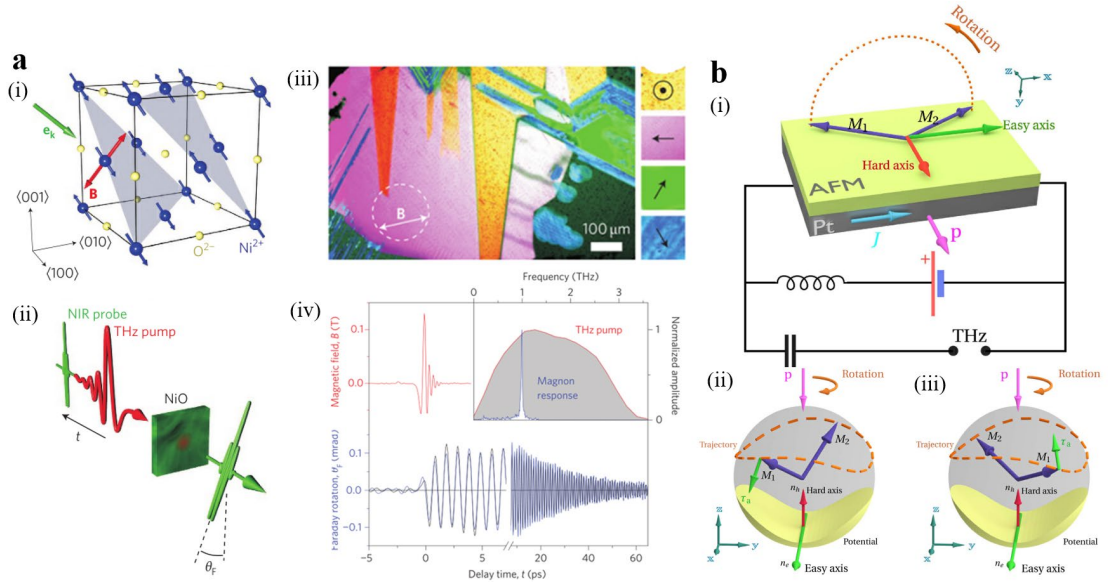

Fig. 8 (a) (i) Crystal lattice of NiO (blue spheres, Ni^{2+}; yellow spheres, O^{2-}) with magnetically ordered spins (blue arrows) of a selected S domain in the (111) planes (light blue) and the direction of the THz magnetic field B (double-ended red arrow)[62]. (ii) Schematic of femtosecond THz spin resonance[62]. (iii) Polarization micrograph (top view) of the 45-mm-thick NiO sample, identifying all four types of T domains[62]. (iv) A pair of 0.5-ps, 40-mT THz transients (grey curve) is applied to antiferromagnetic NiO. The resulting magnetization dynamics (blue curve) shows that the pulse sequence switches a 1-THz spin wave on and off[62]. (b) (i) Schematic view of the THz-frequency oscillator based on a Pt/AFM bilayer[71]. (ii) Schematic representation of the rotating sublattice magnetizations in an anisotropic antiferromagnet under the action of a spin-transfer torque[71].

In the previous section we introduced a Josephson-like oscillator as a THz generator. Despite being theoretical, use spin-dependent technologies to generate high-frequency electromagnetic signals has become a new means of THz generation. There are several approaches to THz-frequency generation nowadays, including the use of free-electron lasers, quantum cascade lasers, superconductor Josephson, backward-wave oscillators, electro-optic rectification of laser radiation, etc [71]. However, the above-mentioned sources of THz-frequency signals require rather complex setups or low temperatures and/or cannot be made sufficiently small, which greatly limits their usability in many important practical applications. As an alternative to traditional THz generator, the following three models of spin-dependent THz generator show excellent emission properties. First, Sulymenko et al. [72] designed of a THz-frequency signal generator based on a layered structure consisting of a current-driven Pt Layer and a layer of an AFM with easy-plane anisotropy (Figure 9a(i). They theoretically proved that radiation frequencies in the range f=0.05~2 *THz* are

possible at the experimentally reachable magnitudes of the driving current density, and they evaluate the power of the signal radiated into different types of resonators (Figure 9a(ii)). Chen et al. [73] then studied THz emission spectroscopy from compensated magnetic heterostructures including CoGd ferrimagnet alloy or IrMn AFM (Figure 9b(i)). Under femtosecond laser excitation, the compensated magnetic base bilayer generates THz radiation through net spin polarization, with the radiation intensity depended on the temperature of the CoGd or IrMn layer (Figure 9b(ii)).In 2019, Zhang et al. [74] investigated THz emission from CoFeB/Cr/Pt trilayers with emphases on the role of Cr as both a spin current transporter and generator (Figure 9c(i)).Both the CoFeB layer and uncompensated spins in Cr near the CoFeB/Cr interface generate spin currents upon femtosecond laser excitation, which are subsequently converted to transient charge current via the inverse spin Hall effect in Pt, and thereby generating THz emission with different polarizations. In this system, the parameters of Cr layer have a significant influence on the wavelength and time delay of transmitting THz (Figure 9c(ii)). Although the three THz generation systems mentioned above are still in the theoretical stage, spin spin-dependent THz generators undoubtedly have broad application prospects.

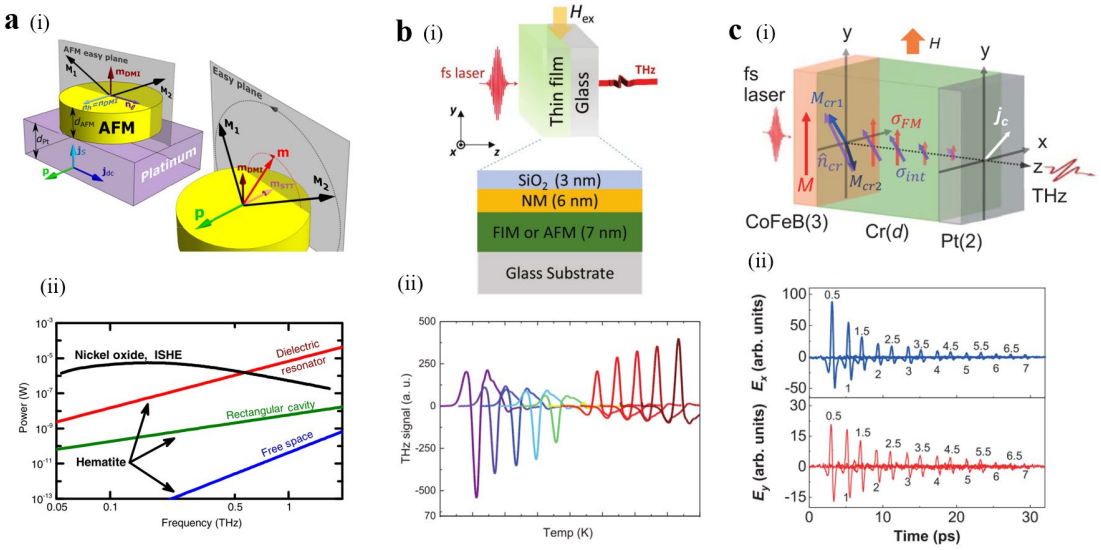

Fig. 9 (a) (i) Schematics of an auto-oscillator based on a layered structure containing Pt layer and AFM layer[72]. (ii) Generated power vs frequency for a SHO based on a layer of a canted AFM providing dipolar radiation into different types of resonance systems[72]. (b) (i) Schematics of film stack and THz emission geometry[73]. (ii) Temperature dependence of the emitted THz signal from the $Co_{63}Gd_{37}$/Pt bilayer[73]. (c) (i) Schematics of the CoFeB/Cr/Pt trilayers and experimental setup[74]. (ii) THz signals from CoFeB/Cr/Pt emitters; the number above or below the waveforms indicates the Cr thickness in *nm*[74].

5. Conclusions

In this review, we elucidate the interaction of THz wave and functional materials from three aspects. Firstly, THz wave can be utilized for investigating ultrafast phenomena in condensed matter. Particularly, strong intensity THz wave could act as an excitation source to trigger collective excitations in solids. So the THz-pump optical-probe technology has been emerged as an unique method for ultrafast science. Secondly, for THz medical imaging, the imaging contrast agents has shown significant promoting effect for improving the imaging quality. This review presents typical contrast agents for this purpose. Referring to the development of imaging contrast agents in the other medical imaging methods, it's strongly believed that the contrast agents for THz medical imaging would be investigated and developed quickly. Thirdly, the interaction of THz wave and spins in condensed matter has also been an emergent topic. It means that we can understand the spintronics using THz technology, and explore advanced THz functional devices based the spintronics.

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