Photothermal conversion for the solar energy use

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Abstract

This work describes the photothermal conversion phenomena, the main mechanisms that take place in this, and the related concepts, avoiding, as far as possible, technicalities and advanced mathematical language to provide a general and accessible overview to students and professionals from diverse fields of knowledge and not only to people related to science and engineering. Some of the most critical applications in the photothermal conversion field are also discussed. Initially, some basic concepts are presented that are necessary to accurately describe the main topics discussed in the article's final part: the photothermal conversion mechanisms and some of their applications. Photothermal conversion for solar energy use is a field of research with a growing interest that, due to its current relevance, is pertinent to widely disseminating and promoting its understanding among students and professionals in different fields of knowledge.

Keywors: Photothermal conversion; solar energy use; thermal radiation; selective surfaces.

Resumen

Este trabajo describe el fenómeno de conversión fototérmica, los principales mecanismos que en él toman lugar y los conceptos relacionados, evitando, en la medida de lo posible, tecnicismos y lenguaje matemático avanzado para proporcionar una visión general y accesible a estudiantes y profesionales de campos del conocimiento diversos, y no solo a personas relacionadas con la ciencia y la ingeniería. También, se describen algunas de las aplicaciones más importantes en el campo de la conversión fototérmica. Inicialmente, se presentan algunos conceptos básicos necesarios para describir de una mejor manera los temas principales tratados en la parte final del artículo: los mecanismos de conversión fototérmica y algunas de sus aplicaciones. La conversión fototérmica para el aprovechamiento de la energía solar es un campo de investigación de creciente interés que, por su relevancia actual, resulta pertinente difundir ampliamente y promover su comprensión entre estudiantes y profesionales de los diferentes campos del conocimiento.

Palabras clave: Conversión fototérmica; energía solar; radiación térmica; superficies selectivas.

For economic, environmental, and political reasons, it is necessary to look for alternative energy sources to fossil fuels, which are at the same time economical, abundant, clean, and preserve the ecological balance [1]. Energy from the sun, wind, and the Earth (geothermal) are the options. However, energy from the sun has extra advantages, and it is the most promising alternative. The sun emits energy 24 hours a day and 365 days a year; all places receive this energy according to their latitude; it is abundant and accessible, it is non-polluting, it does not produce harmful waste, it occupies less area per watt in the energy production, no one can increase its price, etc. [2]. The use of solar energy is widely justified if the statistical data related to the radiation incident in the Earth's atmosphere is observed, with a solar constant of 1,367 W/m² and an energy of 2.16×10^{20} W/h/year [3].

Photothermal (PT) conversion refers to the process of converting light energy into heat. This conversion is typically achieved using materials that can absorb light and transform it into thermal energy. The absorbed light energy raises the temperature of the material, leading to an increase in its thermal energy. PT conversion efficiency depends on the material properties and the wavelength of the incident light. Materials with high absorption coefficients in the desired spectral range are often chosen for effective PT conversion. Photothermal conversion is utilized for different purposes, including solar energy harvesting, PT therapy, water purification, and heat-assisted magnetic recording (HAMR) [4]. This divulgation work describes the main mechanisms of photothermal conversion and some applications, before which some basic concepts are reviewed.

The Electromagnetic Spectrum

The electromagnetic (EM) spectrum represents how EM waves are classified according to regions divided by intervals of wavelengths, or frequency, or corresponding energy. The regions range from those with shorter wavelengths, such as cosmic rays, gamma rays, and X-rays, through ultraviolet (UV) light, visible (VIS) light, infrared (IR) rays, and microwaves to longer wavelength waves, such as radio waves. These are shown in Table1. The EM energy spreads as a wave, an EM wave. In free space it propagates at the speed of light of c_o = 2.99792 × 10^8 m/s, and in a medium with refraction index n as $c = c_o/n$. This speed is related with its wavelength λ, and its frequency ν as

$$c = \lambda\nu \tag{1}$$

The EM energy can interact with matter in the form of packets, called photons, whose value is directly proportional to the frequency of the EM wave:

$$E = h\nu \tag{2}$$

where $h = 6.6256\text{x}10^{-34}$ *Js* is a Planck's constant [5].

Region	Wavelength (nm)	Frequency (Hz)	Energy (eV)
Radio	$>10^8$	$<3\text{x}10^9$	$<10^{-5}$
Microwave	10^8-10^5	$3\text{x}10^9$-$3\text{x}10^{12}$	10^{-5}-0.01
Infrared	10^5-700	$3\text{x}10^{12}$-$4.3\text{x}10^{14}$	0.01-2
Visible	700-400	$4.3\text{x}10^{14}$-$7.5\text{x}10^{14}$	2-3
Ultraviolet	400-1	$7.5\text{x}10^{14}$-$3\text{x}10^{17}$	3-10^3
X-Rays	1- 0.01	$3\text{x}10^{17}$-$3\text{x}10^{19}$	10^3-10^5
Gamma Rays	< 0.01	$>3\text{x}10^{19}$	$>10^5$

Table 1. Regions of the electromagnetic spectrum

Thermal Radiation

Electromagnetic radiation is the EM energy emitted by matter due to changes in atoms and molecules' electronic, vibrational, and rotational states propagating as EM waves. Thermal radiation is that part of EM radiation whose wavelength ranges from ~ 200 nm to ~ 1 mm. It includes the near and middle UV (from 200 to 400 nm), the VIS (from 400 to 700 nm), and IR (from 700 nm to 1 mm) regions of the EM spectrum. All surfaces emit it if their temperature is above absolute zero. It differs from other forms of EM radiation, such as gamma rays, X-rays, microwaves, and radio and TV waves, unrelated to temperature.

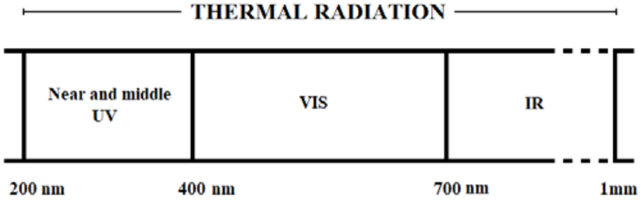

Fig. 1. Thermal radiation region of the EM spectrum.

Thermal radiation is a form of heat transfer different from conduction and convection. It can be transferred between two surfaces at different temperatures. It does not require a medium to propagate and can even spread through free space. It is how we perceive the heat coming from the Sun. Thermal radiation is a volumetric phenomenon. However, it is usually considered a surface phenomenon in opaque solids. The radiation emitted from the interior of these solids does not reach the surface, and the radiation incident from the outside is commonly absorbed within a few microns from its surface [6].

A blackbody (BB) is an ideal body that absorbs all incident EM radiation upon it (zero reflectance and zero transmittance), regardless of wavelength or incidence angle. The BB is a perfect emitter of thermal radiation, depending only on its temperature. The fact that a BB does not reflect incident radiation is the reason for its name. The real substances reflect some radiation. However, some of them approach a BB, as a carborundum (silicon carbide, SiC), gold black, and a thick layer of carbon black, which can absorb approximately 99% of all incident thermal radiation. To our eyes a body may appear black, but our eyes are only sensitive to the VIS region, which is a small portion of the thermal radiation region. Many white paints are good absorbers of IR, and good reflectors of VIS radiation. The concept of BB is useful in science and technology because serves as a tool for modeling the behavior of thermal systems [7,8].

The theoretical spectral distribution of BB radiation was discovered by the German physicist Max Planck in 1901, now called Planck´s blackbody spectral radiation law, given as:

$$M_\lambda = \frac{2\pi hc^2}{\lambda^5\left[e^{hc/\lambda kT}-1\right]} \tag{3}$$

where h = 6.626176 × 10^{-34} $J{\cdot}s$ is Planck's constant and k = 1.380662 × 10^{-23} $J{\cdot}K^{-1}$ is Boltzmann's constant. Here, M_λ is the flux per unit area leaving the surface of a BB at a wavelength λ, called spectral **exitance**, with unit W/m^2 [3,7,8]. Many literature uses the spectral radiance L_λ in Planck´s law, Eq. (3), instead of spectral exitance. But, this is incorrect since the spectral radiance is the area and solid angle density of flux radiant (units: $\text{W}\cdot\text{m}^{-2}\cdot\text{sr}^{-1}$) [7]. Fig. 2 shows a BB radiation spectra obtained from Ec. (3). A log-log scale was used to cover the wide range of values. Note that at room temperature (~300K), the maximum spectral excitation occurs around 10 μm, and it moves to shorter wavelengths with increasing temperature.

The relationship between the wavelength of the maximum intensity of BB radiation and its temperature was formulated by the German physicist Wilhelm Wien in 1893, called Wien´s displacement law, which can be written as

$$\lambda_{max}T = b \tag{4}$$

where b = 2897.8 $\mu m{\cdot}K$ is the Wien´s constant. This relationship can be obtained by differentiating the Planck´s law, Eq. (3), and equating to zero.

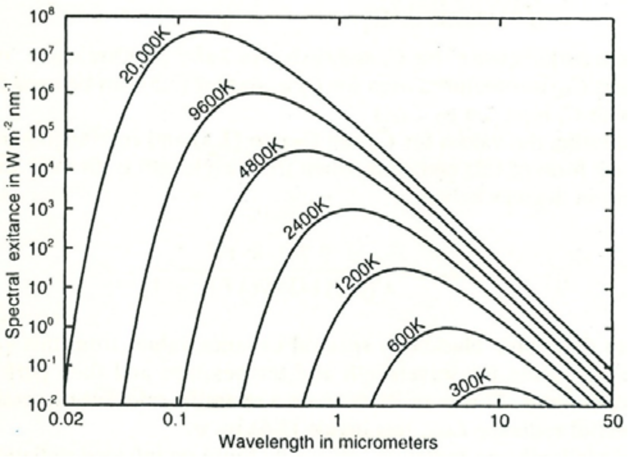

Fig. 2. $M_{BB\lambda}$ at various temperatures [7]

By integrating Planck's law over all wavelengths, the total energy emitted per unit area by a BB is found to be

$$M = \sigma T^4 \tag{5}$$

where M is the exitance (units: W·m^{-2}), and $\sigma = 5.6697 \times 10^{-8}$ Wm^{-2}K^{-4} is the Stefan-Boltzman constant. This equation is known as Stefan-Boltzman law, named after physicists Josef Stefan and Ludwig Boltzmann. This is the radiation emitted by an idealized BB, and it is the maximum limit for a real surface, for which Eq (5) should be expressed as

$$M = \varepsilon\sigma T^4 \tag{6}$$

where ε is called either the **emittance** or the **emissivity** of the surface [7], whose value is in the range $0 \leq \varepsilon \leq 1$, where 0 indicates perfect reflectivity (no emission) and 1 indicates perfect BB behavior (complete emission). Emissivity measures of how closely a surface approximates a BB, for which $\varepsilon = 1$ [6].

In addition to being an ideal emitter, the BB is also a perfect absorber, with an absorptance α equal to 1. A surface's **absorptance** is the fraction of the radiant energy incident absorbed by it. Absorptance depends upon the surface temperature and wavelength of incident radiation. For a real surfaces, like emissivity, the value of absorptivity is in the range $0 \leq \alpha \leq 1$. Kirchhoff's law states that emissivity and the absorptivity of a surface at a given temperature and wavelength are equal. A surface with high absorbance for a given λ in the VIS region at room temperature will also have a high emittance to that λ; it will emit radiation almost like a BB at that temperature and that λ, which is insignificant.

Solar absorptance and infrared emittance are quantities required for most solar energy calculations. Considering energy conservation, it can be shown that, for an opaque surface, energy from all directions, either monochromatic or total, is either absorbed or reflected so that

$$\rho_\lambda + \alpha_\lambda = \rho_\lambda + \varepsilon_\lambda = 1 \tag{7}$$

And

$$\rho + \alpha = 1 \tag{8}$$

where ρ represent the surface´s reflectance; the ratio of the reflected radiant flux to the incident [3,7].

The Sun Radiation

The sun is a hot gaseous matter sphere with 5777 K effective BB temperature. In their interior regions its temperature is estimated at 8 MK to 40 MK. The energy generated inside is transferred to its surface and then radiated into space. The **irradiance** is the incident radiant energy on a surface per unit of time and unit perpendicular area. The **solar constant**, denoted as G, is the solar irradiance that reaches outside the earth's atmosphere at a mean sun-earth distance. Its currently accepted value is 1.353 kW/m^2, with ± 1.5% estimated error [9]. The G constant and its spectral distribution, Fig 3, are fundamental for solar energy conversion systems. For solar energy and its applications, the wavelengths of importance are in the near-UV to the near-IR range, that is, 0.29 to 2.5 μm, the region that includes most of the sun radiation on the earth's surface. Solar radiation in the 0.25 to 3 μm range is significant outside the atmosphere, but a part of it is not received on the ground [3].

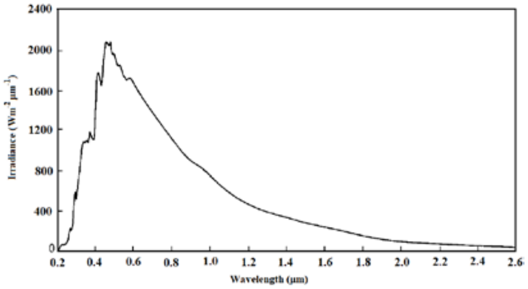

Fig. 3. Spectral distribution of the solar constant [9]

Selective Surfaces

A surface with high absorptance in the solar energy spectrum and low long-wave emittance, to reduce losses, is called **selective surface**. Many solar collectors' surface temperatures are less than 200ºC, for which less than 1% of the emitted radiation is in the region with $\lambda < 3$ μm. Almost all losses due to thermal radiation are in the region above 3 μm. On the other hand, 98% of the extraterrestrial solar radiation is in the region with $\lambda < 3$ μm. These facts give the possibility of designing selective surfaces. Figure 4 shows the concept of selective surface.

Over time, several types of surfaces have been developed to achieve selectivity. Coatings with high solar absorption and high transmittance for long-wave radiation have been used upon low-emittance substrates, called solar selective absorbing coatings (SSACs). A coating with high transmittance for long-wave radiation ensures low absorbance and, therefore, low emittance in the region with the most significant thermal radiation emission at usual temperatures, reducing energy losses. The SSACs for solar collector applications started in the fifties. Metal oxides were used as coating materials and metals as substrates, such as copper oxide on aluminum [10]. Various coating techniques have been used, such as wet chemical methods, electro-deposition, physical vapor deposition (PVD), ion plating, sputtering and evaporation, etc. In the 1990s, multilayer absorbent coating was proposed, significantly interfering with incident light by designing a reasonable composition and thickness between double absorbent layers. The design of coatings gradually changed from layer-by-layer transmission absorption to offset interference, thus improving solar energy selectivity [11,12].

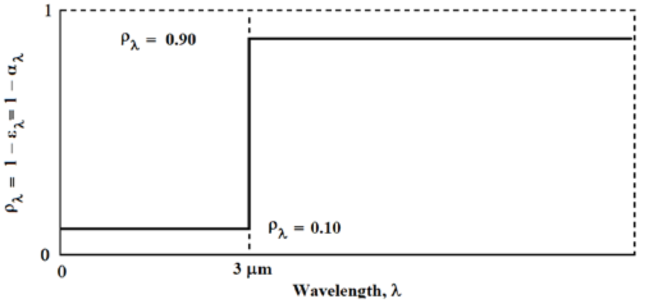

Fig. 4. Reflectance vs λ for a selective surface [3].

Photothermal conversion mechanisms

The process of converting light energy into heat energy is called photothermal conversion. It is a straightforward and efficient way to harness solar energy, commonly classified into three mechanisms: plasmonic localized heating, non-radiative relaxation, and thermal vibration.

Plasmonic localized heating

When metallic nanostructure is irradiated by light, the oscillating electric field causes the conduction electrons to oscillate coherently and redistribute at the nanoparticle surface, Fig. 3. Plasmons are the quanta of the collective of these conduction electron oscillations, termed localized surface plasmon resonances (LSPRs). Plasmons are the analog to photons (the light wave quanta) and phonons (the sound wave quanta).

When LSPRs are excited by light energy, an intense resonant interaction occurs, increasing light absorption and the local field and conducting the LSPR to global non-equilibrium. The thermally equilibrated state is restored when the absorbed energy of the electrons is relaxed through either the radiative re-emissions of photons or the nonradiative generation of electron−hole pairs. The energy transfer process from a plasmon quantum to a single electron−hole pair takes place through electron−electron collisions without loss of the absorbed photon energy. The energetic electrons produced from the non-radiative plasmon decay are called hot electrons, which quickly interact with low-energy electrons through inelastic Coulombic collisions that transform electron energy into heat. Simultaneously, low-energy electrons couple with the metallic lattice by electron-phonon scattering processes conducing to the lattice thermalization. Finally, thermal dissipation occurs in the surroundings through phonon−phonon collisions. The significant absorption and scattering cross-sections at the resonant frequency make the metallic nanostructures an excellent light-to-heat conversion ability, making them an excellent choice for harvesting light and concentrating energy [4,13,14].

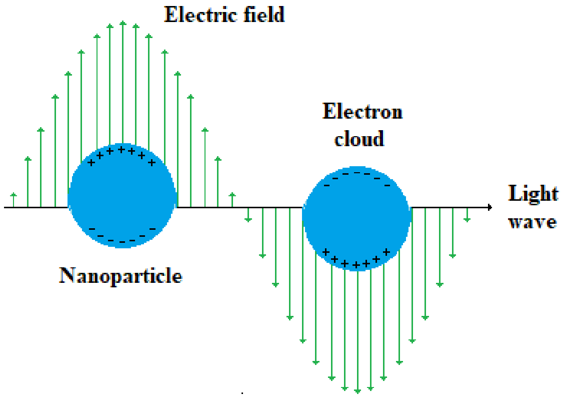

Fig. 3. Oscillation of the electron cloud of a nanoparticle under the electric field of a light wave.

Non-radiative relaxation

The excitation of a non-plasmonic semiconductor by photons with energies up its bandgap generates electron−hole pairs. In de-excitation, the energy can be either released by emitting photons or transferred to the lattice by non-radiative relaxation. The Shockley−Read−Hall and Auger recombination are the non-radiative relaxation processes that are especially applicable to heat generation in semiconductors.

Auger recombination is an intrinsic process in which three charge carriers intervene. In the electron-hole pair recombination, the energy can transfer to either a conduction band electron higher or a valence band hole deeper. The third energetic carrier typically thermalizes back to the band edge through lattice vibrations. The other carrier usually thermalizes back to the band edge by lattice vibrations.

Shockley−Read−Hall recombination is a trap-assisted recombination. Trap levels are the defect states generated within the bandgap by defects and impurities in a semiconductor. In this process, the conduction-band electrons relax to the trap level and then go to the valence band, where a hole is annihilated. This process occurs with an exchange of thermal energy with the material [4,13,14].

Thermal vibration of molecules

Carbon-based materials and some organic polymers are very competent in heat generation by lattice vibrations and have a good capacity for light absorption. Pi bonds (π bonds) are covalent bonds between the carbon atoms, in which two lobes of an orbital of one of them overlap with two lobes of an orbital to the other, and the atomic orbitals overlap laterally. Under low-energy irradiation, the loosely held electrons are excited from the π orbitals (highest-occupied molecular orbital, HOMO) to the π* orbitals (lowest-unoccupied molecular orbital, LUMO), passing from the ground state to a higher energy state. Then, the excited electrons relax to the ground state by vibration−electron coupling, and the excess energy is released as heat [4,13,14].

Applications

In recent years, materials that efficiently convert solar energy into heat have been developed and used for various purposes. Below, we summarize some of their multiple applications.

Solar Energy Harvesting

This is the process of photothermal conversion where sunlight is concentrated onto a material that can efficiently absorb and convert the light into heat. Research in solar panels seeks new photothermal materials to improve the efficiency of solar energy capture and reduce costs [15]. Different synthesis conditions result in different values of the plasmon positions in spray-pyrolyzed nano-cermet coatings for solar absorbers [16]. Photothermal conversion applications based on nanofluids are also being developed to address the growing energy demands [17] sustainably. Recently, it was reported that an ionic gel capable of converting solar energy into heat and subsequently into electricity using photothermal electrodes had been developed [18]. In another recent publication, the improved photothermal properties and solar absorptivity of a nano-enhanced eutectic phase change material (NeUPCM) laden with different concentrations of multi-wall carbon nanotube (MWCNT) to be employed for thermal energy storage purposes were reported. Carbonaceous thermal energy storage involving phase change materials (PCMs) has recently generated increasing interest due to its notable higher thermal conductivity and energy storage density [19].

Pure water can be produced by heating and evaporating seawater and wastewater using photothermal materials [20,21]. Developments have been reported to harvest incident solar energy more effectively to generate electricity during solar absorption, steam generation, and water condensation. A 3D organic bucky sponge was fabricated with broadband light-absorbing, heat-insulating, and shape-conforming abilities integrated with thermoelectric modules that render efficient photothermic vaporization and energy generation. The upper part of the thermoelectric modules receives the heat generated by the sponge when absorbing sunlight, while the lower part is cooled by the water below. The temperature difference between both sides generates electricity due to the Seebeck effect [22]. Electricity can also be obtained from the evaporation-induced salinity gradient in a solar desalination system that uses an ion-selective membrane [23]. A polyvinylidene fluoride film can also harvest the waste energy from solar vapor for electricity generation based on the coupled pyroelectric and piezoelectric effects [24].

Photothermal Therapy

The development of photothermal materials has led to the emergence of a type of phototherapy with minimal invasiveness, low toxicity, and spatiotemporal selectivity: photothermal therapy (PTT) [25]. This therapy is based on the use of PT materials to generate an overheating of abnormal cells induced by light (hyperthermia) to trigger their death. When the tissue temperature exceeds 46o C, the treatment is called thermal ablation and is characterized by direct cytotoxic effects (which eliminate cells, such as cancer cells). External laser irradiation at a specific wavelength activates the PT material, generating heat that accumulates in lesions or abnormal cells. Due to the efficient light absorption of PT materials, relatively low input power is required, minimizing damage to the surrounding healthy tissues [4]. NIR irradiation, particularly the NIR-II window (1000-1700nm), is used for deep tissue penetration. This window can penetrate deeper into soft tissue with reduced scattering. Besides, it takes advantage of the range 800-1400nm, where water absorption is negligible [26].

In recent years, PT materials such as metallic nanostructures, semiconductors, carbon-based nanomaterials (NM), organic polymer NM, two-dimensional NM, hybrid PT NM, etc., have been developed for use in PT therapy with different lighting conditions (wavelength of the irradiation laser, power density, and exposure time) and variable values of PT conversion efficiency. References [4] and [27] list these materials. In particular, for several years, using porous silicon (PSi) as a photothermal material has been reported, taking advantage of its low thermal conductivity and remarkable ability to absorb near-infrared light. Lee et al. [28] used photoexcited PSi nanoparticles as a therapeutic agent, reporting that they generated enough heat to kill cancer cells without chemical toxicity. Subsequently, selective destruction of cancer cells without damaging surrounding healthy cells was reported using PSi nanoparticles irradiated with near-infrared light [29]. These and other in vitro and in vivo studies confirm the photothermal properties of PSi for its application in PTT [30-33].

Water Purification

The photothermal conversion mechanism is a fundamental part of the photocatalysis process used to treat and purify water for human consumption. A sustainable and renewable alternative is using sunlight as an energy source in photocatalytic systems. These technologies are based on semiconductor films that can be excited by sunlight with energy greater than its band gap, generating hydroxyl radicals (OH). These radicals are powerful oxidants capable of oxidizing and mineralizing organic molecules in water, producing CO2 and inorganic anions [34].

Recent works report the study of different microstructures of the surfaces of absorbent materials [35]. These works aim to improve the efficiency of capturing light energy and its subsequent conversion into thermal energy for heating water and its evaporation. Such are the cases of carbon nanotubes [36,37], porous structures, or crystals [38].

Other applications of the photothermal conversion phenomenon have been reported in desalination technologies using solar energy [39,40]. Different authors are already working on hybrid models combining traditional methods with solar energy for the water desalination process through reverse osmosis systems to reduce the use of non-renewable and polluting energies, which consume a lot of energy [40].

Heat-Assisted Magnetic Recording (HAMR)

Hard disk drives (HDD) serve as widely utilized mass storage devices. However, in the prevailing manufacturing technique, known as perpendicular magnetic recording (PMR), as data densities increase, the magnetic regions become smaller, and the risk of bits flipping spontaneously arises, approaching their physical limits. Therefore, a material with high resistance to magnetization is usually implemented. This raises another problem: the magnetic field generated by the write head is not strong enough to record these specific materials [Richter, 2007].

The heat-assisted magnetic recording (HAMR) technique leverages the fact that elevated temperatures diminish the resistance to magnetization on a material. In this recording method, the write head incorporates a near-field transducer (NFT) illuminated by a laser through a waveguide. Surface plasmons in the NFT convert the optical energy to a deep subwavelength heat spot in the media, heating a minute section of the surface of the recording layer and facilitating the magnetization process [42,43].

Currently, NFTs exhibit 3–6% coupling efficiencies. Hence, photothermal materials need to be developed to improve performance. Noble and alkali metals offer good plasmonic properties, yet most are incompatible with environmental conditions. Extensively explored, Silver (Ag) boasts excellent plasmonic features but corrodes, while Gold (Au), a common and compatible choice, faces thermal-mechanical challenges. Even more so, temperatures on NFT can reach up to 300°C, causing instabilities in materials like Au. In summary, photothermal materials are crucial to developing HAMR technology [44].

Conclusions

Interest in photothermal materials and their applications has grown significantly in recent years, and new developments in this field are continually reported. We hope that this divulgation work contributes to the dissemination of knowledge about the photothermal conversion phenomena, the main mechanisms that take place in this, and their applications. This work describes some of the multiple and varied applications of photothermal materials by avoiding specialized terms and without delving too deeply into them to generate interest in the general public. However, a bibliography is provided that can be consulted by those who wish to know more about a specific topic.

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