Spectral selective and photothermal nano structured thin films for energy efficient windows

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HIGHLIGHTS

- Identified the critical issues and ideal models in window thin film designs.
- Applied the novel photothermal nano coatings to windows for the first time.
- A new design of window structure is proposed for energy-efficient windows.

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ABSTRACT

This review deals with critical issues in the development of energy-efficient windows from two fundamentally different approaches, namely, spectral selectivity and photothermal effect. This review is therefore divided into two parts. The first part reviews the engineering considerations based on an ideal window concept in terms of spectral selectivity, glazing scale, seasonal factors, and related thermal transfer. In particular, spectrally selective window designs and metal-based thin films are introduced with optimized engineering parameters and physical properties. The second part introduces a new approach of thermal insulation via the photothermal effect of the nanostructured thin films and coatings. The key that limits the heat flow through windows is the thermal insulation, which is traditionally constructed by multi-pane structures with an insulating layer. A novel concept not relying on any insulating media, but photothermal effects of nanomaterial coatings has been recently proposed and experimental verified. Both concepts of spectral selectivity and photothermal effects are introduced for energy-efficient window applications. A new direction is proposed in the development of the energy-efficient windows via the photothermal effects in various nanostructures of thin films and coatings.

1. Introduction

Windows are one of the most important building envelope components, due to their large areas with required thermal and optical performances. The U.S. Department of Energy (DOE) has reported that the heat loss through windows in cold weather is approximately 3.95 quads (or 1.16 e+12 kWh) of primary energy use in the U.S. based on the statistical data by the 2016 SHIELD program \cite{1}. Preventing heat flow of this type has presented great challenges to both civil/architectural engineers and material/chemical scientists for collaboratively developing more energy efficient structures. Heat transfer through a window occurs via conduction, convection, and radiation. A parameter used to characterize the overall heat transfer rate or insulation capability of a window assembly is the so-called U-factor, which combines the effects of three types of aforementioned heat transfer. A low U-factor indicates a high insulation ability or low heat transfer through a window. The current methods in developing windows with low U-factors are mainly from two directions: structural and spectral designs.

In current structural design, multi-plane glazing is the most popular approach that focuses primarily on conductive heat transfer. Such a structure normally consists of two or more glass panes separated by insulating layers of air, inert gas, vacuum cavities, phase changed materials, silica aerogel, or some dynamic controls, such as airflow or water flow \cite{2–10}. The materials that can serve as transparent thermal
barriers are therefore sought with low thermal conductivity and good visible light transmission. Spectral design mainly deals with radiative heat transfer for energy efficient windows, normally through thin films, tints, or coatings that respond to surrounding thermal radiations. For temperatures of practical interest in the building energy studies, thermal radiation flux occurs in four basic bands: ultraviolet radiation (100 nm < \( \lambda \) < 400 nm), visible light (400 nm < \( \lambda \) < 700 nm), and solar infrared radiation (700 nm < \( \lambda \) < 3000 nm) from the sun, and longwave radiation (3000 nm < \( \lambda \) < 50,000 nm) from the building interior or outdoor environmental temperatures (see Fig. 1). Regulating window transmission, absorption, and reflection properties to control the passage of thermal radiation in these ranges can significantly improve building energy efficiency. Typical conventional technologies include spectrally selective films, anti-reflection films, chromic technologies (e.g., electrochromic, thermochromic, and photochromic materials), angular selective coatings, liquid crystals, and electrophoretic or suspended-particle technologies. These glazing technologies are commonly preferred and used by architects for their strong impacts on building energy efficiency, indoor thermal and visual comfort, façade appearance, and architectural aesthetics. Despite of considerable progresses made in the glazing technologies, challenges remain that limit further optimization of energy efficiency. These include independent multispectral band modulations and unidirectional transparency of infrared thermal radiations. The purpose of this paper is to review representative concurrent spectral selective energy efficient window film designs and trace their fundamental features, and then introduce a recent novel approach in increasing window thermal insulation based on photothermal effect of nanoparticles.

This review is structurally composed of two parts, and respectively dealing with critical issues in developing energy-efficient window structures from two fundamentally different technical approaches – spectral selectivity and photothermal effects. In Part I, we first provide a brief discussion on the fundamental aspects of ideal windows as a baseline for engineering considerations and thin-film technologies. Based on a perfect window, materials structural design is possible in order to simulate these ideal properties. Various approaches will be introduced for this purpose including thin film low-e coatings, modulating of transmission and/or reflection for controlled thermal radiation fluxes, and spectrally selective structures for optimum optical features. We then extend the ideal window concept to the fundamental requirements and strategies of spectrally selective thin film design. The most representative benchmark examples and their optical performance are subsequently introduced in terms of transmittance in visible and infrared regions. In particular, selective absorption properties in designated photon frequency regions can now be tuned via nanostructures, materials compositions, and externally applied electrical field (smart materials) [11–13].

It is pointed out in this review, however, despite of the current window technologies aforementioned, major challenges cannot be easily addressed for further optimization of energy efficiency. Limited by the intrinsic materials properties, development of ideal windows still faces great challenges in both materials synthesis, thin film architecture, and engineering design. To address these critical issues, we introduce a recently developed novel approach fundamentally different from the spectral selectivity, namely, photothermal effect through design of new nanostructures. In this unique approach, energy efficiency is achieved via the photon-activated heating processes in the nanomaterials, which is the core mechanism in the design of the new thin film structures for window applications.

The second part of the review introduces a new design of window structure with significantly reduced heat loss based on the photothermal effects of nanomaterials. It should be particularly noted that although the photothermal effects have been discovered and extensively studied for metallic nanoparticles, such as gold, for medical therapeutics, few has been carried out in the deposition of thin films and window coatings for energy applications. In fact, the research on the photothermal thin films and coatings has just begun very recently, but the initial work has paved a new path in the development of energy-efficient materials in a viable and economic fashion. In particular, the photothermal effects of the Fe\(_3\)O\(_4\) nanoparticles are discussed in terms of nanostructures, defects, fundamental mechanisms responsible for photothermal heating, and the balance between photon transmission and photothermal conversion efficiency. The so-called photothermal effect of nanoparticles is utilized to reduce the center-of-glass U-factor by slightly heating up the window interior surfaces under solar irradiation. Engineering parameter calculations such as photothermal conversion efficiency and center-of-glass U-factor are also provided for window designs. From the energy saving perspective, we address the critical issues of selective absorption of solar-infrared radiation and thermal energy convert efficiency for overall window performance in cold climate. We will finally conclude on both conventional spectral selective and new photothermal thin-film designs that are tailored to the energy requirements.

2. Part I window designs based on spectral selectivity

2.1. Basic concept

The thermal properties of a window, such as the U-factor, solar heat gain coefficient (SHGC), are understood as the essential indicators of window energy performances. Light transmittance (VT) and haze level (h) are particularly important window function parameters that characterize the visual contact with the outside world. To achieve high optical and thermal performances, the concept of a “perfect window” or “ideal window” has been developed [14,15]. Fig. 2 shows the schematic diagrams of the perfect window models.

As is well-known, the visible solar spectrum is considered essential to occupants (e.g., for their well-being, health, work efficiency, etc.)
and useful for other forms of energy such as electric light [16–20]. A perfect window should therefore permit high visible light transmission (VT) from the complete solar spectrum. Regarding thermal aspect, a perfect window should be able to seasonally control all types of radiative emissions for minimum energy consumption and reasonable indoor comfort, as environmental radiation changes in summer and winter (outdoor solar radiation and interior longwave thermal radiation). In the winter season (Fig. 2a), a perfect window needs to be completely transparent to incoming visible and infrared radiations and reflect all longwave radiation flux back to the interior for energy saving. In the summer season (Fig. 2b), a perfect window should reflect 100% solar-infrared radiations from the sun and any longwave thermal radiation from external environment. In addition, the perfect window has to maintain the unidirectional transparency to allow emissions of longwave thermal radiations from building interior to exterior.

Based on the concept of perfect window, thin films are designed and developed to simulate these ideal properties, so that their transmission and/or reflection features are regulated for selected and controlled passages of thermal radiation fluxes. However, limited by the intrinsic materials properties, development of ideal windows still faces great challenges in both materials synthesis, thin film architecture, and engineering design. Current nanotechnology has shed new light on completely different ways of solving these engineering problems from perspectives of thermal insulation, spectral selectivity, and multilayer film deposition [21–23]. In particular, selective absorption properties in designated photon frequency regions can now be tuned via nano-structures, materials compositions, and externally applied electrical field (smart materials) [11–13].

2.2. Spectrally selective thin films

Spectrally selective design aims at permitting particularly selected portions of the light spectrum to pass through a medium, while blocking others. This function is conventionally achieved in the glazing applications via highly-doped conducting/semiconducting materials and metal-based films. On the one hand, one way of solar heat control is through reflecting the heat from the sun mainly near IR. The Indium tin oxide (ITO) and fluorine-doped tin oxide (FTO) are extensively studied with dopants such as Zn, In, and Sn, that enhance IR reflectivity. However, the dopant level can only reach certain limits from the synthesis perspective, and further doping is not without considerable difficulties [24]. On the other hand, if the metal-based films with Ag, Cu, Au, or Al are made sufficiently thin (smaller than wavelength), their visible light transmittance is well enhanced but with strong IR reflection [25]. However, durability of these single-metal films has been an issue when exposed to the atmosphere [26]. Multilayer thin films with a structure of dielectric/metal/dielectric (D/M/D) have therefore been proposed and developed for building fenestration. Presently, most of the high-performance D/M/D thin films are based on ultra-thin silver film, sandwiched between two dielectric or metal oxide layers, such as Zinc oxide (ZnO), FTO, Titanium dioxide (TiO2), and aluminum-doped zinc oxide (AZO) [27–30]. Refraction takes place as light travels from one optical medium to another. Some portion of the light is reflected at the interface between the two media with an angle relative to the surface and incoming light. Two reflected light waves will interfere, and their phase (φ) difference determine the degree of constructive (two reflected waves are in-phase φ = 0) or destructive (two reflected beams have opposite-phase φ = 180°). Consequently, by a proper design of each layer thickness, the destructive optical interference may enhance visible transmittance, while maintaining considerable reflectance of longwave due to the metallic layer. Furthermore, these thin films can be stacked multiply up to hundred layers for optimum visible transparency and longwave reflectance [31]. For instance, adding more pairs of sub-10 nm silver layers between high refractive index oxide layers results in sharp curves and divisions between the visible region (70% transmittance at about 700 nm) and IR region (10% transmittance at about 800 nm) [32]. The techniques for making these metal-based spectrally selective thin films include chemical vapor deposition, physical vapor deposition, thermal evaporation, and plasma ion assisted deposition [33–36]. It has been reported that coatings deposited using chemical vapor deposition technique can lead to more durable and better spectrally selective coatings [37].

In order to compare the metal-based spectrally selective thin films with the perfect window model, we plot various spectral curves of thin films including those of the perfect window using simulation by Window Optics 6 [38], as shown in Fig. 3. In Fig. 3a, for heating- and cooling-dominated climates, two idealized thin films are presented: Type A is characterized by T = 1, R = 0 (T and R respectively denote transmittance and reflectance) for 400 < λ < 700 nm, and T = 0 for 700 nm < λ < 50,000 nm. For Type B, the parameters are set at: T = 1, R = 0 for 400 < λ < 3,000 nm, and T = 0 for 3000 < λ < 50,000 nm. SHGC low-e coatings are commonly used in cold weather conditions, while the low-SHGC low-e coatings for warm weather climates.

Fig. 3b and c presents the spectral curves of reflectance, transmission, and absorption of two as-deposited thin films on a single glass. By comparing with the idealized spectra shown in Fig. 3a, the low-SHGC low-e coating (e.g. triple silver unit) in Fig. 3b exhibits behaviors similar to that of Type A for minimum IR transmission in hot climates. Fig. 4a shows the schematic diagram of the low-SHGC low-e coating with typical optical properties. As shown in this figure, the low-e coating is able to reflect over 90% of solar infrared and longwave infrared and still transmit 61% visible light. The key in this category is to...
further increase visible transmittance while maintaining large IR re-
fection. Several previous studies have focused on anti-reflec-
tive films and wide bandgap semiconductors for developing the low-SHGC low-e coatings [40–43]. The anti-reflective layer is structurally tailored to these optical properties with patterned and porous structures via nanoimprint lithography or gradient refractive index [44,45]. The anti-
reflective coating may not be particularly aimed at improved thermal performances, but the increased visible transmittance has strong po-
tential to save overall energy by reducing cooling loads associated with the electrical lights [46].

It is worth noting that the spectra of the high-SHGC low-e coating (e.g. single silver unit, Fig. 3c) are quite different from those of the idealized (Type B, Fig. 3a), especially in the solar infrared region. It has been a great challenge to achieve coincident high solar-infrared transmittance and low emissivity in longwave radiation via the spec-
trally selective thin films. Fig. 4b shows 50% solar-infrared reflection to outdoor, which is far from the desired property of a perfect window. Destructive optical interference is a possible approach to increase solar-
infrared transmission by adding dielectric or oxide layers with optim-
ized thicknesses and refractive indices. However, in most of the weather conditions, strong solar-infrared transmittance may not be necessary from the practical standpoint, as cooling loads in summer, due to high IR transmittance, may offset the benefits in winter.

2.3. Absorption-based nanoparticle systems for spectral selectivity

A narrow waveband absorption in solar infrared, especially in the near-infrared (NIR) region (750–1300 nm) counting for 40% solar energy, has been studied as an alternative solar heat blocking mechanism in recent years [47–49]. Intrinsic absorptive properties of materials, such as tinting materials, pigments, and dyes, have been utilized in windows in order to absorb NIR. However, these material systems are known to pose negative effects on visible transmittance, instability, and haze conditions. In recent years, absorption-based nanoparticle-com-
posites have been developed for the spectrally selective films. The absorption-based spectral selectivity thin films have been realized via special electronic properties of the nanoparticles, for instance, the local-
ized surface plasmon resonance (LSPR). Several types of materials are known to absorb infrared and suitable for glazing applications. These include gold, ITO, AZO, antimony-doped tin oxide (ATO), lan-
thanum hexaboride (LaB₆), and rare-earth hexaborides (GdB₆) [50–54]. Among these, two candidates – ITO and LaB₆ have been extensively studied for glazing applications [51,54–60]. The ITO and LaB₆ nano-
particles are characterized with high transparency and absorption wa-
vebands in particular infrared regions. The research effort has been focused on manipulating the absorptions into the desired regions. Schelm et al. incorporated both spherical LaB₆ and ITO nanoparticles into Poly(vinylbutyral) (PVB) and obtained strong absorptions at 900 nm and 2350 nm, respectively [54]. Yuan et al. reported the cor-
relation between the particle size of LaB₆ in polymer and absorption level in the region of 600–1380 nm [60]. Adachi et al. found redshift and broadening of the LSPR peak in the disc-like LaB₆ nanoparticles [59]. In addition, these experimental works show considerable compositional effects on the infrared absorptions of the LaB₆ and ITO nano-
particles when dispersed in the PVB matrices. For instance, 0.3 wt% of LaB₆ plus 4 wt% of ITO doped in PVB matrix resulted in transmit-
tance of 72.4% in visible (615 nm) and 55% in infrared (1000–2,250 nm) regions [58]. The optical properties can be further optimized through control of the particle size, shape, orientation, dis-
tribution, concentration, and composition for high-quality glazing

Fig. 4. (a) Typical optical properties of spectrally selective thin films with low SHGC, designed for hot weather or summer season. (b) Typical optical properties of spectrally selective thin films with high SHGC designed for cold weather or winter season.
Thin films incorporating various nanoparticles may isolate visible and infrared radiations from solar spectrum. However, independent multispectral band modulations are still difficult for the visible or infrared radiations. The so-called electrochromic (EC) materials have been developed to address this critical issue in the past several decades.

A new approach based on plasmonic electrochromism has recently been proposed and demonstrated by Milliron et al. [61,62]. One of the unique features of EC materials is the ability to selectively control NIR absorption via modulated LSPR. Fig. 5 schematically illustrates this concept with two types of nanostructure designs of the EC thin films. As shown in Fig. 5a, the nanocomposite electrolyte consists of polymer hosts and transparent conducting nanoparticles such as ITO, AZO, and LaB₆ [63]. Under different electrical potentials, the LSPR absorption level is altered by controlling the electrochemical changes and in turn their electron density. This alteration enables modulation of solar-infrared absorptions with minor effects on the visible region. In Fig. 5b, development of the electrode based on depositions of ITO nanocrystals on niobium oxide (NbOₓ) glass presents another viable approach [62,64]. Both ITO nanocrystals and NbOₓ glass matrix exhibit distinctly different spectral electrochromic responses, therefore each may independently yield modulation in the NIR (ITO nanocrystals) and visible regions (NbOₓ) [62]. Fig. 5c shows three schematic status of the EC windows under 4 V, 2.3 V, and 1.5 V.

As aforementioned, all previous studies focus on optimization of optical behaviors via spectral-selective features of media, associated with either their intrinsic or extrinsic materials properties. In other works, most of the effort has all concentrated on manipulation of optical properties (absorption/reflection in particular wavelength range) for optimum energy efficiency. However, spectral selectivity is often hindered by the intrinsic and extrinsic materials properties that are not easily manipulated via chemical and materials means. Quite often additional physical fields (such as electrical potential in spectral electrochromic) are required to fine-tune the optical properties. These obstacles often introduce additional complications in materials design, synthesis, and large-scale processing, which makes the engineering aspect not economical. Therefore, in further optimization of energy efficiency, new approaches, other than optical spectral selection, must be sought via different physical fields such as thermally-activated nanostructures that not only effective in thermal insulation, but also easily mass-produced with economic advantages.

Photothermal effect, although a well-known phenomenon especially in metallic materials, has been recently utilized, through some novel materials designs, for developing energy efficient architectural materials. A novel concept has been recently formulated in the design of single-pane windows with significantly enhanced thermal insulation.
based on the photothermal effects of oxide nanoparticles, such as Fe₃O₄. The following sections will be devoted to the new design of nanostructures, their synthesis and physical properties, and potential applications in energy-efficient windows especially for the cold climate regions. It should be noted that saving building energy via the photothermal effect of nanostructures is a very new development with the first paper published in 2017 [65]. In particular, all previous photothermal studies have focused only on solutions and particles for medical applications. Investigation on photothermal thin films is also recent therefore with limited literature. Nonetheless, it points to a new direction in the development of optical energy materials with the high possibility of achieving the most energy-efficient materials.

3. Part II window designs based on the photothermal effect of nanomaterials

3.1. The concept of photothermal effect and opportunities in window applications

Recently, photothermal hyperthermia of nanoparticles via NIR irradiation has been developed for various applications including medical therapy [66–76]. The photothermal effects have been found in several nanoparticle systems, such as quantum dots, gold, graphene, and Fe₃O₄ [66,67,69,71,72,74–76]. These nanoparticles all exhibit strong NIR-induced photothermal effects effectively raising the solution temperature by greater than 30 °C. The previous studies show that, upon NIR-laser irradiation, the temperature of the Fe₃O₄ nanoparticle aqueous suspensions can increase, within short periods of time, from room temperature to 45 °C [69,72,74,76]. However, these photothermal studies were all based on NIR radiation (~800 nm). The photothermal effects of these nanoparticles via a much wider spectrum (350–750 nm) have not been rigorously investigated. In particular, the photothermal mechanism under solar light was not investigated for Fe₃O₄ until very recently.

The photothermal effect has been extensively studied for gold and graphene and attributed the energy conversion to LSPR [68,70,73]. A localized plasmon is the result of the confinement of a surface plasmon in a nanoparticle smaller than the wavelength of the incident light. A nanoparticle’s response to the oscillating electric field can be described by the so-called dipole approximation of Mie theory [77]. The fluorescent quantum dots were also found to exhibit highly efficient photothermal effect [75]. Although the photothermal effects of these nanomaterials have been shown to be effective, they are quite costly making them not industrially viable especially for large surfaces and volumes. Furthermore, the operating mechanisms of heat conversion have not been well identified for some of the semiconducting systems. We have recently investigated the photothermal effect of the Fe₃O₄ nanoparticles and explained its mechanism based on the photoluminescence emission in both visible and NIR regions [74,76].

Spectrally selective thin films based on the plasmonic NIR absorption present a promising approach to achieve independent multispectral band modulations. However, regardless of the optical property, be it static or dynamic, these thin films regulate solar spectrum transmission mainly through the absorption rather than reflection. Consequently, glazing systems with these thin films necessitate the use of low-e coatings. In addition, the longwave radiation control still relies on low-e coatings in winter while blocking the external longwave heat in summer. The low-e coating can reflect about 50% solar-infrared radiation in the winter season, which is essentially “free” from the environment (Fig. 4b). There is, therefore, a high incentive to fully utilize this free energy via new window structure designs, especially for retrofitting the existing windows.

3.2. Synthesis and characterization of the Fe₃O₄ nanoparticles

We have recently shown that the Fe₃O₄ nanoparticles, in various forms, can generate sufficient heat when irradiated by NIR light (808 nm) [74,76]. By directing a low-power laser beam into a solution of weak concentration of magnetic Fe₃O₄ nanoparticles, the solution temperature rapidly reached above 42 °C. One of the unique nanostructures is the polystyrene (PS)/Fe₃O₄ composite. Nanoscale Fe₃O₄ nanoparticles (~5–10 nm) are embedded in the matrices of PS spheres that are synthesized by using modified emulsion/miniemulsion polymerization [74]. The Fe₃O₄ nanoparticles with an average particle size about 10 nm were synthesized and dispersed in succinyl octane as a ferrofluid. The ferrofluid was then added to the aqueous solution with sodium dodecyl sulfate (SDS) to obtain miniemulsion after ultrasonication. Meanwhile miniemulsion was prepared from styrene monomer. The mixture was held at 80 °C for 20 h in order to obtained the Fe₃O₄/PS nanospheres (Fig. 6a). The poly(acrylic acid) (PAA) coated Fe₃O₄ nanoparticles was obtained by co-precipitation of iron chloride salts with ammonia, denoted as PAA-Fe₃O₄ [74]. Fig. 6a depicts multiple nuclei of Fe₃O₄ entrapped within a polystyrene matrix while Fig. 6b shows the image of PAA-coated Fe₃O₄. The particle diameters can be estimated in the focal plane if the nanoparticles are known to possess a generally spherical geometry. The nanoparticles that are not surface functionalized are denoted as Uncoated Fe₃O₄. Their morphologies are similar to those shown in Fig. 6b.

3.3. Photothermal effect measurements using near-infrared laser

The photothermal measurement apparatus is schematically shown in Fig. 7. The sample is injected into one well of a 48-well microplate. The microplate is placed on an electric hot plate, which is in an incubator, to provide a 37 °C environmental temperature. A 785 nm laser with controllable power supply (0–1 A, 6 V) is used as the light source, as shown in Fig. 7. The shape and size of the light spot is set to exactly cover the sample well. The sample surface temperature is recorded by

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Fig. 6. (a) TEM image of PS/Fe₃O₄ microspheres showing the polystyrene spheres entrapping multiple Fe₃O₄ nanoparticles, and (b) TEM image of PAA/Fe₃O₄ [65].
an infrared camera (FLIR-T640). The well bottom area is 0.95 cm², and an optical power meter is used to measure the laser power on the sample surface. A standard power meter can be used to determine the relation between the applied current and the optical power output. A linear function can also be fit to the data to allow calculation of the laser power and consequent intensity over an applied area. For a given nanoparticle concentration, laser intensity and wavelength, a heating and cooling curve can be generated. The infrared camera is oriented to monitor the temperature of the nanoparticle solutions. For determination of the heating curve, temperatures are normally recorded every minute for the first 8 min and every two minutes for the next 12 min. The cooling curve is obtained by recording the temperature at 30 s, 1 min, and every following minute for the next 7 min after removal of the laser.

Fig. 8 shows the heating curves for 150 µl of PAA-Fe₃O₄ [74]. The photothermal effect was observed by application of 38.5 kW/m², 785 nm NIR laser for 15 min. Temperature was measured through IR thermal imaging by a FLIR-T640. Sapareto and Dewey showed that concentration of 0.2 mg/ml was the minimum expected for inducing saturation afterwards. It is also observed in this figure that the nanoparticles exhibit considerable photothermal effects even at low concentrations such as 0.1 mg/ml, raising temperature above 40 °C.

3.4. Photothermal effect measurements using solar light

Zhao et al. recently investigated the photothermal effects of Fe₃O₄ nanoparticles and thin films in a much wider spectrum [65]. In their experiments, a white light was applied using a solar simulator for generating the photothermal heat in Fe₃O₄ nanoparticle suspensions and thin films. In the “sample-in-well” experiment, 0.15 mL solution with different Fe₃O₄ concentrations (0.25, 0.5, 1.0 mg/mL) was added into a 48-well plate [65]. For the “sample-on-glass” experiments, a solution with 0.1 mg Fe₃O₄ nanoparticles was coated on a 25 mm × 25 mm glass slide by drop casting in order to develop a thin film [65]. Both the liquid and thin film samples were irradiated by a white light from a solar simulator. The power density on the samples from both light sources is 0.1 W/cm², which is about the sun radiation density on the Earth. The sample temperature was measured by the thermal imaging camera. Light was turned on for 15 min, but the thermal imaging camera continued to record the temperature after the light was turned off. All preliminary experiments started from room temperature.

Fig. 9 shows the heating curves of PAA-Fe₃O₄ solution at various concentrations (0.25, 0.5 and 1.0) mg mL⁻¹. A solar simulator was used as the light source at the light intensity of 0.1 W/cm², which provides approximately the radiation density similar to the surface of Earth from sun. As can be seen in this figure, as expected, the photothermal effect has a clear concentration dependence. At 0.1 W/cm², the 1.0 mg mL⁻¹ sample results in a temperature increase of 11 °C (from 24 °C to 35 °C) within 15 min. Even at 0.25 mg mL⁻¹, the temperature of the solution could reach 32 °C, indicating a strong photothermal effect. Upon turning off the light source, as shown in Fig. 9, all samples exhibit approximately the same cooling rates indicating similar heat losses to the surroundings [65].

The heating curves of the same PAA-Fe₃O₄ solutions are shown in Fig. 10. These curves were obtained by using a 785 nm NIR laser irradiation with light intensity of 0.1 W/cm². The NIR laser generates, as can be seen in this figure, much less heating compared to the white-light irradiation at 1.0 mg mL⁻¹. The temperature only increases slightly from ∼23.5 °C to 27 °C, resulting a gain of 3.5 °C within 15 min.
Expectedly, even weaker heating is observed at 0.25 mg mL$^{-1}$ for an insignificant temperature increase. These results clearly show different photon absorptions and energy conversions between NIR and white light irradiations. It is evident that white light produces much greater photothermal effect and heating efficiency.

### 3.5. Coating of polymer thin films on glass

For energy efficient window applications, spin coating was preferred and used to deposit thin films on the glass substrate in an experiment recently reported by Zhao et al. [65]. Spin coating is economically viable and technically straightforward, therefore commonly used to deposit uniform thin films to flat substrates [79]. The solution containing Fe$_3$O$_4$ nanoparticles of various concentrations is applied on the center of the substrate, that is spinning at a controlled low speed. In the experiments reported by Zhao et al., the substrate was kept still for obtaining a film of certain thickness. Different polymer materials may be selected for thin film coatings on glass that exhibit most efficient heating but high transparency. Note that the balance between the photothermal efficiency and transparency has to be well controlled for the optimum optical properties. Ideally, the thin film coating should exhibit the highest transparency while exerting the strongest photothermal heating. The balance is difficult as well-diluted solution coating may have a high transparency but attenuated photothermal effect. Further, the window should also have good spectral selectivity, as described above that most of NIR should be well absorbed in the winter for energy saving. It is therefore important to develop nanomaterials with both strong photothermal and spectral selective properties for energy efficient window applications.

By carefully selecting the type and thickness of the polymer layers, one can deposit Fe$_3$O$_4$ nanoparticles on a single pane using the spin coating method, as it is the most economic approach compared to the vapor deposition for building structures.

### 3.6. Photonic properties of the Fe$_3$O$_4$ nanoparticles

As briefly described above, the photothermal effect has been attributed to the LSPR of the nanoparticles under light irradiation. The LSPR effect has been previously demonstrated for both noble metals and conducting metal oxides (CMOs) [68,70,73]. Even for low charge carrier densities of CMOs ($n \approx 10^{23}$ electrons/cm$^3$), compared to that of typical noble metals ($n \approx 10^{25}$ electrons/cm$^3$), LSPR effect can arise from limited conductivity. LSPR behavior is associated with conducting electrons of any materials with considerable charge carrier densities oscillating in response to electromagnetic waves. According to Drude free electron model [80]:

$$\omega_p = (\mu / \varepsilon_0)^{1/2}$$  \hspace{1cm} (1)

where $\omega_p$ is the plasma frequency, $\mu$ is the effective mass, $n$ is the charge carrier density, $\varepsilon$ is the electron charge, and $\varepsilon_0$ is the permittivity of vacuum. Based on this equation, for typical conducting metal oxide, the plasma frequency is on the order of 1 eV in the NIR region. For gold of vacuum. Based on this equation, for typical conducting metal oxide, Urbach energy is a parameter related to the crystal defect density associated with impurities and disorder. Both $\omega_u$ and $E_u$ in Eq. (2) are material-dependent constants, and observed for many ionic crystals, degenerately doped crystalline, and amorphous semiconductors [83]. Some of the defects are thermally activated such as point defects in oxides, leading to an Urbach exponential absorption tail. In Fig. 11, one can see that the Urbach energy is obtained from the linear portion of the log $\alpha$ vs. photon energy curve for various Fe$_3$O$_4$ nanoparticles indicated. These include the PAA-coated Fe$_3$O$_4$ nanoparticles (PAA/Fe$_3$O$_4$) and Fe$_3$O$_4$ nanoparticles embedded in polystyrene nanospheres (PS/Fe$_3$O$_4$). Si/PS/Fe$_3$O$_4$ denotes the silica-surface-functionalized PS/Fe$_3$O$_4$. The Urbach Energy values were determined to be 0.572 eV, and 0.418 eV respectively for the Uncoated Fe$_3$O$_4$ and PAA-Fe$_3$O$_4$. The lower Urbach Energy (0.418 eV) is an indication of effective modification of Fe$_3$O$_4$ nanoparticles by PAA resulting in reduced surface defects [82]. By plotting $(\rho E)_2$ as a function of photon energy, the direct band gap can also be estimated from extrapolation of the linear portion of the curve to the x axis which gives the value of the direct band gap. The extrapolation shows the energy difference (0.31 eV) between O(2p) and ($\varepsilon_0$) of the octahedral site [82,83].

The previous experimental results show that Fe$_3$O$_4$ nanoparticles exhibit continuous decrease in photon absorption up to the NIR region (i.e. no obvious strong absorption in NIR), while strong absorptions in the visible region (0.530 nm) have been well observed for gold nanoparticles, responsible for strong photothermal effect [72,84,85]. According to the discussion on the ideal window, it is preferred to have strong absorption in the NIR region for that to be converted to the photothermal energy in winter. To deal with this issue, a Fe$_3$O$_4$-Ag hybrid may offer the required optical properties [85]. Bankole and Nyokong developed a Fe$_3$O$_4$/Ag (Fe/Ag) core–shell structure that exhibits considerable photon absorption near 690 nm [85]. They attribute photon absorptions to the LSPR effect for the Fe$_3$O$_4$–Ag hybrid and explained the red shift by the depleted electron density at the Fe$_3$O$_4$–Ag interfaces. However, the mechanism of NIR absorption is still not well identified for the Fe$_3$O$_4$/Ag (Fe/Ag) core–shell structure. Nonetheless, the NIR absorption observed in the Fe$_3$O$_4$–Ag composite nanoparticles present some potential for making the energy efficient energy windows.

Sadat et al. observed photoluminescence (PL) in both visible and
NIR regions for Fe$_3$O$_4$ nanoparticles in various forms [82]. Fig. 12 shows the PL spectra of the PAA/Fe$_3$O$_4$, PS/Fe$_3$O$_4$ and Si/PS/Fe$_3$O$_4$ measured at 10 mg/mL with a solid state laser of 4.5 mW and excitation wavelength 407 nm (3.04 eV). They found the most intensive peak at $\sim$ 540 nm (2.296 eV) for PAA/Fe$_3$O$_4$ while those for the PS/Fe$_3$O$_4$ and Si/PS/Fe$_3$O$_4$ are at $\sim$ 565 nm (2.194 eV). The emissions near 540 nm and 565 nm were respectively assigned to the energy gap of crystal field splitting (2.2 eV) of octahedral site and the electron transitions between the defect sites[82].

Zhao et al. also found the PL emissions from the PAA-functionalized Fe$_3$O$_4$ nanoparticles (Fig. 13). In particular, they observed a clear NIR peak at 674 nm (1.84 eV). As can be seen in Fig. 13, the peak at 550 nm (2.10 eV) in the visible region is much broader. This is consistent with the experimental data that the photothermal effect is more pronounced when irradiated by the white light compared to 785 nm laser, as the former contributes to photon absorption in a wider frequency range. The PL peak at NIR was suggested by Sadat et al. to correspond to the recombination of trapped electrons from the octahedral site to O(2p)[82].

For window applications, as mentioned above, transparency, upon nanoparticle coatings, is important while maintaining the optimum optical properties such as considerable absorption in NIR, strong photothermal effect, and high photon transmission in the visible range. Fig. 14 shows the absorption and transmission for various thin film coatings on the glass substrates. As can be seen in this figure, the highest absorption, thus lowest transmission, is observed for the thin film containing the uncoated Fe$_3$O$_4$ nanoparticles. A peak near 400 nm is also evident, rendering this film rather dark under visible light. The situation improves when the nanoparticles are coated with poly acrylic acid (PAA), as shown in Fig. 14. Much higher transmission is achieved when the Fe$_3$O$_4$ nanoparticles are embedded in the polystyrene nanospheres, however with compromised photothermal effect. Fig. 15 shows the heating curves of thin films containing Fe$_3$O$_4$ nanoparticles in various forms. Consistent with Fig. 14, the film with the uncoated-Fe$_3$O$_4$ nanoparticles exhibit the strongest photon absorption and highest photothermal effect (Fig. 16). The film with PAA-coated Fe$_3$O$_4$ nanoparticles shows reduced visible absorption, and correspondingly lower photothermal effect. The substrate with the PS/Fe$_3$O$_4$ coating is quite transparent, but suffers from the significantly weakened heating ability. It is thus important to consider these optical and photothermal properties in thin film design and nanoparticle development so that both transparency and photothermal heating efficiency are enhanced simultaneously.

Sadat et al. calculated the extinction ($Q_{ext}$), absorption ($Q_{abs}$), and scattering ($Q_{sca}$) efficiencies using the following equations [82,86]:

$$Q_{ext} = \frac{2}{\pi^2} \sum_{n=1}^{\infty} (2n+1) \text{Re}[a_n + b_n]$$

(3)
Calculation of the photothermal conversion efficiency

For the photo energy transferred to heat, the conversion efficiency can be calculated. Han et al. calculated the photothermal conversion efficiency, \( \eta \), of silica-functionalized Fe\(_3\)O\(_4\) composites using formulations developed by Roper et al. The photothermal conversion efficiency \( \eta \) can be expressed as \([88,89]\):

\[
\eta = \frac{hS(T_{\text{Max}} - T_{\text{Surr}}) - Q_s}{(1 - 10^{-\alpha_{\text{med}}}) S}
\]

where \( h \) is the proportionality constant \( \text{h}(\text{mW}/\text{m}^2 \cdot \text{°C}) \) is the heat transfer coefficient; \( S \) (m\(^2\)) is the surface area of the container; \( T_{\text{Max}} \) (°C) is the system maximum temperature; \( T_{\text{Surr}} \) (°C) is the ambient surrounding temperature; \( Q_s \) (mW) is the energy input by the sample cuvette and the solution; and \( I \) is the incident light power.

The value of \( hS \) is obtained by the following equation \([88]\):

\[
hS = \sum_{i=1}^{n} \frac{m_i C_{P,i}}{\tau_i}
\]

where \( m_i \) and \( C_{P,i} \) are respectively the mass and heat capacity of the sample including nanoparticle suspension and sample cell. \( \tau_i \) (s) is the sample system time constant which is given by \([89]\):

\[
\tau_i = \frac{t}{\ln 2}
\]

where \( t \) is defined as the ratio of \( (T - T_{\text{Surr}}) \) to \( (T_{\text{Max}} - T_{\text{Surr}}) \), and \( T \) (°C) is the solution temperature. \( \phi \) can be expressed as \([88,89]\):

\[
\phi = \frac{T - T_{\text{Surr}}}{T_{\text{Max}} - T_{\text{Surr}}}
\]

where \( (T_{\text{Max}} - T_{\text{Surr}}) = \Delta T \) and is experimentally determined. With all experimental conditions and parameters provided in the study by Han et al, they calculated the \( \eta \) value of 31.9% for the nanoparticle solution \([89]\). The general formulations and calculations will have to be established for the \( \eta \) values of thin films on the glass substrates with given materials properties and dimensions. The photothermal conversion efficiency will also have to be optimized through both nanomaterials development and multilayer thin film structure designs.

4. Discussion

As we discussed in Parts I and II, spectrally selective thin films and photothermal thin films focused on different fundamental physical mechanisms related to solar light, which is mainly about optical and thermal, respectively. Utilizing both spectral selective features and photothermal effects of nanostructured thin films may achieve independent multispectral band modulations while fully utilizing “free” solar energy which is normally reflected by low-e coating and converting it to thermal energy in winter. Fig. 17 shows the schematic diagram on a new window design based on the photothermal effect and spectral selectivity. In this proposed schematic design, we selected Fe\(_3\)O\(_4\) nanoparticles as the photothermal medium. One of the most investigated nanomaterials is Fe\(_3\)O\(_4\) for its pronounced photothermal effect, and the Fe\(_3\)O\(_4\) nanoparticles can be dispersed in various solutions upon surface functionalization. Deposition of thin film coatings on windowpanes is therefore possible to improve the overall winter center-of-glass U-factor of windows with strong Fe\(_3\)O\(_4\) photothermal effect. The working mechanism is as follows.

The adjacent low-e coating layer is heated up by conductive heat transfer from the Fe\(_3\)O\(_4\) layer. The convective heat transfer at the interior window surface plays an important role in the overall window
Conductive heat to increase inner surface temperature

Fig. 17. A typical glazing structure with absorption-based spectrally selective thin films.

thermal performance in the winter season. This is a particularly important architectural feature that the forced airflows via air vents are generally located under windows in a building. The solar-induced photothermal heating on the inner surface of windowpane can then be used to effectively reduce the temperature difference $\Delta T$ between the warm room interior and the window glass interior surface in the winter season, therefore diminishing the convective heat loss significantly. Meanwhile, the low-e coating still serves as a longwave radiation reflector to keep indoor warm conditions. Unlike the conventional “heat-absorbing” tinted glasses with low visible transmittances, the nanocomposite coating shown in Fig. 17 absorbs insignificant visible light, but the narrow waveband near-infrared radiation. In this way, there will be little or no change in visual appearance and transmittance.

Regarding possible summer overheat situation, one can design a window external layer (Surface 1 in Fig. 17) based on optical constructive interference on a selective waveband according to the solar energy incident angles, while still allowing maximum transmission in winter. Similarly, angular selective films with nano structural characteristics have been developed to reflect, divert, and scatter light into designated directions for angular dependent transmittance [90,91]. Expected absorption intensity curves for the combined effects from the photothermal layer and the external summer heat control layer are shown in Fig. 18. In winter, the photothermal layer selectively absorbs the incident solar-infrared and the low-e coating layer reflects NIR radiation, focusing the thermal energy to heat up the inner window surface for reduction of convective heat transfer. In summer, upon mitigation effect by the external interference layer or angular selective layer, the absorption intensity of the photothermal layer is reduced to a lower level compared with that in winter, rendering a minor temperature increase.

Regarding the effects by different orientations of windows on buildings, this window structure design could still operate as what we designed to convert the absorbed NIR solar energy to thermal energy but more thermal energy will be obtained during the early morning for east façade and the late afternoon for west façade due to the strong incident solar light at the low solar altitude. Detailed data collections on solar irradiance and its NIR portion for different vertical orientations should be conducted in future works for this analysis.

In order to understand the improvements of window thermal insulation, we calculated U-Factor using hypothesized photothermal effects on single-pane windows. In the United States, National Fenestration Rating Council (NFRC) implements a national rating system for energy performance of fenestration products, and NFRC has standardized the environmental conditions for U-factor calculations (interior air temperature: 21.1 °C, exterior air temperature: −17.8 °C, wind speed: 12.3 km/h) [77]. $U$ can be expressed as [92]:

$$ U = \frac{1}{\frac{L}{8.07 \times 10^{20} + \frac{1}{4.46 \times \left( \frac{T_2 - T_1}{2} \right)^{25} + 0.09 \left( \frac{T_2 + 273.16}{T_2 + 273.16} \right) \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \Delta T}} + \frac{1}{\frac{1}{5.67 \times 10^{-8} \sigma (T_1^{4} - T_2^{4}) \Delta T}}} \right)$$

(10)

where $L$ is the total height of a window, $\sigma$ the Stefan-Boltzmann constant ($5.67 \times 10^{-8}$ W/m$^2$K$^4$), $e$ is emissivity, $T_1$, $T_2$, and $T_3$ are the window’s inner surface temperature, window’s outer surface temperature, and indoor air temperature, respectively.

Eq. (10) can be used to analyze the possible impacts of the inside surface temperature $T_1$ (which can be controlled by the photothermal effect) on the center-of-glass U-factor. In this estimation, we hypothesized two groups of glazing systems: high emissivity ($e = 0.87$) and low emissivity ($e = 0.03$). In addition, each group has three different baseline insulation referring to the three possible outside surface temperature $T_2$. Regarding the group with the high emissivity ($e = 0.87$), increasing temperature $T_1$ can dramatically lower U-factor for all three types of glazing systems. The decrease is $\sim 28$–68% depending on the increase of the temperature $T_1$ for the three glazing systems. For low emissivity ($e = 0.03$), the reduction percentage is around $\sim 21$–65% for the three glazing systems.

Under the NFRC standards, based on Eq. (10), the possible impacts...
of $\Delta T$ on the center-of-glass U-factor of Fe$_3$O$_4$ thin films. In their photothermal experiments, they found the temperature of the Fe$_3$O$_4$ thin film typically increased approximately 5 °C after white light irradiation. Assuming a similar $\Delta T$ under the experimental conditions, the center-of-glass U-factor was found, according to their calculations, reduced to 0.08–0.15 W/m$^2$ K. The U-factors in this range would correspond to an energy saving of 85–159 KJ/m$^2$ in one-hour white light irradiation. This U-factor estimation demonstrates the potentials of the photothermal effect under white light in the design and application of the energy efficient windows.

Based upon a DOE report, the stock of sing-pane window is declining fairly slowly. About 30% of residential buildings in cold U.S. climates uses the single-pane windows [1]. The concept depicted in Fig. 17 paves a new way for the most efficient window thermal insulation without relying on sandwiched window structures of two or three panes for heating-dominated locations. Furthermore, the Fe$_3$O$_4$-nanoparticle-containing polymer films can be applied using various coating methods, representing an ideal candidate for wide-scale-energy-efficient window retrofits with low balance-of-system costs. However, to achieve the goals illustrated in Fig. 18, the photothermal effect has to be studied in terms of various thin film parameters such as concentration, thickness, and heating efficiency. The operating physical mechanisms governing the photonic heat conversion will also have to be identified. Based on the photonic property study, the overall window thermal transfer mechanisms under all conditions can be investigated using both computational and experimental models. Upon optimization of photothermal efficiency of nanoparticles, prototypical single-pane models may be built for proof of concept.

5. Conclusions

This review concludes that it is possible to achieve a significant reduction in building energy consumption via design of novel nanosstructures for window applications. Two conventional approaches are introduced for achieving the so-called “perfect window,” categorically, structural and spectral. The former deals with conventional glazing using sandwiched structures with the transparent insulation materials and/or air gas layers. The latter is concerned with spectral selectivity of windows in different wavelengths (from visible to NIR). Low-e coatings are spectrally selective control films that fall into this category. There is an abundant solar energy, 50% of which is directly reflected when it encounters the high-SHG low-e coatings for cold climates, but can be otherwise utilized via the photothermal effect. Based on the perfect window concept, unidirectional NIR radiation is needed, yet difficult to achieve with the static thin films. In contrast, dynamic thin films, including electrochromic, thermochromic, electrophoretic, and suspended-particles, are capable of responding to external stimuli by changing their optical and physical properties, therefore highly promising for independent modulation in the visible and NIR regions.

Conducting nanoparticles exhibit strong plasmon absorptions in NIR region, while semiconducting oxides are less investigated for their photothermal effects. Recent studies on the Fe$_3$O$_4$ nanoparticles show photo-fluorescence in both visible and NIR regions, suggesting a possible mechanism for the photothermal effects that have been experimentally well observed. Although the photothermal effects of nanoparticles have previously and primarily used for cancer treatment, new studies suggest high possibilities for applications in energy efficient window structures. The traditional thermal insulation is accomplished via a gaseous gap between the double panes. The performance of the traditional double pane is therefore solely dependent on the thermal insulation properties of medium. It has been established in a recent study that the center-of-glass U-factor can be effectively reduced by photothermal heating of the window interior surface. By a straightforward coating method, a thin film containing Fe$_3$O$_4$ nanoparticles can be applied on the glass substrate. Upon simulated solar light irradiation, the surface temperature can be considerably increased resulting in reduced convective heat loss in winter. This is a fundamentally different approach in reducing window heat loss in winter via the photothermal effect of nanomaterials. This approach lifts some of the major obstacles to building energy savings and paves a new path for novel window designs.

The advantages of the photothermal thin films are several-folds: (1) no insulating medium is needed as in the traditional double-pane structure, (2) the Fe$_3$O$_4$ nanoparticles can be mass-produced with low cost, (3) the polymer coating containing Fe$_3$O$_4$ can also be easily applied using various coating methods, (4) $\Delta T$ between the warm room interior and the inner window glass surface temperature can be tuned by adjusting the nanoparticle concentration and film thickness, (6) the condensation resistance in glass corners and edges can be increased by directing magnetic Fe$_3$O$_4$ nanoparticles to the specific areas of glass, and (7) adhesive products built upon this approach can be applied in wide-scale energy-efficient window retrofits with low balance-of-system costs. These advantages in energy saving profoundly points a new research direction in the design of the novel building materials in terms of both fundamental science and architectural engineering.

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