

Plasmon-Enhanced Solar Energy Harvesting

by Scott K. Cushing and Nianqiang Wu

Solar energy can be directly converted to electrical energy via photovoltaics. Alternatively, solar energy can be converted and stored in chemical fuels through photoelectrochemical cells and photocatalysis (see front cover image), allowing continued power production when the sky is cloudy or dark. The conversion of solar energy is regulated by four processes: light absorption, charge separation, charge migration, and charge recombination. An individual material cannot be optimized for all four processes. For example, TiO_2 has excellent charge migration qualities. However, the ultraviolet (UV) band gap limits charge separation to less than 5% of the solar spectrum. Visible light band gap semiconductors such as Fe_2O_3 often have small charge minority diffusion lengths, ~ 4 nm in Fe_2O_3 , and suffer from photoinstability.¹

Several alternatives have been investigated to overcome the deficiencies of existing semiconductors. Doping of UV band gap semiconductors increases the absorption of visible light. However, the isolated mid-gap states are detrimental to charge mobility and lead to high charge recombination.² No single material excels in efficient conversion of solar energy. Instead, two materials can be combined synergistically to compensate the individual weakness in a hetero-structured design. Sensitizers are one type of heterostructure where an efficient visible light absorber converts radiation and transfers the photoexcited charge to a semiconductor support. The semiconductor support, unlike the sensitizer, has favorable redox potentials or favorable charge migration and recombination properties. For example, sensitizers have been applied in dye sensitized solar cells to improve the energy conversion efficiency levels to 11.8%.³ Sensitizers are usually organic dyes or quantum dots, but both are plagued by photostability issues, especially for applications related to photocatalysis or photoelectrochemical cells (PECs).⁴

Incorporation of plasmonic nanostructures with semiconductors offers an alternative route to improve the solar energy conversion efficiency. Localized surface plasmon resonance (LSPR) describes the collective charge oscillations in metal nanoparticles created by an incident field resonant with the periodic displacement of electrons against the positive nuclei background. LSPR is, at its core, a damped harmonic oscillator whose resonance conditions are determined by the geometry of the particle, the dielectric constant of the metal, and the local environment.⁵ At resonance, the charge oscillations create a local electric field with

strength up to $\sim 10^3$ times the incident field and greatly increase far-field scattering. In a plasmonic heterostructure the energy stored in the LSPR can (1.) be converted to heat in the metal lattice, (2.) re-emit as scattered photons, or (3.) transfer to the semiconductor.

Plasmonic nanostructures improve solar energy conversion efficiency via the following mechanisms: (a) enhancing the light absorption in the semiconductor by photonic enhancement through increasing the optical path length and concentrating the incident field;⁶ (b) directly transferring the plasmonic energy from the metal to the semiconductor to induce the charge separation in the semiconductor by direct electron transfer (DET);^{7,8} or by plasmon-induced resonant energy transfer (PIRET).⁹

Plasmonic Enhancement of Light Absorption and Scattering

The first enhancement mechanism, referred to as *photonic enhancement*, requires engineering the metal nanostructure or pattern to direct and concentrate light at the interface or bulk of the semiconductor. This is possible because the LSPR causes both absorption and scattering with strengths dependent on the size of the nanoparticle. A 15 nm sized gold nanoparticle (Fig. 1a), primarily localizes the EM field as depicted in Fig. 1c. A 100 nm sized particle primarily scatters the incident field (Fig. 1b) in the forward and backward directions (Fig. 1d).

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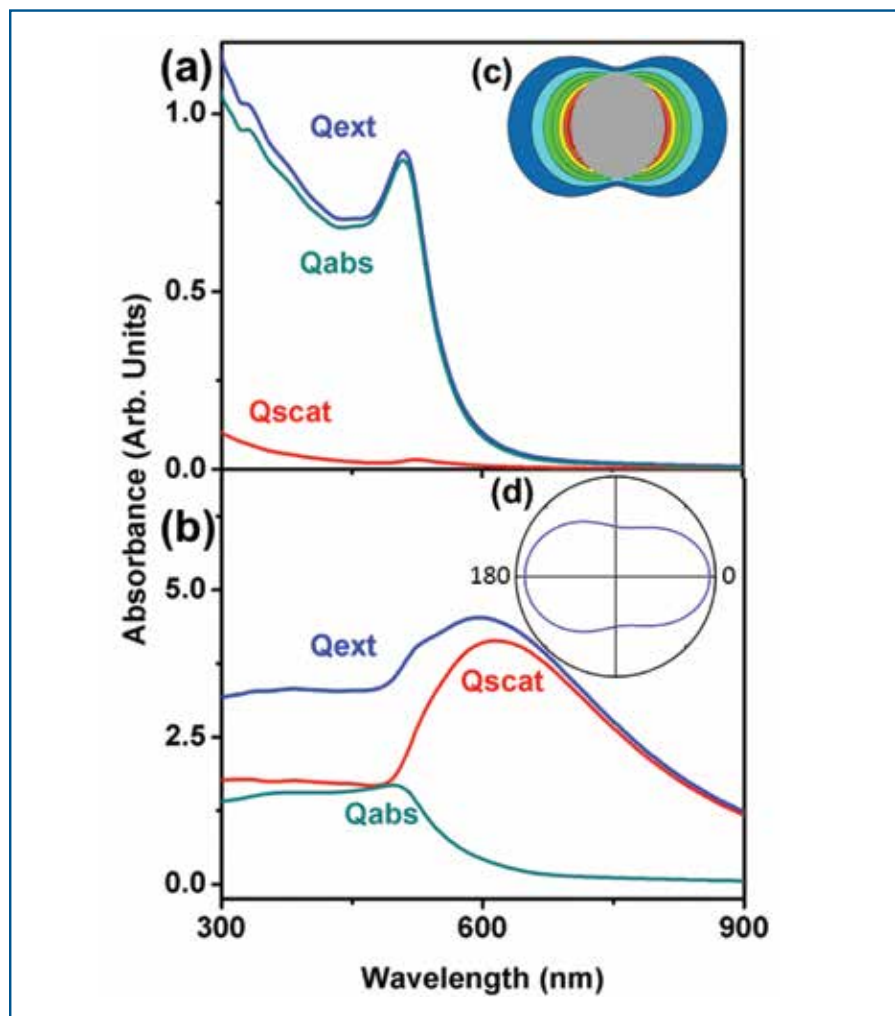


FIG. 1. Extinction, scattering, and absorption for (a) a 15 nm sized gold sphere and (b) a 100 nm sized gold sphere. As the sphere size increases, the LSPR shifts from localizing (c) to scattering (d) the incident EM field.

Combinations of these two characteristics have allowed close to 90% light trapping over the entire visible spectrum.¹⁰ The *photonic enhancement* mechanism can only increase the efficiency of the semiconductor at the energies above the band gap.

Thin film solar cells overcome the short carrier diffusion lengths of visible light band gap semiconductors but remain inefficient because of the small absorption coefficient. The optical path length inside the semiconductor can be increased by using the scattering properties of large metal nanoparticles to effectively trap light.^{6,10} The large metal nanoparticles forward scatter incident light into the cell. A plasmonic reflector at the back of the cell (Fig. 2a) reflects the light that is not absorbed. The reflected light backscatters off the metal nanoparticles at the front of the cell, causing multiple reflections and increasing the optical path length. This strategy has increased the photocurrent of Fe₂O₃-based cells to 4 mA/cm².¹¹

A similar problem is faced in PEC and photocatalysis where semiconductor nanoparticles are favored because of the increased surface area for reactions. The total efficiency is limited because of the small absorption cross section of the nanoscale particles. The light absorption can be increased by attaching small metal nanoparticles on the semiconductor, which localize the incident field. The concentrated electromagnetic (EM) field of the plasmon increases the absorption cross section of the semiconductor nanoparticle and enhances the carrier creation rate.¹² In a Ag@TiO₂ system, the local EM field led to a 10 times enhancement in water splitting rate.¹³ The same strategy can be applied at the interface of two semiconductors, concentrating the incident field in the p-n junction where light absorption is critical.

Direct Electron Transfer (DET) from Plasmonic Metal to Semiconductor

The second design pathway, referred to as *plasmonic energy transfer enhancement*, uses LSPR to convert solar radiation to the plasmonic energy stored in the metal, which is then transferred to the semiconductor. The process directly creates electron-hole pairs in the semiconductor, independent of the semiconductor's light absorption characteristics. Energy is stored in a plasmon by (1.) hot electrons and (2.) the local electromagnetic field. The *plasmonic energy transfer enhancement* allows for charge separation at the energies below the semiconductor's band gap.

The *plasmonic energy transfer enhancement* mechanism was first reported in Au@TiO₂, where the photocurrent increased proportional to the LSPR spectrum.^{7,8} The

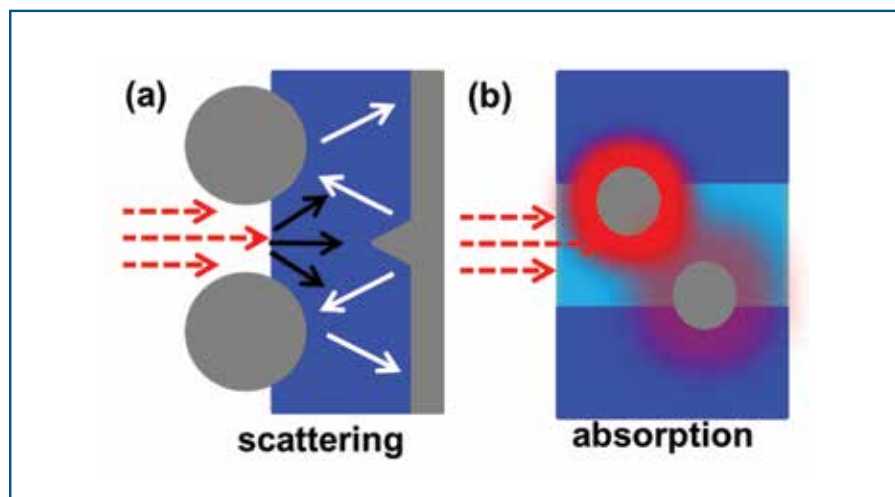


FIG. 2. Photonic enhancement in plasmonic metal-semiconductor hetero-structures, including (a) increasing the optical path length through scattering and (b) increasing the absorption cross section by localizing the incident field.

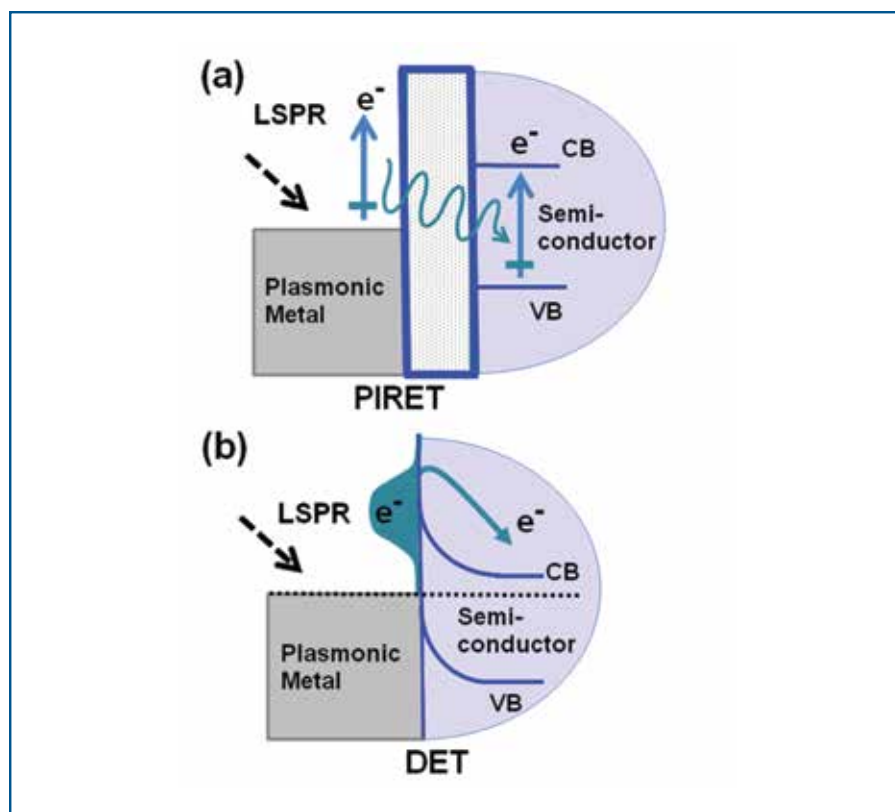


FIG. 3. Two different mechanisms of plasmonic energy transfer enhancement: (a) plasmon-induced resonant energy transfer (PIRET) from the metal to the semiconductor, leading to charge separation, and (b) direct electron transfer (DET).

work of Furube *et al.* confirmed that the plasmonic electrons were overcoming the Schottky barrier and transferring into the Au (Fig. 3b) using transient absorption spectroscopy.¹⁶ The plasmonic electrons have an energy distribution centered on the LSPR peak wavelength. The plasmonic electrons mimic hot, or short lived, electron hole pairs due to the energy associated with the charge oscillation. The oscillations are quickly damped by nonradiative electron–

electron and electron–phonon scattering, or radiative scattering by emission of a photon. The strong dampening means the plasmon has a lifetime of $\sim 10^{-15}$ s.¹⁴ For comparison, the electron hole pairs in a dye or quantum dot have a lifetime of $\sim 10^{-9}$ s. Despite the difference in lifetimes, the interfacial charge transfer process for the plasmonic electrons is still well explained by Marcus theory for charge transfer between an organic dye and a semiconductor.¹⁵

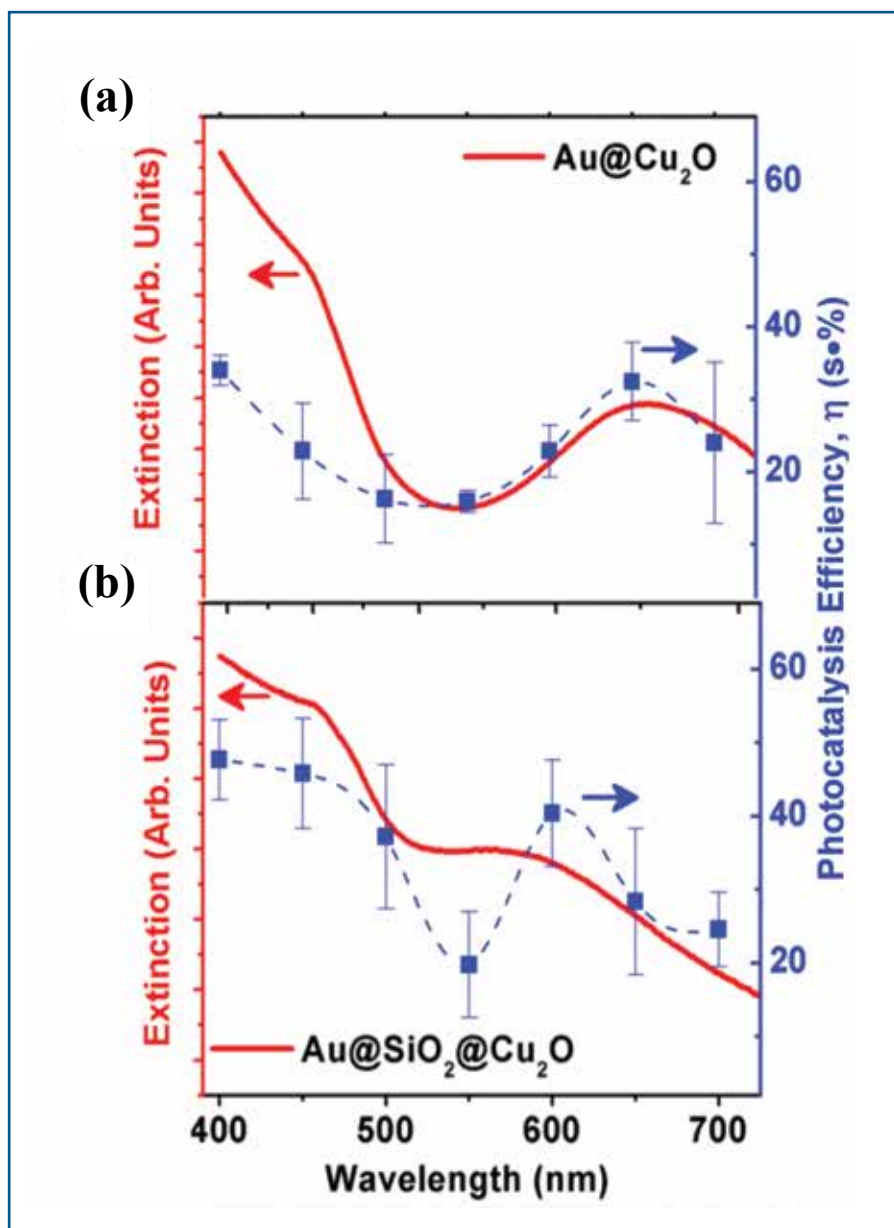


Fig. 4. Photocatalysis enhancement versus wavelength compared to the extinction spectrum for (a) $\text{Au@Cu}_2\text{O}$, and (b) $\text{Au@SiO}_2\text{@Cu}_2\text{O}$ core shell nanoparticles. (Reprinted with permission from Ref. 9. Copyright 2012 American Chemical Society.)

The plasmonic charge transfer process is referred to as direct electron transfer (DET), as shown in Fig. 3b. DET has been investigated in a myriad of systems using both Au and Ag as the plasmonic metal.¹⁷⁻¹⁹ The enhancement of photocatalysis and photovoltaics at the energies above and below band gap has been found to be nearly universal, whether the base material is a semiconductor or graphene.¹⁷⁻¹⁹ DET is similar to electron transfer from a dye to a semiconductor in that direct contact and electronic alignment are necessary for efficient electron transfer (Fig. 3b). However, DET differs in that the plasmon does not have a band gap which determines the charge transfer kinetics. Rather, the plasmonic carriers have the energy

proportional to the incident photon's energy plus the Fermi level, so they can easily overcome the energetically unfavorable barriers at the interface, leading to more flexibility in materials selection.

Plasmon-Induced Resonant Energy Transfer (PIRET) from Metal to Semiconductor

The strong local EM field of LSPR allows for energy transfer mechanisms outside of DET which are not possible with dyes or quantum dots. The plasmonic photocatalysis enhancement even occurs in the presence of a SiO_2 insulating layer between the plasmonic metal and the

semiconductor (Fig. 4b), which prevents from the DET process. Hence DET alone cannot interpret the existence of multiple plasmonic enhancement phenomena.²⁰⁻²³

Recently our group discovered an unprecedented *plasmonic energy transfer enhancement* mechanism, that is, plasmon-induced resonant energy transfer (PIRET)⁹ as shown in Fig. 3a. PIRET can proceed even in the presence of an insulating layer between the plasmonic metal and the semiconductor.⁹ PIRET describes the nonradiative transfer of energy from the LSPR dipole of the metal to the transition dipole of the semiconductor. In other words, the strong local EM field of the LSPR can preferentially relax by exciting an electron hole pair in the semiconductor without the emission of a photon. The strength of PIRET depends on the overlap of the semiconductor's band edge (absorption band) with the LSPR resonance band, as well as the distance between the two dipoles (the plasmonic metal and the semiconductor), similar to Förster resonant energy transfer.^{25,26} Interestingly, our studies showed that only PIRET, not DET, was present in $\text{Au@Cu}_2\text{O}$, independent of the existence of a spacer layer. However, when a Ag core was used, both DET and PIRET were present in $\text{Ag@Cu}_2\text{O}$. These results suggest that both DET and PIRET can coexist dependent on material parameters.²⁷

PIRET is an attractive route for plasmonic enhancement. PIRET depends on spectral overlap and does not require physical contact or electronic alignment to transfer energy like DET, which provides flexibility in design of solar energy materials and structures. As shown in Fig. 4, PIRET can generate electron-hole pairs in the semiconductor above and below the band gap of Cu_2O , suggesting strong coupling to the weak band edge states. The broad plasmon resonance can easily be tuned, allowing for enhancement of solar energy harvesting in the entire visible spectrum (Fig. 5). PIRET is useful when charge transfer creates undesirable effects, such as the carrier equilibration issues or the material degradation.

Plasmonic Photosensitizers

As described above, plasmonic nanostructures can harvest solar light, and transfer solar energy to the semiconductor, enhancing the charge separation in the semiconductor. Therefore, a plasmonic nanostructure can be thought of as an effective "photosensitizer," although plasmonic and traditional sensitizers vary in several key aspects. LSPR has a broad resonance (often 100 nm or larger) compared to dyes and quantum dots. Whereas quantum dots and dyes have a Stokes-shifted emission, the absorbance and "effective" emission of a plasmonic sensitizer are almost identical spectrally. The multiple electron process responsible for LSPR also creates a much

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larger absorption and scattering cross section.²⁸ The LSPR is tunable across the entire UV-NIR spectrum by varying the shape, composition, and environment of the particle, as depicted in Fig. 5.⁵ The metal structure allows stability in the harsh environments of chemical cells while also acting as a co-catalyst and prolonging carrier lifetimes at the semiconductor metal interface.²⁹⁻³²

The same engineering principles used to enhance photovoltaics and photocatalysts with sensitizers can be applied to plasmonics. Plasmonics can replace, supplement, and even enhance current sensitizer based designs.^{12,33-35} The strength of plasmonic sensitizers is that, unlike traditional photosensitizer, multiple plasmon-induced enhancement mechanisms exist. In one system, the photonic and light conversion enhancements can be combined to enable harvesting of full spectrum solar light as outlined: a plasmonic nanostructure will reflect incident light, increasing the optical path length. The increased optical path length allows for more chance of light conversion at the energies below the semiconductor band gap because of the increased plasmonic absorption cross section. The increased light trapping will also enhance the conversion of below-bandgap light by plasmonic energy transfer to the semiconductor. Both DET and PIRET are possible to reduce the constraint in material/device design.

Remarks and Perspectives

Plasmonic nanostructures are an attractive alternative and supplement to dyes and QDs in photovoltaics and photocatalysts. Two mechanisms, DET and PIRET, allow plasmonic sensitization of semiconductors at the energies above and below band gap. Plasmonic enhancement is applicable to a large variety of materials and designs where contact may or may not be possible. Further, the enhancement can be tuned throughout the wavelength range by changing the geometry of the plasmonic nanostructure. Plasmonic nanostructures will play an increasing role in solar energy harvesting. Current plasmonic sensitizers have an EM field enhancement of ~10. Plasmonic nanostructures can be designed with orders of magnitude larger EM field enhancements, creating the possibility of highly efficient photocatalysts and solar cells.

Acknowledgments

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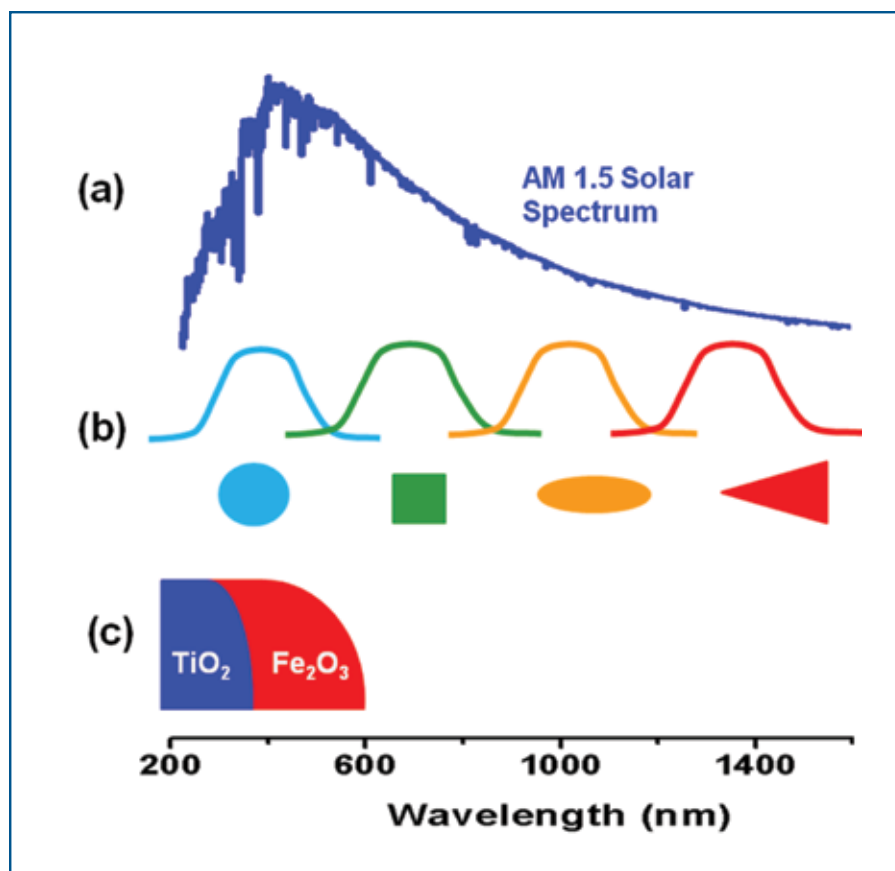


FIG. 5. (a) Solar spectrum;³⁶ (b) representative tuning range for LSPR showing the full solar spectrum harvesting with LSPR as a sensitizer; and (c) the absorbance of common semiconductors used in water splitting.

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