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NANOPARTICLE PHYSICS FOR ENERGY, LIGHTING AND ENVIRONMENTAL CONTROL TECHNOLOGIES

G. Smith

Institute of Nanotechnology & Department of Applied Physics. University of Technology, Sydney
PO Box 123, Broadway, NSW 2007

ABSTRACT

Performance of everyday systems such as windows, skylights, painted car panels, roofs and walls and lighting installations, can be improved markedly using nanoparticles, nanocoated micro-particles and nanocomposites. Additional functionality such as self cleaning and power generation is also possible. Properties and applications using polymer and conductor nano- and micro-particles, metal coated particles and nano-voids in metals are covered. Engineering of novel optical and thermal properties based on surface plasmons and surface plasmon polaritons is outlined. The diversity of responses and technical opportunities demands modelling. Empirical exploration by itself is time consuming and risky. Representing an inhomogeneous nanocomposite optically by an "effective" homogeneous medium is shown to be useful when correctly applied, but is seen to be prone to misuse. The current controversy about negative refractive index nanostructures is a recent example. Opportunities in solar cells, thermal-to-electric conversion and refrigeration, separation, energy storage and power management systems are outlined, along with new decorative and display options.

1. INTRODUCTION

The cost/performance barrier to more general use of environmentally friendly, energy saving and life enhancing technologies is set to fall dramatically as we learn to apply new ideas in nano-science in the context of renewable energy sources, energy efficiency, environmental control and remediation. Making interiors and outdoor spaces more safe, appealing and enjoyable will be a bonus. The areas and volumes required in solar energy, building energy systems and large environmental projects mean that high technology products in these areas should come at capital and running costs which equate with, or marginally exceed, costs of products like paint, glass, polymer sheet and household appliances. Materials with special features or extra functionality rarely meet this criteria. For example conventional approaches to photovoltaic solar energy are running into both cost and performance barriers. While sales volumes are increasing, costs are not falling at the rate one might hope. Approaches instinctively expected to yield lower costs, for instance thin film photovoltaics, or new approaches to polycrystalline PV, are caught in a dilemma. To maintain low cost, undesirably low efficiencies have to be accepted, since enhancements such as multi-junction or multi-layer cells which can lift performance, come at an unattractive cost penalty. In these circumstances PV technologies, without fundamental new approaches, might only be widely used if there is an energy crisis, government subsidy or regulations mandating their use. Energy efficient windows for warm climates have similar problems, which inhibit wider usage. The multi-layer thin films typically with at least two silver layers, that are needed to block solar heat while staying clear and allowing in light, add a multiplier to the cost of a window, by up to a factor of three. Thus, despite their considerable advantages to comfort and energy savings, only select large building projects tend to use them while, in the residential case, use is marginal. The proposed new Australian Building Codes for Energy Efficiency to be implementated in 2003 [1], could not immediately insist on performance windows for energy savings since these codes have to be cost sensitive. As a result most residential glazing will have to be either shaded or limited in area to contain energy impacts. Light gain and view, and hence overall appeal and value of interiors is then diminished compared to what it could be. Lighting itself has enormous scope for energy savings, superior visual comfort, better safety, and greater decorative options. Both glare reduction and the need to spread light, are a major source of energy inefficiency in lighting. In many light fittings, diffusers can be made to be much more energy efficient with polymers containing special additives, while new lamps based on nanotechnology are on the way which may cut lighting energy by 90%. Coloured lighting today is technically quite crude compared to what is possible.

Lighting is one aspect of a core reason why energy savings and renewable technologies fail to attract consumers. They all too often reduce decorative and visual options, or impose ugly or disconcerting aesthetics. Other impediments include difficulty to install, sometimes requiring major structural work, mechanical complexity, maintenance and additional requirements on space for energy storage. Roof mounted solar panels, tracking mirrors, storage tanks, some lamp types, battery arrays, and most skylights suffer from one or more of these drawbacks. Nano-based systems can alleviate each of these problems.

Colour itself is integral to appeal of spaces, roofs and facades, and of course fabrics. Traditionally, to reflect heat required white or pale colours, and to absorb it in solar collectors required black. A bright white or pale metal roof gives too much glare while people like car bodies in many colours. Nano-systems involving new types of pigments can provide solar rejection with a full range of colours, or efficient solar collection and colour [2,3]. They also open up new options such as stunning pearlescence, colour shifting with direction of view, or with environmental conditions - the so-called chameleon effect. Nanoparticles in or on polymer, wool, and cotton fibres promise even more opportunities in colour, appearance, feel and functionality in clothing and furnishings.

This article will indicate how a number of materials utilising nanocomponents, especially those involving nanoparticles and nanostructured layers and films are contributing to ultimately making these systems the technology of choice and opening up quite new opportunities for energy savings and interior design. In addition to those systems noted already we will touch on refrigeration, energy storage, self cleaning surfaces and air cleaning. Nanotechnology is impacting already in some of these markets.

2. ENERGY AND ENVIRONMENTAL APPLICATIONS OF NANOPARTICLES, NANOSTRUCTURED SURFACES AND FILMS

An overview of existing activity in nanotechnology using nanoparticles and structures, sometimes on or with microparticles, for energy efficiency, power supply, energy storage and environmental management is presented in tables 1 and 2. The first table emphasises (except for heat collection), passive systems for lighting and decoration, cleaning and air quality, and passive cooling. Table 2 emphasises active nano-systems for direct solar power, cooling, refrigeration and air conditioning, plus energy storeage and power management. In each case concrete examples of a system used to implement each technology is given. A wide variety of nanoparticles and nanostructures are required.

Table 1. Nanosystems for solar thermal collection, radiation control, lighting, decoration and environmental control

Material	Uses	Example
Solar selective cermets (metal nanoparticles in ceramic matrix)	Flat plate collector Parabolic concentrator Evacuated collector	Black chrome Ni pigmented alumina co-sputtered Mo in oxide
Conducting nanoparticles in polymer	Solar control laminations and polymer sheet in glazing	ITO nanoparticles in PVB between two glass sheets
Oblique metal nano-columns	Angular selective glazing for glare and thermal control	Ag in Al_2O_3 or SiO_2
Nanoimprinted polymer sheets and films on glass	Anti-reflecting coatings with wide angle functionality	Nanostructured PMMA surfaces or sol-gel films
Clear polymer light pipes doped with clear polymer	Continuous general illumination, display, safety lighting, light control	Flexible and rigid acrylics plus clear polymer additives
Holographic polymer sheets	Sunlight redirection and angular selective control	UV interferences gratings in polymer film, nano-imprinted layers
Nanostructured membranes	Water purification Ultra filtration Nanoengineering	Nanoholes in polymer and metal, metal coated polymer fibre arrays
Nanostructured photocatalytic and self cleaning surfaces	Remove organic pollutants and bio hazards from air Auto-Clean windows Water collection	TiO_2 and SiO_2 nanoparticle or nanostructured film layers on glass, polymer or metal surfaces
Nanolayers on metal flakes	Roof, wall, and car energy efficient solar control or low emittance paints of any desired colour Colour variation with viewing angle (pearlescence)	Fe_2O_3 single or Fe_2O_3/SiO_2 double layers on aluminium flakes as pigment in a paint

Table 2. Nanosystems for power generation, power management, and electrical energy storage

Material	Uses	Example
Dye coated semiconductor nanoparticles	Solar power using screen printed dye solar cells (DSC)	Ruthenium dye coated titania in iodide electrolyte
Fullerenes and nanotubes in or on doped conducting polymers Nanorods of semiconductor in organic conductors Porphyrin dye coated nanoparticles embedded in organic conductors	Solar power using hybrid-organic-inorganic solar cells Dye sensitized organic solar cells	Fullerene films on polyphenylvinylene (PPV) Nanorods of CdS in organic electron donors Porphyrin, perylene or pthalocyanine on acceptor nanoparticles in layered heterostructures or blends
Nanostuctured electrodes	Super and ultra capacitors for energy storage and power management including for wind and solar power Low energy electrolytic separation technologies	Activated carbon or metal nanostructured layers plus electrolytes Nanotube "forests" on plates
Low work function surfaces separated by nanogaps Multi- nanolayer thermoelectric devices	Thermionic (thermoelectric) cooling, refrigeration and power sources	Alkali metals plus oxygen or Ag-O-Cs layers on metal separated by 5 to 15 nm Ballistic electron semiconductor multilayers

Radiation management includes spectral and directional control of incoming light and heat, thermal insulation, and light transport or dispersion into space, while radiation usage includes heat capture, current and voltage generation, and chemical processing. A feature increasingly enabled by nanotechnology is evident in the tables, namely increasing multi-functionality in basic building elements, including the coloured paints and windows. Windows were initially for provision of light but as architecture has evolved they have become increasingly multi-functional, with external view and internal ambience now also prime functions. Nanotechnology allows us to add further functions to a window, without compromising these core purposes. Additional functions include self-cleaning, air cleaning, optical switching, emittance control, and power generation using the non visible near IR component of solar radiation. The solar PV aspect comes up in table 2.

3. IMPORTANCE OF PHYSICS TO ENERGY RELATED NANOTECHNOLOGY

3.1 Modelling and physics in development and business processes

Nanotechnology is multidisciplinary and its best developments are coming from professional teams. We will present several reasons and examples from the energy field, why understanding the physics of nano-systems, in the context of nanoparticles and nano-structured films, is even more important than the traditional role of physics in technology evolution to date. It is needed here, not just to underpin R&D and technology optimisation, but to assist in business decision making. Costs are intimately tied up with nanoscale variants, which may lead to similar functional outcomes, say in optical response. The wealth and breadth of opportunity in the nano-scale landscape itself represents a business risk. Management of that risk is easier if the models and the understanding physics supplies is used to elucidate potential competition and help formulate intellectual property strategies.

Knowledge of nano- and micro-composite material physics in the optical and thermal domain has led to several practical energy and decorative technologies from UTS nano-researchers going back to the 1970's and 1980's, through to today. Modelling, based on the underlying physics played a central role in these developments. Successful modelling goes hand in hand with understanding the key issues, which in turn makes the development process much easier. Influences on optical and radiative properties including spectral transmittance, absorptance and reflectance plus directional effects, in an array of nanoparticles include: particle composition and density, the host matrix material, spacing between particles or voids, local order, particle shape and orientation, particle size and size distribution, nanostructure within and on a nanoparticle, changes in electron properties at the nanoscale due to quantum effects, tunnelling and increased collisions, electrical continuity on a scale larger than smallest features but smaller than the wavelength, and polarisation of incident radiation.

The number of potential array structures that can be engineered, as shown schematically in Figure 1, is quite vast. For the same material each has a different optical and electrical response. All can create spectral control, and some directional and polarisation control, but which are easier to make and which give sharper spectral tuning capability? Some new phenomena have only been recently observed in these systems, and are unique to the nanoscale, such as light transmittance along lines of metal nanoparticles via near field coupling across nano-gaps between particles [4] , giant transmittance through nano-holes in metal layers [5], broad band spectral tuning with just two materials using metal coated nanoparticles [6], and special light transport properties of clear polymer doped with clear polymer [7,8]. New fundamental developments such as these open up a range of new technological options. Proven physical models allow exploration of these numerous material and geometric design options without the need for daunting empirical experimental studies. While models are not restrained by laboratory pragmatics, ability to engineer specific particle arrays and in particular the extent that geometric features are narrowly defined in practice must be considered in the modelling process. As an example in our own work [9,10] until recently, we have found that predicted sharp spectral features are rarely found in practice.

Instead multiple or single absorption bands, represented by multiple polarisation eigenmodes, were typically washed out and broadened. This is because there was an admix of local nano-structures, and even just with dilute particles an admix of shapes or sizes. Better engineering precision at the nanoscale will be essential for many *but not all* applications to fully exploit the theoretical options. Many of the applications in tables 1 and 2, however actually benefit from broad bands. Engineering focus may itself be driven by modelling which can provide incentives to achieve new structures and hence evolve new production and layout techniques.

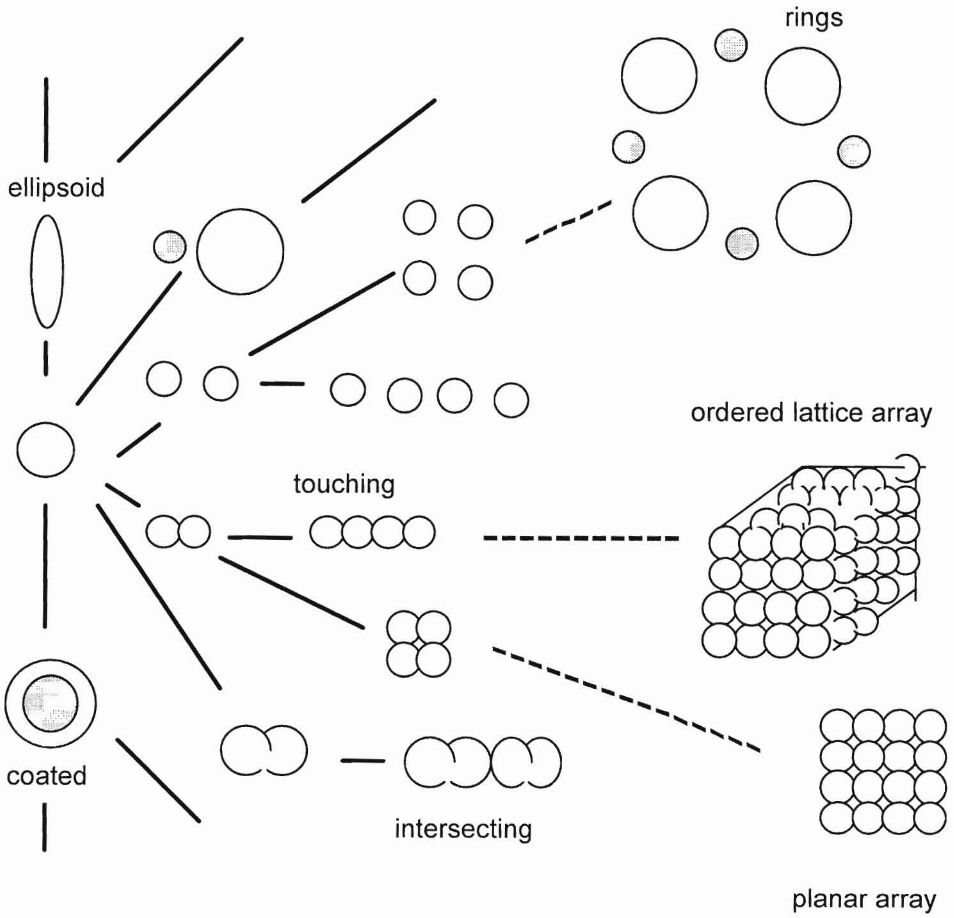
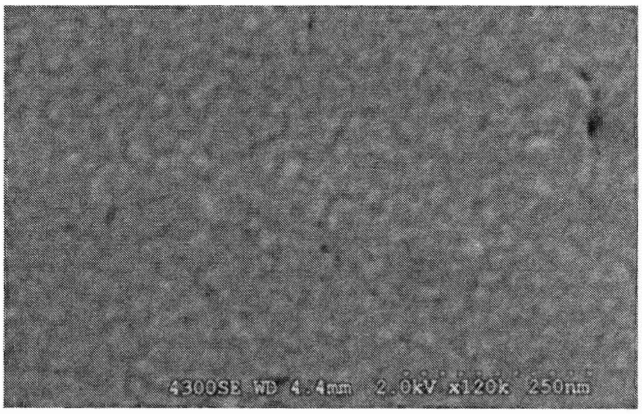


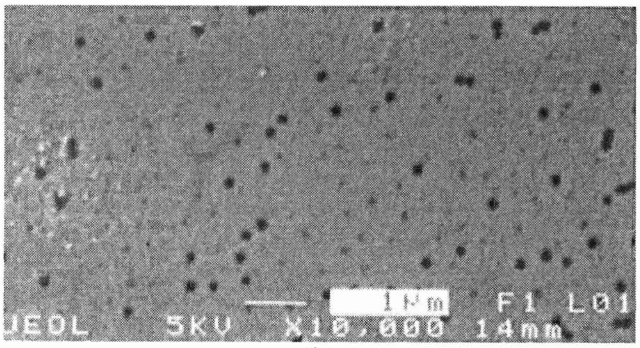
Figure 1. Overview of the nanotechnology "landscape" in terms of different classes of conducting particle arrays that might be made, each of which will have a different effective optical response. Shading represents a different material and is only shown for a few cases but could be used in all.

3.2 Nanostructural hierarchies

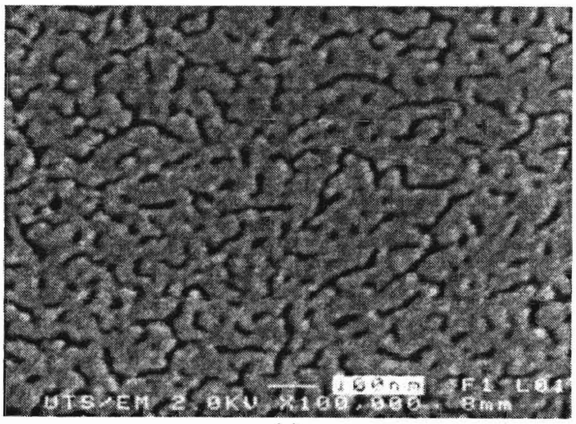
A feature that has emerged in our studies of both nanoparticles and thin films with nano-void arrays, especially when metals are present, is that accurate modelling of optical data often requires consideration of the co-existence of two or more hierarchies of nanostructure in the same system. This is often neglected, despite the fact that their impacts are rarely additive, but rather interact or convolve. For example, we can achieve interesting new effects if we make after deposition, or during deposition, circular nano-holes 20 nm to 100 nm across in a thin electrically continuous metal layer that itself has properties shifted from bulk values due to its 20 to 40 nm grains and possibly 0.5 nm to 1.0 nm wide voids [10]. Nanoparticles themselves may contain substructure such as nano-grains, voids or nano-structured surfaces. Figure 2(a) shows an example of a sputtered 10 nm thick, electrically continuous metal whose infrared properties differ from those of its bulk counterpart due to the obvious nano-structure and figure 2(b) and 2c) are a similar film plus engineered nano-holes.



(a)



(b)



(c)

Figure 2. Thin metal films (a) intrinsic nanostucture (b) and (c) different types of nano-voids in metal itself containing lower order nano-features

The important new area of thin metal coatings on nano and micro size dielectric spheres exemplifies this issue with three to four levels of substructure each needing distinct nano-physics (i) the combination of shell and core in isolation (ii) the nano-thick film on the sphere which lifts the polarisation modal degeneracy found in an all metal particle (iii) the inevitable nanostructure within the shell via current production routes (iv) interaction properties between metal coated nanoparticles. When dealing with many nanoparticles and thin films the material refractive indices used in modelling cannot be simply taken over from known bulk values.

Semiconductor nanoparticles and structures change in another way, with quantum confinement leading to new energy levels which can change apparent colour or fluorescence output, and offer new opportunities in opto-electronics or solar energy conversion. This is a major field in its own right, but again additional nano-substructure can come into play to modify the results of simple theoretical models.

Polymer nano and micro particles can have internal nanostructure which is quite different to the bulk, with new molecular chain configurations and increased cross linking between chains leading to shifted properties. Among those we have used in lighting work are changed melting and softening points to aid in composite manufacturing, and small but significant shifts in refractive indices which allow important new optical effects to be simply achieved. Examples of their unique optical properties appear in Figure 3(a) which shows flat spectral response as high as that for un-doped clear sheet, despite variations with wavelength of the diffuse and specular components: Figure 3 (b) shows insensitivity to thickness at the same doping level of total transmittance at 520 nm as thickness changes from 1 mm to 4 mm.

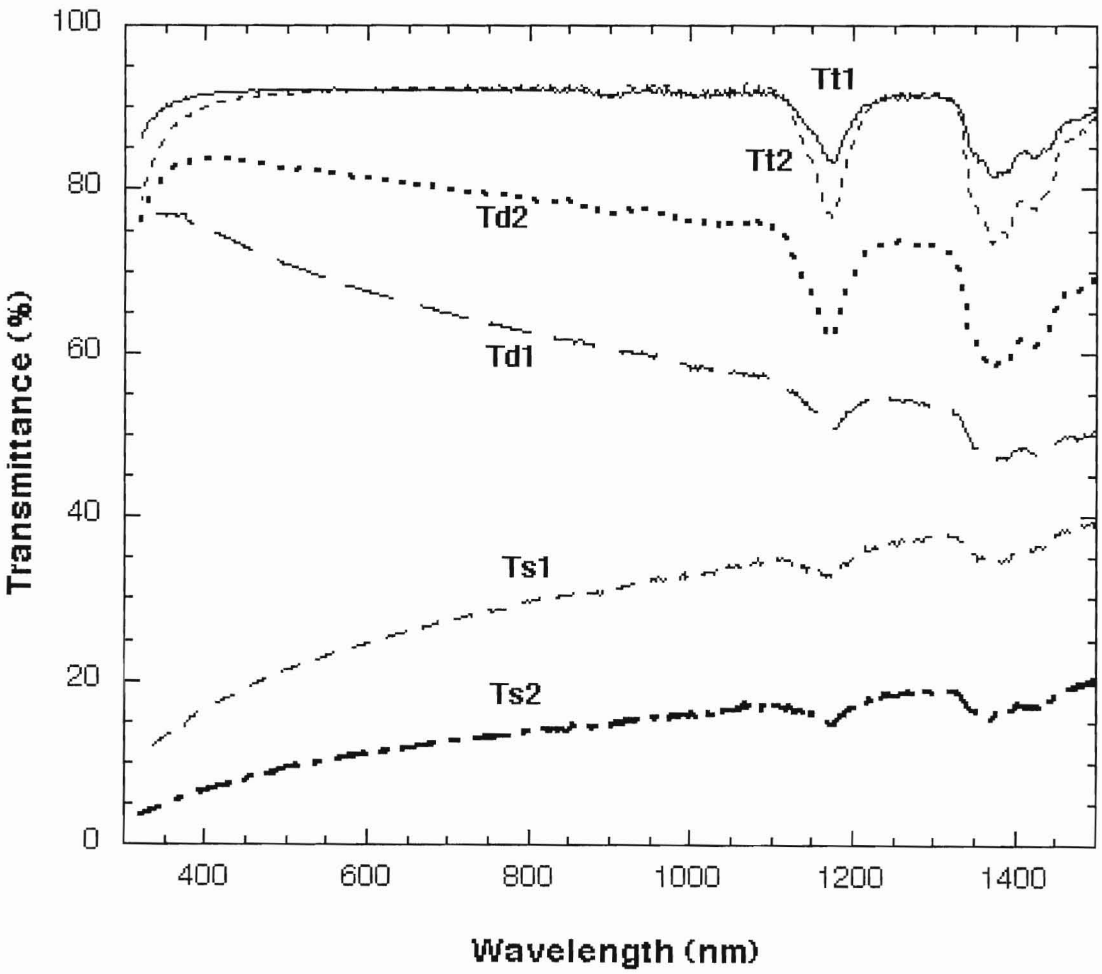


Figure 3(a). Hemispherical spectral response of 1 and 2 mm thick clear PMMA doped with clear cross linked PMMA spheres components[s = specular , d = diffuse and t = total].

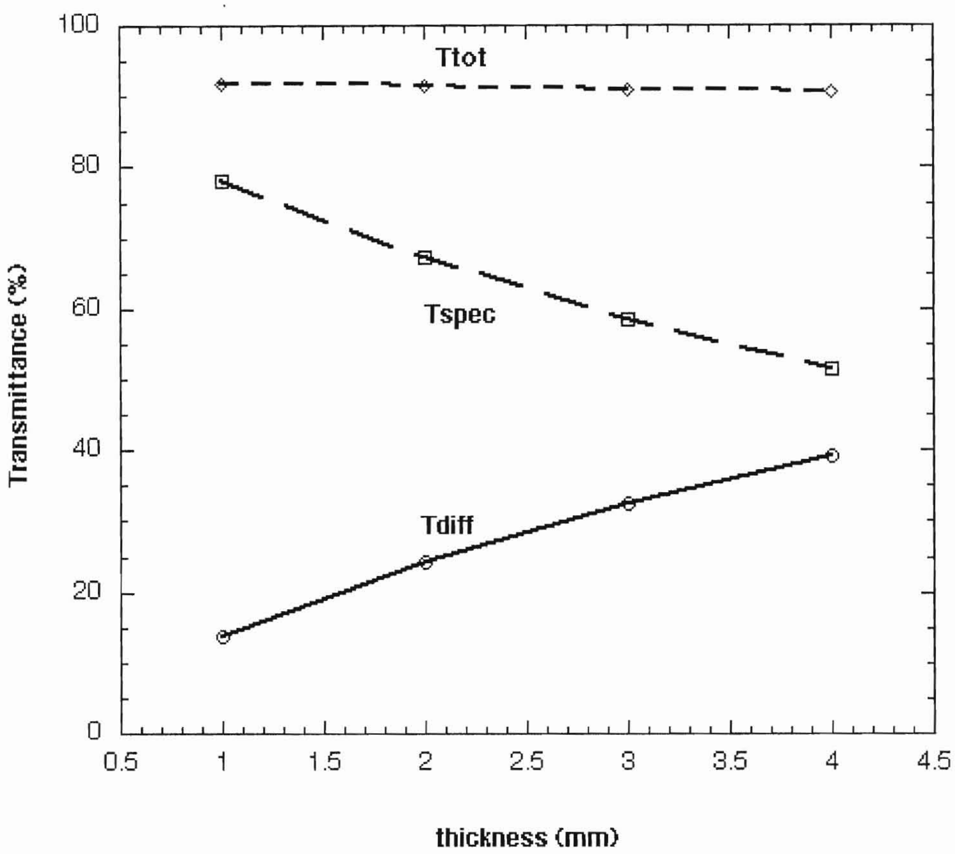


Figure 3(b). Measured hemispherical transmittance at 520 nm of clear PMMA doped with clear cross linked PMMA sphere as a function of thickness

3.3 Nanostuctures using conducting materials

Good conductors, including metals plus oxide, nitride and boride conductors such as indium tin oxide, zinc oxide, titanium nitride and lanthanum hexaboride [11] have special properties at the nanoscale due to the fact that the real part of their dielectric constants are negative below a specific frequency called the plasma frequency ω_P. The plasma frequency is determined by the charge carrier density and a negative dielectric constant means light cannot travel far in such materials – *if continuous* – but their impact on light transport can change dramatically if the conductor is nanostructured. For metals at lower frequencies than ω_P (longer wavelengths), their reflectance starts to rise sharply so aluminium and silver with high densities of carriers reflect all visible light strongly with ω_P clearly into or at the edge of the UV, while for gold and TiN ω_P is in the middle of the visible, and for ITO and ATO with much lower carrier densities it is in the near IR. At still lower frequencies labelled $\omega_{SP,n}$ one or more resonant absorption modes in nanosystems of these materials can then arise. These are due to surface electromagnetic excitations called surface plasmons or surface plasmon polaritons (label SP or SPP) which lead to enhanced absorptive properties in some structures, and enhanced light transport in others, for limited spectral ranges. The values of $\omega_{SP,n}$ depend on geometric details in the nanostructure so many different values can arise for the same metal, as in thin films with different nanohole arrays, isolated particles of different shape such as spheres and ellipsoids, metal coated nanoparticles and clusters of conducting particles. ω_{SP} is also lower in a dielectric matrix than in air, and lower in high index matrices such as TiO_2 than in glass or PMMA.

For small enough particles with no interparticle interactions only the n = 1 dipole mode arises except where surface plasmon degeneracy in say an all metal sphere is split if the metal is instead a shell on a dielectric sphere. Interactions usually give rise to multiple modes, except in the approximation where only dipoles exist on each particle as in the simple classical effective medium models known as Maxwell-Garnett and Bruggemann which are standard in many of the computer programs which are used to simulate optical data. These simplest models also require that particles be much smaller than the wavelength (< ~0.1λ is a good rough guide) otherwise scattering occurs, but as noted below host medium is also important. When small enough that scattering is negligible, the nanoparticles do not disperse transmitted light and cause haze. Thus they can still be used to give spectral control in a visibly clear window by attenuating at the resonances located at ω_{SP} if they lie in the near IR. An example of such use is LaB_6 nanoparticles in the laminate layer of a solar control glass window.

This case, and other solar systems such as nanometal cermets, can be accurately modelled as an "effective medium". The effective medium concept is very useful for modelling work. It replaces an inhomogeneoues medium with an "effective" homogeneous medium and requires nano-scale features for optical frequencies.

Until recent new nano-work involving very local induced currents [12], it was thought to be a valid approach whenever scattering was weak or negligible. This issue is complex and covered further at a number of points in a new book on complex media coming out shortly (see the chapter by Smith, and others [13]). The validity of the quasistatic effective medium approach for isolated particles depends on the host matrix refractive index is often neglected. It is unfortunate that much of the chemical literature on these systems is based on optical data for particles in water whose refractive index is around 1.33. A misleading impression of their usefulness can than be acquired. In polymer with index near 1.5 the situation is very different. In water scattering will be much stronger than in the polymer so in water particles may cause visible haze and NIR scattering, while in PMMA or polycarbonate there may be no change in visible haze and negligible NIR scattering. Thus the quasistatic approximation and effective medium approach may be fine in polymer or higher index materials but not in water.

One feature of the surface plasmon resonance in nanoparticles, which has important economic benefits is that it is very strong and creates a cross section much larger in area than the particle's projection. It in effect draws in or attracts electromagnetic radiation like a sponge. Thus very low concentrations can be sufficient to absorb all incident radiation at resonance. In the ITO and ATO example we find in 0.7 mm layer of PVB or PET less than 0.5 % by weight is needed while for particles with higher $\omega_{SP,}$ such as LaB_6 under 0.05% has sufficed. If metal coated shells can be improved it is probable that even smaller concentrations will suffice. Thus even if expensive particles are used effect on total cost can be very small. Clear nanoparticle-in-laminate glazings have great potential for car windscreens as well as for buildings. They are already available.

There are many other interesting and exciting issues in the physics of these metal containing structures currently under study. Some of the metal nano-systems are throwing up scientific surprises [5], and controversies [13,14] such as whether left-handed or negative refractive index optical materials can exist. These materials, which have to be nano-composites for use at optical frequencies, effectively bend light the wrong way when it enters (though it is arguably not "light" inside these materials). Controversy has arisen because different physicists in both supporting and opposing camps have treated these nanostructured materials in ways, which are physically inappropriate. They have misused the effective medium concept, which as noted can describe some (but not all) optical measurements by replacing an inhomogeneous material with an effective homogeneous material. Transmitted and reflected intensities, amplitudes and phases measured at distances removed from the material by more than many wavelengths (the far field) may be representable by such an effective medium. *This is only a representation* and does not describe how electromagnetic energy actually divides up as it enters a medium nor its distribution in the immediate near field vicinity. Thus you cannot dismiss effective left handedness on the basis of what cannot happen in a continuous left handed material since that can never exist and nor is it what is under discussion. On the other hand uses of such a material based on interactions of evanescent waves, with sub-wavelength spatial periods, with the effective medium to form a super lens are just as inappropriate, since *the effective medium representation cannot be used in the near field.* A super lens is an optical system, which would allow direct imaging of sub-wavelength features with light by collecting and focussing evanescent waves. New optics may arise if we can combine negative effective permeability and negative effective dielectric constant but just how it will be of use remains to be seen. Revolutionary technologies may well follow as the scientific "dust" settles or it may be a technological "red herring".

4. CONCLUSION

Systems using nanoparticle, special microparticles and nanocomposite films are already finding many applications in the field of energy, and environmental management and aesthetics. As we increase our engineering skills in forming various nanostructures and improve the range of physical models available for modelling their optical and radiative responses, many further applications will emerge. Understanding and using physics is essential to stay ahead in this field and to most efficiently exploit the opportunities it presents. In solar power nanoparticles have already contributed to the titania dye solar cell made in Australia, while there is much emerging activity in hybrid organic/inorganic PV cells utilizing combinations of organic conductors and nanoparticles or nanotubes which also has overlaps with the rapid progress on organic light emitting diodes. Lighting sources and lighting effects will undergo major changes as nanotechnologies develop.

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