

Nanomaterial Research with UV-Vis-NIR Spectroscopy



Essential
Knowledge
Briefings

1st Edition, 2021



Agilent

© 2021 John Wiley & Sons Ltd, The Atrium, Southern Gate,
Chichester, West Sussex PO19 8SQ, UK
Microscopy EKB Series Editor: Dr Julian Heath
Spectroscopy and Separations EKB Series Editor:
Dr Christina Poggel

CONTENTS

- 4** INTRODUCTION TO NANOMATERIALS
- 7** CHARACTERIZATION WITH UV-VIS NIR - THEORY AND BACKGROUND
- 17** CHARACTERIZATION WITH UV-VIS NIR – IN PRACTICE
- 21** CASE STUDIES
- 27** COMMON CHALLENGES IN NANOMATERIAL CHARACTERIZATION
- 33** WHAT'S NEXT IN NANOMATERIAL RESEARCH
- 36** FURTHER INFORMATION

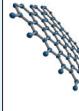
About Essential Knowledge Briefings

Essential Knowledge Briefings, published by John Wiley & Sons, comprise a series of short guides to the latest techniques, applications and equipment used in analytical science. Revised and updated annually, EKBs are an essential resource for scientists working in both academia and industry looking to update their understanding of key developments within each specialty. Free to download in a range of electronic formats, the EKB range is available at www.essentialknowledgebriefings.com

INTRODUCTION TO NANOMATERIALS

By their very nature, nanomaterials are difficult to see. With at least one of their dimensions less than 100 nanometers (one billionth of a meter) in size, they encompass everything from spherical particles to long nanotubes to flat sheets with a thickness of a single atom or molecule (see *Table 1*).

Their tiny size makes them interesting, by giving them a whole host of useful properties, from great strength, to high electrical conductivity to bright fluorescence to efficient catalysis. These properties are a consequence of nanomaterials having a large surface area relative to their size and being small enough to be influenced by quantum effects, leading to them being utilized in areas as diverse as computing, solar cells, batteries and chemical manufacturing.

Type of nanomaterial		Examples ¹	Uses	Relevant optical properties
Metal nanoparticles		Gold nanorods, silver nanowires, titanium dioxide nanoparticles	Photocatalysts, medical imaging and treatment, sun protection, sensing, displays	Absorption, scattering
Semiconducting nanomaterials		Quantum dots, tungsten disulfide, copper(I) oxide	Photocatalysts, solar cells, computing, photodetectors, displays	Absorption, fluorescence, reflection
Carbon-based nanomaterials		Carbon nanotubes, graphene	Composites, batteries, computing, sensing	Absorption, scattering
2D materials		Graphene, molybdenum diselenide, MXene	Photocatalysts, computing, composites, sensing, electromagnetic shielding	Absorption, scattering

1. Some nanomaterials straddle different types e.g. graphene is both a carbon-based material and a 2D material.

Table 1: Different types of nanomaterials

Nanomaterial analysis techniques

Nanomaterials may be difficult to see, but their interaction with light can reveal a great deal of information about them, which is why UV-Vis-NIR spectroscopy has become an important technique for characterizing them.

In UV-Vis-NIR spectroscopy, a beam of light is shone at a sample and a detector placed behind the sample measures the intensity of the light transmitted through it. The difference between the intensity of the original light beam and that measured by the detector indicates how much of the light is absorbed by the sample. By doing this for individual wavelengths of light that can stretch from the ultraviolet (UV) across the visible to the near-infrared (NIR), an absorption spectrum for the sample can be built up, showing those wavelengths of light that are most effectively absorbed.

Not only does this reveal the optical properties of the sample, which is important for nanomaterials designed to interact with light, such as photocatalysts, photodetectors and solar cell materials. It can also reveal various other properties of the nanomaterials, such as their size, shape, composition and electrical properties, all of which can influence their absorption of light.

This is more difficult than it sounds, because as well as absorbing incoming light, some nanomaterials can reflect and scatter it, which also determines how much light reaches the detector. The effect of this reflection and scattering thus needs to be taken into account when calculating the absorption spectrum, which can be done with various accessories available for modern UV-Vis-NIR spectrophotometers. As an add-

ed bonus, this information on reflection and scattering can also be useful in its own right.

With the ability to produce all this information, UV-Vis-NIR spectroscopy has joined transmission electron microscopy and inductively coupled plasma-mass spectrometry in becoming a standard and widely used technique for characterizing nanomaterials, as this technology briefing reveals.

CHARACTERIZATION WITH UV-VIS NIR - THEORY AND BACKGROUND

UV-Vis-NIR spectroscopy

Like most forms of spectroscopy, UV-Vis-NIR spectroscopy monitors the interaction between materials and electromagnetic radiation, but with a focus on the wavelengths either side of visible light. As its name suggests, in practice these wavelengths can stretch from the ultraviolet (200–400nm) through the visible light spectrum (400–800nm) to the NIR (800–2500nm).

All non-transparent materials will absorb, scatter and reflect specific visible wavelengths, as this determines their color, as well as certain UV and NIR wavelengths. As such, UV-Vis-NIR spectroscopy can be used to determine the optical properties of materials, in terms of what specific wavelengths they absorb, scatter and reflect. But it can also be used to probe various other properties that influence a material's optical properties, such as its structure, composition and electronic properties.

UV-Vis-NIR spectroscopy works by shining specific wavelengths of light at a material and recording the intensity of the light that reaches a detector behind it, known as transmittance. Any loss of intensity recorded by the detector, compared with the original beam, means that some of the light at that specific wavelength has been absorbed, reflected or scattered by the sample, collectively known as extinction.

For many non-reflective samples, any light that doesn't reach the detector can be assumed to be absorbed by the sample, and thus the transmittance is directly related to the ab-

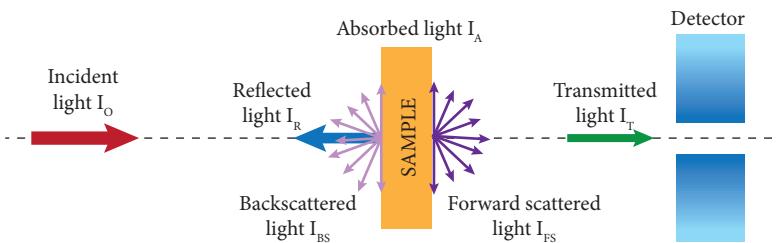


Figure 1: Absorption, reflection, scattering and transmission in UV-Vis-NIR spectroscopy

sorbance. Doing this for a range of different wavelengths allows an absorption spectrum to be built up, which reveals those wavelengths of light that are most effectively absorbed by the sample.

For samples that can reflect or scatter light, however, such as smooth films or milky solutions, the same assumption can't be made, as some of the light will have been reflected or scattered rather than absorbed (see *Figure 1*). This might not matter, as the extinction will often vary with wavelength in a similar way to absorption, producing a similar spectrum. In many cases, however, scientists will want to discover exactly how much light is absorbed, reflected or scattered by a sample, which means finding a way to determine the contribution of each to the measured extinction.

Nanomaterial characterization

UV-Vis-NIR spectroscopy is commonly used to probe a wide variety of materials, both solid and liquid, from thin films to oil shale to DNA. More recently, it has proved to be a useful technique for studying various nanomaterials, including metal nanoparticles, semiconducting nanomaterials such as quantum

dots, carbon nanotubes, and two-dimensional (2D) materials such as graphene. These nanomaterials are usually dispersed in some form of solvent, often just water, as they tend to be easier to analyze as dispersions than as concentrated powders.

As with other materials, UV-Vis-NIR spectroscopy is not just used to probe the optical properties of nanomaterials, but also to characterize attributes that influence their optical properties, which for nanomaterials include size, shape and stability. A related form of optical spectroscopy known as fluorescence spectroscopy can reveal further information about nanomaterials. Rather than record the wavelengths absorbed by a nanomaterial, this uses a similar set-up to analyze the fluorescence emitted by certain nanomaterials as a result of their absorption of the original light.

A nanomaterial's electrons are responsible for its absorption of light at UV and visible wavelengths, because the energy in the light excites the electrons up to higher energy levels. In some nanomaterials, this can be the case for NIR wavelengths as well, but these wavelengths can also be absorbed by inducing vibrations in the bonds between the component atoms, causing the nanomaterial to heat up. Because bonds between different atoms absorb at different NIR wavelengths, this can reveal information about the composition of a nanomaterial.

Metal nanoparticles

In metal nanoparticles, UV and visible light interacts with a sea of electrons at their surface, which are no longer bound to an atom and so are free to roam over the nanoparticles. These surface electrons all tend to resonate at a set frequen-

cy, producing what is known as a localized surface plasmon resonance (LSPR), which absorbs light with similar frequencies and scatters light at different frequencies. As a consequence, metal nanoparticles are being developed for applications ranging from photocatalysis, where the absorption of light powers their catalytic abilities, to transparent electrodes that can absorb and reflect light at specific wavelengths, for use in smart windows and touchscreen displays.

The frequency of a nanoparticle's LSPR is determined by various factors, including what the nanoparticle is made of, and its size and shape. These factors can be revealed by measuring the wavelengths of light absorbed by the nanoparticles in a sample (because the frequency and wavelength of light are inversely related), but only if the optical properties for that nanoparticle have already been determined. Modifying these factors also offers a useful way to produce nanomaterials with desired optical properties.

The absorption spectrum for a metal nanoparticle resembles a bell-shaped curve, rising to a peak of maximum absorption (see *Figure 2*). If this maximum absorption is known for a specific metal nanoparticle of a certain size, then UV-Vis-NIR spectroscopy can determine whether metal nanoparticles of the same type in a different sample are larger or smaller from the position of the peak. This is because smaller metal nanoparticles absorb light at shorter wavelengths.

UV-Vis-NIR spectroscopy can determine various other properties of a solution of metal nanoparticles as well. One is the size distribution of the nanoparticles, because a narrow

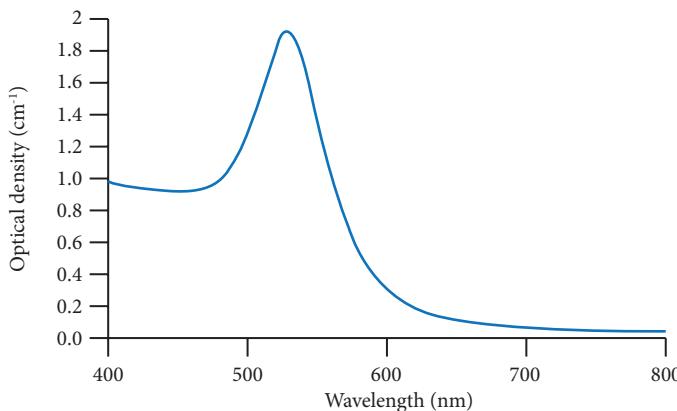


Figure 2: Absorption spectrum for 50 nm gold nanospheres

absorption peak means that all the nanoparticles in the solution are of a similar size, as they absorb a small set of wavelengths. Whereas a broad peak means a greater size range, because the nanoparticles absorb a larger set of wavelengths.

It can determine the concentration of nanoparticles in a solvent, because a higher concentration means more nanoparticles and thus more absorption of light, producing a larger peak. It can also determine nanoparticle aggregation, because this reduces and broadens the peak, due to the fall in the number of distinct nanoparticles (see *Figure 3*). Finally, it can determine whether any molecules bind to the surface of the nanoparticles, because this changes the LSPR and thus the wavelengths absorbed, which allows metal nanoparticles to act as sensors for molecules that bind to them.

Researchers have synthesized metal nanoparticles from many different metallic materials, ranging from nanoparticles of pure gold and silver, which shine different colors depend-

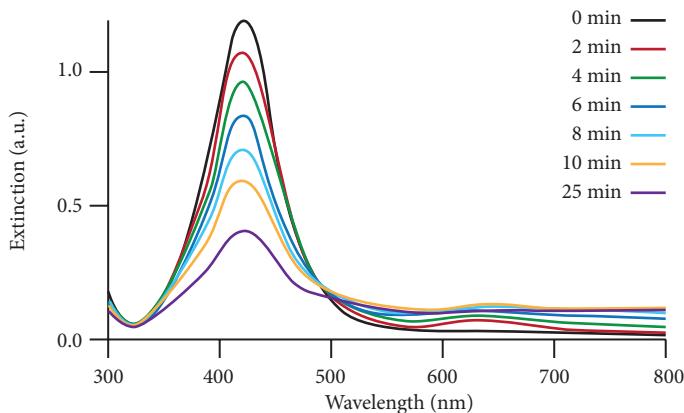


Figure 3: Absorption spectrum for silver nanoparticles as they transition from a well-dispersed state to an aggregated state following the addition of a concentrated salt solution

ing on their size, to complex iron- and titanium-based nanoparticles, which are being developed as photocatalysts. But they all possess metallic properties and thus absorb light via their LSPRs.

Semiconducting nanomaterials

Other metal-containing nanomaterials, however, behave as semiconductors rather than metals. These include the semiconductor nanocrystals known as quantum dots, made from materials such as cadmium selenide and zinc sulfide, and certain 2D materials, like tungsten disulfide, which consist of a single layer of molecules. Although they also absorb light via their electrons being excited up to higher energy levels, the process works in a different way, because it doesn't involve LSPRs.

Rather, the energy levels that the electrons in semiconducting materials can adopt have a large gap in them, be-

tween the levels making up the lower valence band and the levels making up the higher conduction band. This is known as the band gap. Because shorter wavelengths of light possess more energy, wavelengths below a certain point can give the electrons in semiconducting materials sufficient energy to cross this gap, exciting them from the valence band to the conduction band.

By monitoring the absorption of light at different wavelengths, UV-Vis-NIR spectroscopy can determine the point at which the wavelengths have sufficient energy to excite the electrons from the valence band to the conduction band. This is reflected as a clear peak in the absorption spectrum, known as the exciton peak (see *Figure 4*). Because more energy is required to excite electrons over larger band gaps, the wavelength of the exciton peak can be used to determine the size of the band gap. This knowledge can be useful when developing semiconductor nanoparticles as replacements for the silicon in conventional solar cells, for example.

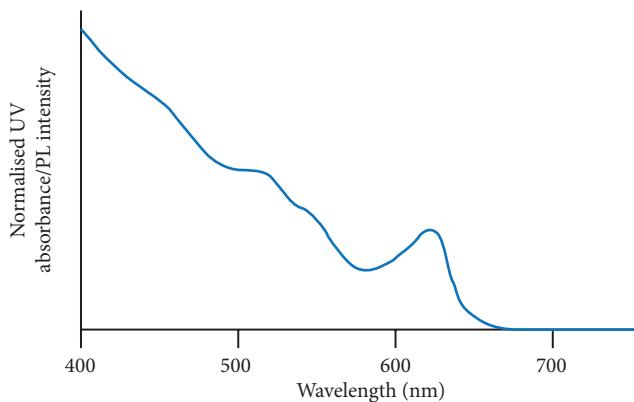


Figure 4: Absorption spectrum for cadmium selenide quantum dots

For quantum dots, the size of this band gap depends on the size of the quantum dots, which usually vary between 2nm and 10nm, with smaller dots having a larger band gap. This means smaller dots absorb light of shorter wavelengths, allowing UV-Vis-NIR spectroscopy to be used to determine their size. As with metal nanoparticles, UV-Vis-NIR spectroscopy can also determine the size distribution of a sample of quantum dots, as well as the concentration, aggregation and the presence of any binding molecules.

In quantum dots, the excitation to the conduction band is unstable and the electrons quickly fall back down to the valence band, releasing the excess energy as a photon. This means that quantum dots are fluorescent, with the wavelengths they emit depending on the size of their band gap and thus on their physical size, although their fluorescence is always at longer wavelengths (and thus a lower energy) than the excitation light. This is because the electrons first drop down through the various energy levels that make up the conduction band by losing energy as vibrations, before crossing the band gap by releasing a photon. Thus, they have already lost some of the excitation energy before emitting the fluorescence.

Because different size quantum dots fluoresce different colors, they are being developed for various imaging and display applications. They can also be analyzed by fluorescence spectroscopy, as the wavelengths of light they emit provide additional information about their optical properties and can be used to determine their size and band gap.

Carbon-based nanomaterials

Carbon-based nanomaterials such as carbon nanotubes and graphene tend to be less straightforward to analyse with UV-Vis-NIR spectroscopy, because they have a greater tendency to scatter and reflect light rather than absorb it. But by utilizing the accessories that are available with modern UV-Vis-NIR spectrophotometers for distinguishing between absorbed, scattered and reflected light (see *Problems and solutions*), their optical properties can still be studied.

Other characterization techniques

Although UV-Vis-NIR spectroscopy can be used to characterize various properties of nanomaterials, researchers often just use it for probing their optical properties, relying on other techniques to determine properties such as size, especially for novel nanomaterials. One reason for this is that UV-Vis-NIR spectroscopy can only determine properties such as size and aggregation by comparing the absorption spectra with the spectra of an identical nanoparticle of known size.

Techniques such as transmission electron microscopy (TEM) can determine the size of a nanoparticle without knowing anything about it. However, TEM is more complex to conduct than UV-Vis-NIR spectroscopy, which requires minimal sample preparation and is entirely non-destructive.

In addition to TEM, UV-Vis-NIR spectroscopy is often combined with inductively coupled plasma mass spectrometry (ICP-MS) for determining the elemental composition of nanoparticles. ICP-MS works by using an electrically charged plasma to break the nanoparticles in a sample down into their

component elements, which are then identified by mass spectrometry, and is sensitive enough to analyze individual nanoparticles (see the related publication *Nanoparticle Analysis Using the Sensitivity of ICP-MS* for more details).

CHARACTERIZATION WITH UV-VIS NIR – IN PRACTICE

UV-Vis-NIR spectrophotometer

A standard UV-Vis-NIR spectrophotometer consists of a light source, a monochromator or diffraction grating for isolating a single wavelength from the wide range produced by the light source, optics for directing the beam of light to a sample held in a sample compartment, and a detector behind the sample (see *Figure 5*).

Several light sources are often used to cover all the required wavelengths. A deuterium lamp can be used to produce UV wavelengths, while a tungsten or halogen lamp can be used for visible wavelengths. Increasingly, these are being

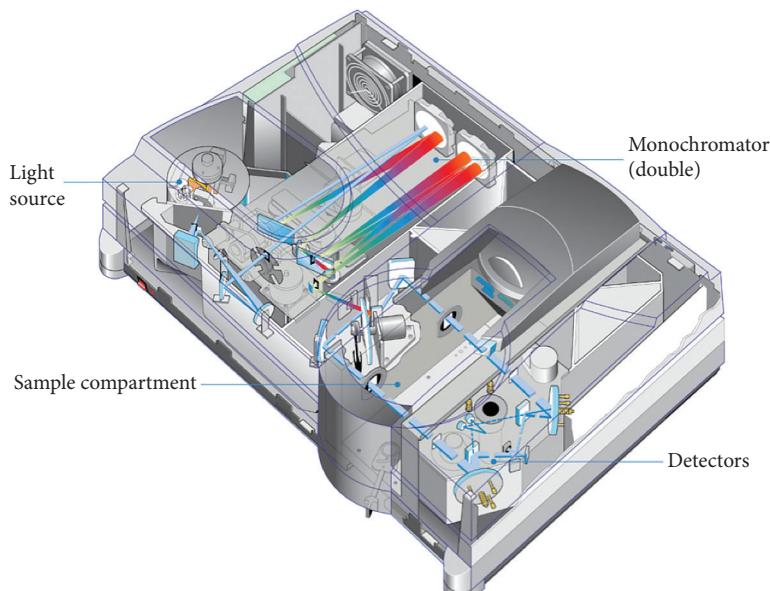


Figure 5: Schematic of a UV-Vis-NIR spectrophotometer

replaced by xenon lamps, which are more long-lasting and able to cover all wavelengths.

Different instruments are designed to study different wavelength ranges. Some just study UV and visible wavelengths, from around 200nm to 900nm, but others extend into the NIR. For example, Agilent produces a range of spectrophotometers under its Cary brand, all start at UV wavelengths, but the wavelengths they extend to vary from 900nm, just past visible wavelengths, to 3300nm, deep into NIR.

The detector works by using a semiconducting material such as indium gallium arsenide (InGaAs) to convert the light that hits it into an electric current, with the size of the current proportional to the intensity of the light.

Optical design

The beam from the light source is usually split and sent along two different paths to produce a reference signal (see *Figure 5*). This can be done using a rotating disc with transparent and mirrored sections that alternate between letting the light beam pass straight through to the sample and reflecting it so that it travels along a different path to the detector. This double-beam approach accounts for any variation in the source intensity or source over time and any changes in temperature or other environmental conditions. It achieves this by subtracting any signal produced by the reference beam from the beam that interacts with the sample. Spectrophotometers that employ this approach are known as double beam spectrophotometers.

Nanomaterials are normally analyzed when dispersed in a solvent held in a glass or quartz cuvette with a volume of

between 100 μ L and 3.5mL. But this introduces the problem that both the solvent and cuvette will absorb certain wavelengths of light, and this obviously needs to be accounted for when producing the absorption spectrum for a nanomaterial. In modern spectrophotometers, this is done by first taking a reference measurement for the solvent and cuvette, without the sample, and then subtracting this reference measurement from any subsequent sample measurements.

Sample handling

The choice of cuvette and solvent is important because both will have absorption cut-off wavelengths, below which the solvent or cuvette will absorb all the light, making them useless for assessing absorption by the sample. For water, this wavelength is 180nm, which means all but the shortest UV wavelengths will pass through, but for acetone it is a more problematic 329nm, which is bordering on visible wavelengths. Similarly, the absorption cut-off wavelength for glass is around 300nm, but for quartz is 160nm, making quartz cuvettes more suitable when studying nanomaterials that absorb at UV wavelengths.

Of course, many materials don't just absorb light at UV, visible and NIR wavelengths, but also reflect and scatter it, which will obviously affect the transmittance and thus the calculated absorbance. This can be important when studying nanomaterials, as nanomaterials suspended in water are often very effective at scattering light, although smaller nanoparticles tend to scatter less.

Fortunately, there are several accessories available for

UV-Vis-NIR spectrophotometers, including specular reflection and diffuse reflection accessories, that can determine the degree of reflection and scattering. Not only do these accessories allow a more accurate measure of absorption by a sample, but the degree of reflection and scattering can also be useful information in its own right, such as when analyzing thin films or developing materials for smart windows. These accessories will be discussed in more detail in the *Common challenges in nanomaterial characterization* chapter.

Case study 1: Splitting water with graphitic carbon nitride (Dong-Liang Peng, Xiamen University, China)

Electric cars may finally be starting to challenge the dominance of petrol-powered cars, but that doesn't mean researchers have stopped trying to improve their performance. One way they're doing this is by developing better batteries that can store more charge, allowing electric cars to travel for longer between charges. Another is by developing fuel cells that generate electricity from a clean fuel such as hydrogen, which may one day replace batteries.

Novel nanomaterials are central to both efforts, and researchers such as Dong-Liang Peng, professor in the College of Materials at Xiamen University, are busy developing those nanomaterials and then characterizing them with techniques such as UV-Vis-NIR spectroscopy.

The cleanest way to produce the hydrogen for fuel cells is by splitting water. This can be done via electrolysis, which involves passing an electric current through the water, but an even cleaner way is to use a photocatalyst that can split water powered purely by sunlight. One nanomaterial that has shown a lot of potential as a photocatalyst for hydrogen production is graphitic carbon nitride ($g\text{-C}_3\text{N}_4$), which is a semiconductor.

When sunlight hits $g\text{-C}_3\text{N}_4$ it excites the material's electrons to the conduction band, where they can provide the energy for splitting water. The problem is that the excited electrons tend to fall back down to the valence band quite quickly, often before they get a chance to split any water. So Peng and his team have been

experimenting with combining g-C₃N₄ with other nanomaterials to prevent this from happening.

In recent work, they tried combining g-C₃N₄ with molybdenum diselenide (MoSe₂), which is a type of two-dimensional material known as a transition metal dichalcogenide. They characterized the resulting nanocomposite using a variety of techniques, including TEM, energy dispersive X-ray spectroscopy and UV-Vis spectroscopy.

With UV-Vis spectroscopy, they were able to determine that the nanocomposite had the same band gap as g-C₃N₄ and thus could also split water, but that it was much better at absorbing wavelengths above 420nm, meaning in the visible spectrum. As a consequence, it proved to be a much more effective photocatalyst, able to produce hydrogen from water at a faster rate than g-C₃N₄ on its own.

Zeng D, Wu P, Ong W-J, et al. Construction of network-like and flower-like 2H-MoSe₂ nanostructures coupled with porous g-C₃N₄ for noble-metal-free photocatalytic H₂ evolution under visible light. *Appl Catal, B* 2018;233:26–34. (<https://doi.org/10.1016/j.apcatb.2018.03.102>)

Case study 2: Optical properties of copper oxide nanoparticles (Kathryn Knowles, University of Rochester, US)

A whole range of factors can influence a nanomaterial's optical properties, including its composition, size, shape and electronic properties. Using UV-Vis-NIR spectroscopy, Kathryn Knowles and her colleagues at the University of Rochester have recently shown that surface oxidation states can also be added to this list, at least for metal nanoparticles.

Knowles and her team were investigating nanoparticles of copper(I) oxide (Cu_2O), which have proven to be effective photocatalysts for various organic reactions. These include the reduction of carbon dioxide to carbon monoxide, which is the first step in converting carbon dioxide into useful products such as fuels. Nanoparticles of metallic copper can also make effective photocatalysts, but they work in a different way, because their absorption of light is mediated by an LSPR. In contrast, Cu_2O nanoparticles are semiconductors and don't possess an LSPR.

But copper nanoparticles and Cu_2O nanoparticles can transform into each other, via oxidation and reduction. This process can also produce hybrid versions, such as nanoparticles with a pure copper core covered in a layer of Cu_2O . Knowles and her team were interested in discovering what happens to the LSPR during this oxidation and reduction.

So they synthesized several forms of copper nanoparticle and probed their optical properties with UV-Vis-NIR spectroscopy. This involved synthesizing Cu_2O nanoparticles and then removing all the oxidized copper species from their surface by expos-

ing them to nitrogen, and synthesizing copper nanoparticles and then exposing them to air to form a surface layer of Cu_2O containing oxidized copper species.

Removing all the oxidized copper species from the surface of the Cu_2O nanoparticles led to the formation of an LSPR, because the surface was now covered in unoxidized copper. This LSPR absorbed light at similar wavelengths to the LSPR on metallic copper nanoparticles. Copper nanoparticles with a covering of Cu_2O and oxidized copper species also possessed an LSPR, but this LSPR absorbed longer, lower-energy wavelengths than the LSPR on metallic copper nanoparticles.

This shows that the surface oxidation state of copper nanoparticles can have a strong influence on their optical properties, potentially offering a novel way to tune their optical and catalytic properties.

Tariq M, Koch MD, Andrews JW and Knowles KE. Correlation between surface chemistry and optical properties in colloidal Cu_2O nanoparticles. *J Phys Chem C* 2020;124:4810–4819. (<https://doi.org/10.1021/acs.jpcc.9b10753>)

Case study 3: Semiconducting nanoparticles for transparent electrodes (Enrico Della Gaspera, RMIT University, Australia)

In general, metal-containing nanomaterials can either behave like metals, in which case they possess an LSPR, or behave like semiconductors, in which case they don't. But by doping metal-containing nanoparticles with elements such as gallium and lanthanum, scientists have managed to develop metal-containing nanoparticles that behave like semiconductors and also possess an LSPR, although one that absorbs light at NIR wavelengths rather than visible wavelengths.

Enrico Della Gaspera and his colleagues at RMIT University are developing such nanoparticles as the next generation of transparent electrodes. At the moment, transparent electrodes are mainly used in touchscreen displays, but they could also find use in smart windows and solar cells. Indium tin oxide is the most widely used material for the transparent electrodes in touchscreens, but the search is on for alternative materials that are cheaper and utilize more abundant elements than indium.

Such materials obviously need to be electrically conductive and transparent to visible light, but for applications such as smart windows they also ideally need to reflect or absorb light at NIR wavelengths. Hence the interest in developing semiconducting nanoparticles with an LSPR that interacts with NIR wavelengths.

Della Gaspera and his colleagues have developed several such nanoparticles, including zinc oxide (ZnO) nanocrystals doped with gallium, barium stannate ($BaSnO_3$) nanocrystals doped with lanthanum and tin oxide (SnO_2) nanocrystals doped with

fluorine. The doping is what gives these nanocrystals their LSPRs, because the dopants leave behind excess electrons after they bind with the elements making up the nanocrystals. These excess electrons then form the LSPR.

After synthesizing the nanocrystals, Della Gaspera and his colleagues assess their optical properties with UV-Vis-NIR spectroscopy. For example, with the fluorine-doped SnO_2 nanocrystals, they used UV-Vis-NIR spectroscopy to determine that the nanocrystals had an absorption peak at a wavelength of around 275nm, due to their band gap, but also possessed an LSPR that absorbed at NIR wavelengths above around 1000nm. They further confirmed that this LSPR wasn't present in undoped SnO_2 nanocrystals and that its strength increased with greater fluorine doping.

Kendall O, Wainer P, Barrow S, *et al.* Fluorine-doped tin oxide colloidal nanocrystals. *Nanomaterials* 2020;10:863. (<https://doi.org/10.3390/nano10050863>)

COMMON CHALLENGES IN NANOMATERIAL CHARACTERIZATION

Reflection and scattering

Operating as standard, UV-Vis-NIR spectroscopy determines the extinction at different wavelengths, meaning the combination of absorption, reflection and scattering that prevents light from passing through a nanomaterial sample to a detector behind it (see *Figure 1*). But scientists often want to distinguish the specific contributions of absorption, reflection and scattering, in order to obtain a full characterization of a nanomaterial's optical properties.

To make matters more complicated, this reflection and scattering can come in several different forms (see *Figure 6*). Materials with flat, shiny surfaces, such as mirrors, display specular reflection, in which the beam of light is reflected at the same angle that it hits

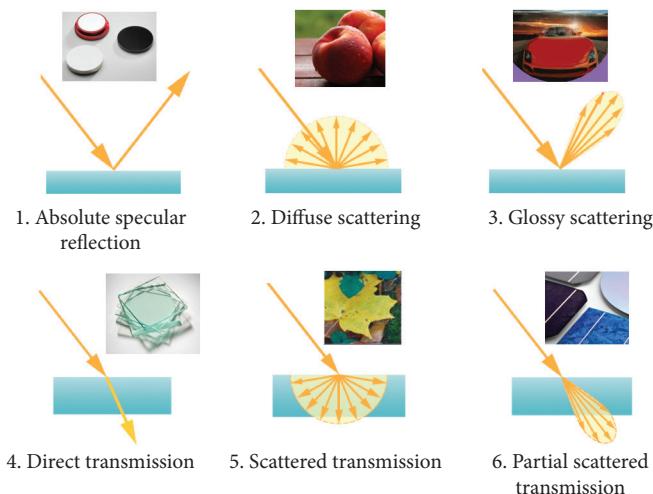


Figure 6: Different forms of reflection, scattering and transmission

the surface. Materials with rougher surfaces, such as paper, display diffuse scattering, in which the light is reflected at many different angles. There is also glossy scattering, as displayed by the surface of a polished car, in which the light is reflected at a narrower range of angles than in diffuse scattering.

This kind of reflection and scattering happens when the light hits the surface of a material and is reflected or scattered back, but scattering can also occur when light exits a material after travelling through, known as forward scattering. If the nanomaterial sample is transparent at a specific wavelength, then the light will pass straight through without any scattering at all, allowing it to reach the detector. Even here, the angle that the light exits the sample will be different from the angle that it enters, because of the refraction caused by the light travelling through the sample at a slightly different speed than through air.

For materials that are translucent rather than transparent at specific wavelengths, such as a leaf, the light is scattered as it travels through the material, emerging at a wide range of different angles. This is known as scattered transmission and will result in some of the light being scattered away from the detector. There is also partial scattered transmission, where the light emerges at a narrow range of angles.

Specular reflection accessories and diffuse reflectance accessories

Various accessories are available for UV-Vis-NIR spectrophotometers to measure reflected and scattered light. To use them, they must be fitted into the sample compartment. Specular reflection accessories are placed in front of the sample

and are designed to vary the angle of the incoming light (see *Figure 7*). They then collect the resulting specular reflection and use a system of mirrors to direct it around the sample to the detector.

Diffuse reflectance accessories possess their own detector, located within an integrating sphere, and can detect both diffuse and specular reflection, and scattered transmission (see *Figure 8*). An integrating sphere is a sphere with a reflective inner coating, such that light entering the sphere is repeatedly reflected until it encounters a detector on the inner surface.

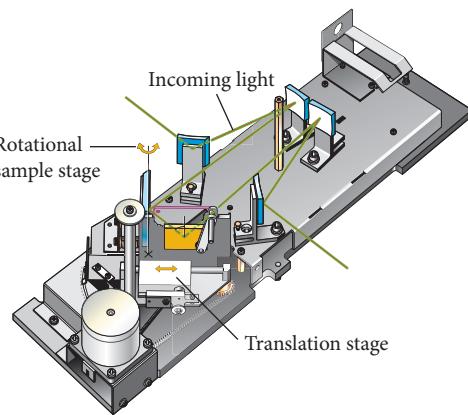
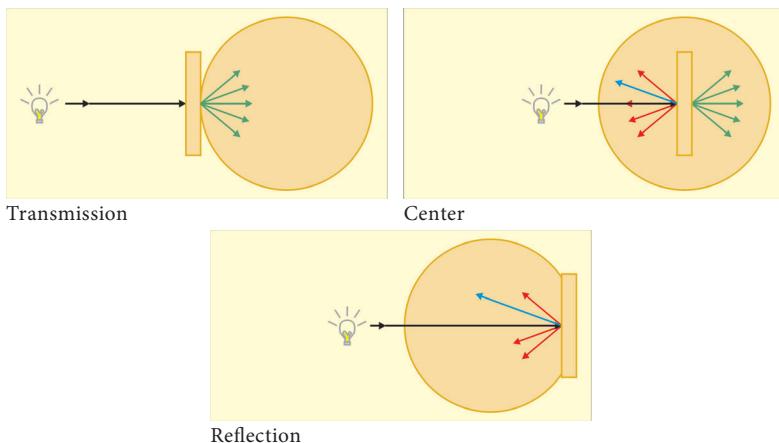


Figure 7: Specular reflection accessory



Figure 8: Integrating sphere from a diffuse reflectance accessory, with detector at bottom

The sample and sphere are placed in various arrangements to detect different forms of reflection and scattering (see *Figure 9*). To detect specular and diffuse reflection, the sample is placed against a hole in the side of the sphere and opposite a second hole through which light is shone so that it



Schematics showing transmitted and reflected light. Diffuse R (red), specular (blue) and diffuse T (green).

Figure 9: Different arrangements of sample and integrating sphere for measuring reflection and scattering

hits the sample. All the light reflected and backscattered by the sample is then directed towards the detector.

To detect the direct and scattered transmission, the sample is placed in front of the sphere, so that it covers the hole. This ensures all the transmitted and forward scattered light passes through the hole and into the sphere, where it is directed towards the detector. Alternatively, the sample can be placed at the center of the sphere, with light shone at it through the hole. In this case, all the light that is reflected, scattered or transmitted by the sample is directed towards the detector.

Universal measurement spectrophotometer

Recent advances in technology have allowed Agilent to develop a new system that can embrace broad measurement types. Known as the universal measurement spectrophotometer (UMS), this

single system can distinguish between reflected, scattered and transmitted light. By mounting the sample in the center of the sample compartment and utilizing a detector that can be moved all around the sample, the UMS can automatically measure light reflected or scattered at any angle (see Figure 9).

By performing multiple measurements, the UMS can replace all other accessories in most cases. Being able to use a single accessory is convenient, but also minimizes error as the sample is in a constant position, so measurements are always through the same point in the sample. For collecting scattered light over a wide arc, however, a diffuse reflectance accessory is still recommended.

With angular control over light collection, the UMS can provide more insight into the optical properties of a sample,

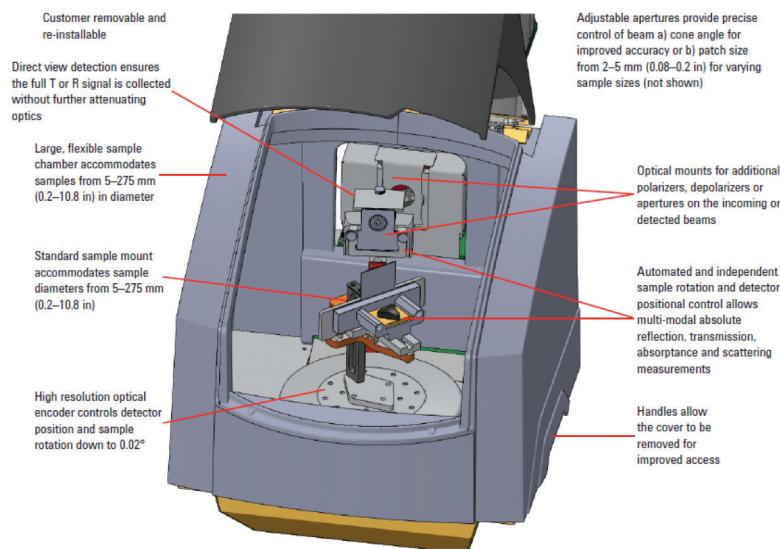


Figure 10: Agilent's Cary 7000 UMS

by recording exactly how much light is reflected at each specific angle, rather than simply measuring all the diffuse scattering or scattered transmission simultaneously. It is well-suited for analyzing solid samples, such as deposits of nanoparticles on glass or thin films, but isn't routinely used to analyze dispersions of nanoparticles in a liquid solvent.

The type of accessory employed and how it is used depends on the optical properties being probed. Determining separate and individual contributions from reflection, scattering, transmission and absorption has traditionally required various specular reflection accessories and a diffuse reflectance accessory with the sample placed both in front of the integrating sphere and behind it. Alternatively, this can all be done with the UMS. When angular information relating to diffuse and transmissive scattering is not required, absorptance can be accurately determined by placing the samples inside the integrating sphere to measure all reflected, scattered and transmitted light in a single collect.

WHAT'S NEXT IN NANOMATERIAL RESEARCH

Nanomaterials research

UV-Vis-NIR spectroscopy has become an important component of the suite of analytical techniques that researchers use for characterizing newly developed nanomaterials. Not only is UV-Vis-NIR spectroscopy the only practical option for probing their optical properties, but the interaction between materials and light can reveal a whole lot of additional information about the materials. Unlike other commonly used characterization techniques, such as TEM or ICP-MS, UV-Vis-NIR spectroscopy is also entirely non-destructive, able to analyze nanomaterials without destroying them or needing them to be modified in any way.

As a consequence, UV-Vis-NIR spectroscopy is playing a central role in the most exciting and active areas of nanomaterials research. These include the creation of stacks, or heterostructures, of different 2D materials, such as graphene and transition metal dichalcogenides like tungsten disulfide. Whereas stacks of graphene layers produce graphite and stacks of tungsten disulfide layers produce bulk tungsten disulfide, stacks containing layers of graphene and tungsten disulfide simply don't exist in nature and could thus possess some novel and interesting properties.

They also include nanocrystals of a mineral known as perovskite, which encompasses a family of materials comprising an organic cation, an inorganic cation and a halide anion such as iodide, bromide or chloride. Certain perovskites have proven to be very effective absorbers and emitters of light,

and so are being explored for use in solar cells and light-emitting diodes. As an added bonus, unlike the silicon that forms the basis of conventional solar cells, perovskite nanocrystals can be processed in solution, which offers the possibility of producing solar cells very cheaply by printing.

As with perovskite nanocrystals, many of these nanomaterials are being developed for applications that take advantage of their optical properties, such as photocatalysts, photo-detectors and optical sensors for use in electronic devices such as mobile phones. But they are also being developed for a range of other applications, including as novel battery materials and as materials for novel forms of computing, such as spintronics. In this case, researchers just want to provide a full characterization of the properties of these novel nanomaterials, including their optical properties.

Advances in UV-Vis-NIR spectroscopy

Recent advances in the technology for UV-Vis-NIR spectroscopy is helping in this regard. The latest xenon light sources, diffraction gratings and detectors are all enhancing the sensitivity and versatility of the technique. The light sources are generating a wider range of wavelengths, the grating technology provides better wavelength selectivity in smaller and smaller packages, and the detectors are able to detect wider dynamic ranges. As an added bonus, some of these advances are also reducing the cost of ownership; the latest xenon light sources, for example, are more robust than previous versions, meaning they last for longer.

In addition to increasing the sensitivity and versatility,

manufacturers are also looking to make their UV-Vis-NIR spectrophotometers easier to use, by automating as much as of the analytical process as possible. The ideal is for the instrument to accurately and reliably determine all the required optical information about a sample at the push of a button.

The UMS moves towards that goal by allowing the transmittance, reflection and scattering of different wavelengths by a sample to be distinguished and determined in a single automated operation, albeit one comprising lots of individual measurements. As does the data analysis software that comes with the latest instruments, which can automatically calculate the absorption spectrum from the data generated on the transmittance, reflection and scattering of different wavelengths, however determined.

As the range of nanomaterials being developed and their potential applications continue to expand, these kinds of technological advances will ensure UV-Vis-NIR spectroscopy continues to be an essential technique for characterizing nanomaterials. Even if they remain exceedingly difficult to see.

FURTHER INFORMATION

C&EN webinar. Advancing Nanomaterial Research with Optical Spectroscopy. Focus - Wet Chemical Synthesis of Semiconductor Nanomaterials. https://connect.acspubs.org/CENWebinar_Agilent_6_16_20?partnerref=Agilent

Mourdikoudis S, Pallares RM and Thanh NTK. Characterization techniques for nanoparticles: comparison and complementarity upon studying nanoparticle properties. *Nanoscale* 2018;10:12871. (<https://doi.org/10.1039/C8NR02278J>)

Nair AK, Mayeen A, Shaji LK, *et al.* Optical Characterization of Nanomaterials. In: *Characterization of Nanomaterials: Advances and Key Technologies*. Edited by Bhagyraj SM, Oluwafemi OS, Kalarikkal N and Thomas S. Duxford: Woodhead Publishing, 2018. (<https://www.sciencedirect.com/book/9780081019733/characterization-of-nanomaterials>)

