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Recent advances on the characterization of nanoparticles using infrared spectroscopy

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ABSTRACT

Infrared (IR) spectroscopy provides highly discriminatory information due to the excitation of inherently specific fundamental vibrational transitions characteristic of molecular species. Nanoparticles of diverse nature have been characterized and determined using different spectroscopic techniques in the infrared range. Nanoparticles with inherent infrared absorptions or functional groups present at their surface may thus be directly characterized via infrared spectroscopy. Furthermore, different ligands attached to nanoparticles may readily be identified according to their vibrational signatures in a rapid, precise, and non-destructive way. Next to the direct characterization of such materials, some nanostructures modify the local optical field, thereby yielding enhanced IR signals facilitating advanced infrared imaging procedures for nanoparticles. In this review, recent examples for the characterization of nanoparticles and their surface functionalization via IR spectroscopy are discussed, and exemplary application examples including toxicological studies and adsorption processes are highlighted.

Contents

Abbreviations: CDs, Carbon dots; DR-FTNIR, Diffuse reflectance Fourier transform near-infrared; DRIFTS, Diffuse reflectance infrared Fourier transform spectroscopy; EC-IRRAS, Electrochemical-infrared reflection-absorption spectroscopy; FTIR, Fourier transform infrared spectroscopy; GQDs, Graphene quantum dots; IR, Infrared; IR-ATR, Attenuated total reflection infrared spectroscopy; IRRAS, Infrared reflection-absorption spectroscopy; MIR, Mid-infrared; MWNTs, Multiwalled carbon nanotubes; NC, Nanocellulose; NIR, Near-infrared; NPs, Nanoparticles; SEIRAS, Surface enhanced infrared absorption spectroscopy; SERS, Surface enhanced Raman spectroscopy; SFG, Sum frequency generation; s-SNOM, Scattering near-field microscopy; SWIR, Short wave infrared; SWNTs, Single-walled carbon nanotubes; TERS, Tip enhanced Raman spectroscopy; VCD, Vibrational circular dichroism; 2D-IR, Two dimensional infrared.

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1. Introduction

The past two decades have seen the full expansion of nanoscience and nanotechnology into almost any area of research. One of the roles of analytical chemistry in this context is the analysis and characterization of nanoparticles (NPs). A variety of analytical techniques are available for characterizing NPs and their surface chemistry including microscopic, separation, and spectroscopic techniques. Regarding the spectroscopic techniques, the infrared (IR) spectral range – in particular in the near-infrared (NIR; 0.9–3 μm) and the mid-infrared (MIR; 3–20 μm) region – provides highly discriminatory information due to the excitation of inherently specific fundamental vibrational and vibro-rotational transitions characteristic of molecular species, NIR spectra bands corresponding mainly to overtones and combination bands of fundamental transitions. Nanoparticles may be directly evaluated owing to inherent infrared absorptions or may be characterized via functional groups attached to their surface (e.g., carboxyl and hydroxyl groups present at the edge of graphene quantum dots, etc.). IR spectroscopy also enables the identification of different ligands attached to the surface of nanoparticles according to their vibrational signatures in a rapid, precise, and non-destructive way. We are aware of the undoubted potential of Raman spectroscopy –including surface enhanced Raman spectroscopy (SERS) and tip-enhanced Raman spectroscopy (TERS)- for the characterization of nanomaterials (i.e. carbon nanotubes or graphene) as well as of microscopic and separation techniques (i.e. capillary electrophoresis) for nanoparticle evaluation. Nevertheless, the aim of this review is not to compare the suitability of IR versus Raman –neither other analytical techniques- for the characterization of nanomaterials, but to focus on the utility of IR spectroscopy for this purpose.

Analytical nanoscience and nanotechnology (AN&N) considers nanomaterials with particular emphasis on the analytical scope either as tools for the development of advanced analytical processes or as sampled objects (i.e., the subject of analysis). However, most recently a third aspect of nanomaterials has emerged proposing the simultaneous use of nanomaterials, i.e., as tools for the characterization/determination of other nanoparticles within the same analytical process [1]. In the present review, we will focus on the applicability of infrared spectroscopy for the characterization and determination of nanomaterials. Nevertheless – and as explained later – the utility of nanoscale materials goes beyond their characterization via IR spectroscopic techniques, since some nanomaterials, i.e., in particular metallic nanoparticles have been widely used to enhance the analytical signal, thereby increasing the achievable sensitivity for the detection of low-concentrated analytes taking advantage of so-called surface enhanced infrared absorption spectroscopies (SEIRAS). Fig. 1 gives a summarizing overview on the various roles of NPs in infrared spectroscopy.

In this review, we specifically focus on the characterization and determination of nanomaterials via different infrared spectroscopic methodologies. Due to the fact that the characterization of nanoparticles and their surface functionalization accounts for most publications on the use of IR spectroscopy for evaluating nanomaterials, only selected examples are discussed exemplarily highlighting recent developments. Moreover, indirect methods facilitating the IR analysis of nanoparticles based on their effects on local optical fields (i.e., surface enhanced infrared absorption (SEIRA)

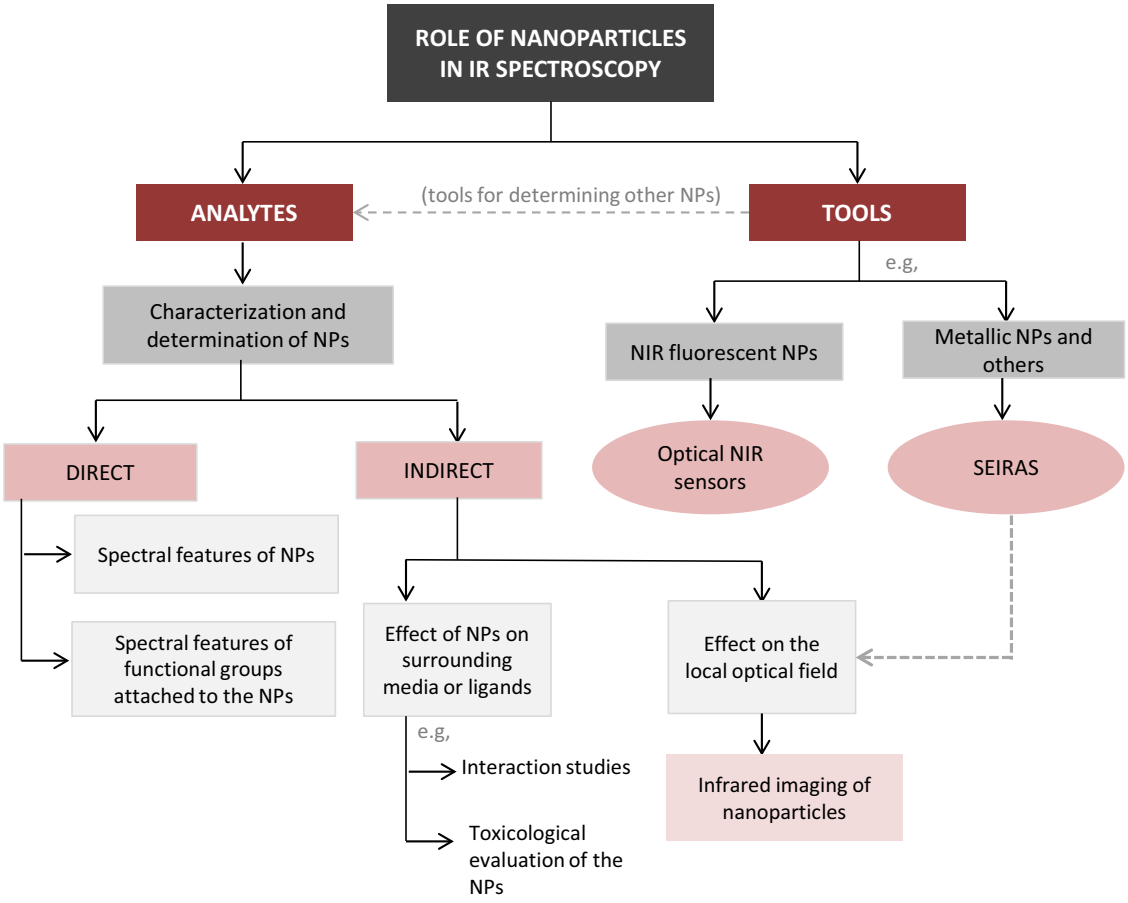

Fig. 1. Scheme of the different roles of nanoparticles in infrared spectroscopy, namely, as analytes, that can be characterized direct or indirectly, and tools for the determination of compounds or other nanomaterials.