Video Article

Diffuse Reflectance Infrared Spectroscopic Identification of Dispersant/ Particle Bonding Mechanisms in Functional Inks

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Abstract

In additive manufacturing, or 3D printing, material is deposited drop by drop, to create micron to macroscale layers. A typical inkjet ink is a colloidal dispersion containing approximately ten components including solvent, the nano to micron scale particles which will comprise the printed layer, polymeric dispersants to stabilize the particles, and polymers to tune layer strength, surface tension and viscosity. To rationally and efficiently formulate such an ink, it is crucial to know how the components interact. Specifically, which polymers bond to the particle surfaces and how are they attached? Answering this question requires an experimental procedure that discriminates between polymer adsorbed on the particles and free polymer. Further, the method must provide details about how the functional groups of the polymer interact with the particle. In this protocol, we show how to employ centrifugation to separate particles with adsorbed polymer from the rest of the ink, prepare the separated samples for spectroscopic measurement, and use Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS) for accurate determination of dispersant/particle bonding mechanisms. A significant advantage of this methodology is that it provides high level mechanistic detail using only simple, commonly available laboratory equipment. This makes crucial data available to almost any formulation laboratory. The method is most useful for inks composed of metal, ceramic, and metal oxide particles in the range of 100 nm or greater. Because of the density and particle size of these inks, they are readily separable with centrifugation. Further, the spectroscopic signatures of such particles are easy to distinguish from absorbed polymer. The primary limitation of this technique is that the spectroscopy is performed *ex-situ* on the separated and dried particles as opposed to the particles in dispersion. However, results from attenuated total reflectance spectra of the wet separated particles provide evidence for the validity of the DRIFTS measurement.

Video Link

The video component of this article can be found at http://www.jove.com/video/52744/

Introduction

Additive manufacturing has recently emerged as a promising technique for fabrication of everything from ceramics to semiconductors to medical devices[1]. As the applications of additive manufacturing expand to printed ceramic, metal oxide, and metal parts, the need to formulate specialized functional inks arises. The question of how to formulate the required functional inks relates to a fundamental issue in surface and colloid science: what are the mechanisms by which particles in colloidal dispersion are stabilized against aggregation? Broadly, stabilization requires modification of the particle surfaces such that close approach of particles (and hence aggregation) is prevented either by Coulombic repulsion (electrostatic stabilization), by the entropic penalty of polymer entanglement (steric stabilization), or by a combination of the Coulombic and entropic forces (electrosteric stabilization)[2]. In order to achieve any of these mechanisms of stabilization, it is usually necessary to modify the particle surface chemistry through attachment of polymers or shorter chain functional groups. Thus, the rational formulation of stable functional inks demands that we know whether a given chemical additive attaches to the particle surface and what chemical group attaches to the particle surface.

The goal of the method presented in this protocol is to demonstrate rapid characterization of chemical species adsorbed on particle surfaces in functional inks. This goal is particularly important as functional ink formulation transitions from a specialized task for surface and colloid scientists to an activity broadly practiced by the range of scientists and engineers interested in printing ceramic, metal oxide, and metal devices. Achieving this goal requires designing an experiment that overcomes the challenges of characterizing opaque, high solids loadings dispersions. It also requires discriminating between chemical species that are present in the dispersion but not adsorbed on the particles from those that are actually adsorbed. It further requires distinguishing between those species that are chemically adsorbed on the particles from those that are weakly physisorbed. In this experimental protocol, we present the use of diffuse reflectance infrared spectroscopy for characterization of dispersant attachment in functional inks. The diffuse reflectance infrared spectroscopy measurement follows a pre-analysis sample preparation technique necessary to distinguish adsorbed species from those merely present in the dispersion.

A variety of methods are currently used to gain insight into the nature of the interactions between chemical ink components and colloidally dispersed particles. Some of these methods are indirect probes in which measured properties are presumed to correlate with surface

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functionalization. For example, changes in slurry rheology or sedimentation rates are presumed to correlate with adsorption of surface modifiers[3]. Particle size distribution, as characterized by dynamic light scattering (DLS), and zeta potential, as characterized by electrophoretic mobility, provide insight into the adsorption of polymers or species with surface charge[4,5]. Similarly, sample mass loss as probed by thermogravimetric analysis (TGA) relates to the presence of desorbing species and the strength of interaction between the adsorbate and the particle[6]. The information from the above mentioned indirect probes suggest changes in surface chemistry, but they do not provide direct insight into the identity of the adsorbing species or the mechanism of its adsorption. Direct insight is particularly important for functional inks in which a large number of components are present in the dispersion. To provide detailed molecular level information, X-ray photoelectron spectroscopy (XPS)[7], ^{13}C nuclear magnetic resonance (NMR) [4,6], and infrared spectroscopy[8-12] have been explored. Of these three options, infrared spectroscopy is particularly promising. In comparison to ^{13}C NMR, infrared spectroscopy does not require that inks be formulated with analytically pure solvents to prevent interferences during measurement[13]. In comparison to X-ray photoelectron spectroscopy, standard infrared spectroscopy can be conducted at ambient pressure, avoiding the need for ultrahigh vacuum conditions during measurement.

There is literature precedent for the use of infrared spectroscopy to probe the interaction between colloidally dispersed ceramic, metal oxide, and metal nanoparticles. These works can be separated into attempts to measure interfacial chemistry *in situ* using attenuated total reflectance infrared (ATR-IR)[9], and attempts to measure interfacial chemistry *ex situ* using solid sampling[8]. While there are advantages to *in situ* measurements, the uncertainties that arise due to the necessity for spectral manipulation make the method difficult for multi-component inks in which there are solvents and multiple polymeric components. Therefore, this protocol focuses on solid sampling and *ex situ* measurement. All of the solid sampling methods entail a pre-treatment step where a solid is obtained by separating the particles from the solvent, and an analysis step where infrared measurements are performed on the solid particles. The difference between methods arises in the choice of sample pre-treatment and in the choice of experimental technique used for infrared analysis of the solid. Historically, the traditional way to use infrared spectroscopy to analyze solids was to grind small quantities (< 1%) of the solid sample with potassium bromide (KBr) powder, and then subject the mixture to high pressure sintering. The result is a transparent KBr pellet. This procedure has been attempted successfully with powders derived from aqueous suspensions of zirconia nanoparticles functionalized with polyethyleneamine[10], with fatty acid monolayers on cobalt nanoparticles[7], and with catechol-derived dispersants on Fe_3O_4 nanoparticles[14]. Despite these successful applications of the KBr pelleting technique for detection of adsorbed dispersants, diffuse reflectance infrared spectroscopy provides several advantages. One advantage is simplified sample preparation. In contrast to KBr pelleting, the solid sample in diffuse reflectance can be simply ground by hand. There is no sintering step as the powder itself is loaded into the sample cup and the diffusely scattered infrared light is measured. The other advantage of diffuse reflectance over KBr pelleting is the increased surface sensitivity[15]. The increase in surface sensitivity is especially useful for the present application in which the critical questions are the presence and nature of adsorbates on the nanoparticle surfaces.

Among works that have used the diffuse reflectance sampling technique to probe the adsorption of chemical species on colloidally dispersed samples, the primary differences arise in the method of separating the nanoparticles from the liquid medium. This step is critical because, without the separation, it would be impossible to distinguish specifically adsorbed dispersants from dispersants simply dissolved in the liquid medium. In several examples, the method of separation is not obvious from the experimental protocol[12,16,17]. When specified, the most frequently practiced method involves gravitational separation. The rationale is that the ceramic, metal oxide, and metal nanoparticles are all more dense than the surrounding media. When they settle, they will drag down with them only the specifically adsorbed species. Chemical species not interacting with the particles will remain in solution. While dispersions may readily settle under normal gravitational force[18], a stable inkjet ink should not observably settle over a time period of less than a year. As such, the method of employing centrifugation for pre-analysis separation is preferred. This has been demonstrated in several studies of dispersant adsorption on glass particles[19,20], dispersant binder adsorption on alumina[8], and anionic dispersant functionalization of CuO[11]. Most recently, we have used it to evaluate mechanisms of fatty acid binding in non-aqueous NiO dispersions used for inkjet and aerosol jet printing of solid oxide fuel cell layers[21].

Protocol

1. Pre-analysis Sample Preparation

1. Separation of functional particles from ink vehicle: centrifugation
    1. Based on the initial ink formulation, calculate how much ink sample is needed to obtain a minimum of 2.0 g of particle sediment. For example, if the ink is 10 vol% ceramic and the density of the ceramic is 6.67 g/cm^3, then a minimum of 3.0 ml of ink is needed to generate 2.0 g of sediment.
    2. Pipet at least the minimum required ink quantity into a centrifuge tube. Choice of centrifuge tube should be made based on quantity of ink required and on inertness of tube material to ink solvents.
    3. Place tube in centrifuge. Choice of centrifuge and rotational rate will be dictated by the gravitational force required to sediment the ink particle. A standard lab centrifuge like the Sorvall ST16 centrifuge with a TX-200 swinging bucket rotor is usually adequate.
    4. Program centrifuge to spin ink at a rotational rate and time necessary to produce a clear supernatant. For the centrifuge used here, typical rates and times are 3,000 – 4,000 rpm for between 30 min and 90 min. Arriving at the correct rotational speed and time necessary to sediment the ink may require trial and error because even inks of the same average particle sizes may have different particle size distributions.

2. Post-separation sample handling: removal of supernatant, sample washing, drying
    1. Once a clear supernatant has been achieved, remove the centrifuge tube from the centrifuge.
    2. Decant the supernatant and save in a capped glass sample vial for possible future analysis. The functional particles are now residual in the centrifuge tube.
    3. After decanting, place the uncapped centrifuge tube upside down on a paper towel and allow additional supernatant to drip out for 1 min.
    4. Remove the tube from the paper towel and rinse the sedimented particles by adding to the tube approximately 2 ml of fresh solvent of the same composition used in the ink formulation. Note that this solvent will only touch the top most layer of the particles sedimented in the centrifuge tube. Decant solvent. Repeat the rinse cycle three times.

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5. After the final rinse cycle, place the uncapped centrifuge tube upside down on a paper towel and allow the additional solvent to drip out for approximately 5 min.
6. Use a thin metal spatula to remove the sediment from the bottom of the centrifuge tube, and spread onto a clean, dry watch glass. Use a lint-free non-abrasive cotton swab or the tip of a clean spatula to remove excess particles from the spatula tip.
7. Place the watch glass into a 50 °C oven and allow the particles to dry for 24 hr. The temperature of the oven should be kept relatively low to minimize the possibility of decomposing adsorbed species. The time required for drying the particles will depend on the vapor pressure of the solvent. 24 hr is typical, but results are usually insensitive to wait times as short as 12 hr and as long as 3 weeks.

2. Diffuse Reflectance Infrared Spectroscopy Measurement

1. Preparation of infrared spectrometer: align accessory, purge compartment
    1. Turn on IR spectrometer.
    2. To prepare for diffuse reflectance infrared spectroscopy measurements, place the diffuse reflectance sampling accessory into the infrared spectrometer sampling compartment. The infrared spectrometer may be any Fourier transform infrared spectrometer capable of interfacing with a diffuse reflectance sampling apparatus. A Shimadzu IR Prestige 21 spectrometer interfaced with a Pike Technologies EasiDiff accessory was utilized for this protocol. For most ink particles, a standard deuterated, L-alanine doped triglycine sulfate (DLaTGS) detector provides enough sensitivity for measurement. A liquid nitrogen cooled mercury cadmium telluride (MCT) detector provides a four to tenfold increase in sensitivity, but this is not usually necessary for identifying adsorbates on ink particle surfaces.
    3. Align the diffuse reflectance sampling accessory as per the manufacturer's instructions.

2. After alignment, close the infrared sampling compartment and begin purging with nitrogen or with CO_2-free, dry air (purge rate of 10 L/min). A standard Parker Balston FT-IR purge gas generator provides air with less than 1 ppm water and CO_2. The amount of purge time necessary to obtain a stable water and CO_2 free chamber will depend on the sample compartment configuration and the humidity in the lab. The necessary purge time can be determined experimentally by comparing background spectra taken at 1 or 2 min intervals and assessing the intensities of the water and CO_2 bands as a function of time.
3. Prepare sample for diffuse reflectance infrared spectroscopy measurement
    1. Obtain the following sample preparation accessories: small (35 mm) agate mortar and pestle, small metal spatula, straight razor blade, and two diffuse reflectance infrared sample cups. Wipe the accessories clean with ethanol, then acetone, and allow them to dry for 10 min in a 50 °C oven.
    2. Remove clean, dry sample preparation accessories from the oven, place them on a large Kimwipe, and allow them to cool to RT.
    3. While the sample preparation accessories are cooling, remove the dried ink particles from the oven, and use an analytical balance to measure 0.025 g of the particle sample. Leave the sample sitting in the analytical balance.
    4. Return to the sample preparation accessories and pour 0.5 g of KBr into the agate mortar. Always use KBr sold for infrared applications. Pre-measured individual 0.5 g packets of KBr (Thermo Scientific) are recommended because they minimize weighing time and exposure of the hydroscopic KBr to the ambient water vapor. Grind the KBr to a uniform appearance, usually 1 min of continuous manual grinding.
    5. Completely fill one of the diffuse reflectance infrared sampling cups with the ground KBr powder. Lightly press the powder with the blunt end of the pestle, and top off the sampling cup with KBr.
    6. Use the side of the razor blade to flatten the top of the KBr in the sample cup. This filled and flattened sample is the reference or background.
    7. Dispose of any KBr remaining in the mortar, and wipe clean.
    8. Open a new 0.5 g packet of KBr powder (or add 0.5 g of KBr powder), and pour into the mortar.
    9. Add the previously weighed 0.025 g of ink particles to the 0.5 g of KBr, and grind with the pestle to form a uniform powder, usually 1 min of continuous manual grinding. This ratio of ink particles to KBr provides a 5 wt% sample during the measurement. This is within the standard range (1 – 10 wt%), but can be adjusted up or down depending on the absorptivity and signal strength of the sample.
    10. Follow steps 2.3.5 and 2.3.6 to create a sample cup filled with the particle/KBr mixture.

4. Infrared spectroscopic measurement
    1. Place the reference and sample cups into the holder, and place the holder into the diffuse reflectance infrared spectroscopy sampling accessory. Position the holder so that the cup containing the background (pure KBr) material is exposed to the infrared radiation.
    2. Close the infrared sampling compartment and allow the compartment to purge for 5 min. This purge time may be adjusted depending on the amount of time determined to be necessary in step 2.2.
    3. After 5 min of purging, obtain an infrared spectrum of the background in the region of interest. The number of scans should be set to maximize the signal to noise ratio while minimizing measurement time. 128 scans at 4 cm^{-1} resolution is usually adequate.
    4. After the background scan is completed, open the infrared sample compartment and move the cup containing the particle/KBr mixture so that it is now exposed to the infrared radiation.
    5. Repeat steps 2.4.2 and 2.4.3 to obtain a spectrum of the particle/KBr mixture.

Representative Results

The experimental procedure described in this protocol has been applied to gain insight into the mechanism of NiO particle stabilization in an ink used to print the anode of solid oxide fuel cells. This ink is a dispersion of NiO particles in 2-butanol, alpha terpineol, and a range of dispersants and binders[22]. Representative results are shown here for a simplified dispersion of NiO in 2-butanol with an oleic acid dispersant. In **Figure 1A**, we show raw diffuse reflectance infrared spectroscopy data. To interpret this data, it is necessary to compare the spectrum of the NiO particles obtained from the dispersion to the spectrum of the NiO particles before dispersion (**Figure 1B**) and to the spectrum of the neat dispersant, oleic acid (**Figure 1C**). We note here that none of the data in **Figure 1** has undergone baseline subtraction or mathematical transformation.

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Thus, there is no question of artifacts arising from data processing. Because the spectroscopic signature of the dispersed NiO is different from the NiO that did not undergo dispersion, it is evident that an adsorbate species is present on the NiO obtained from the NiO/2-butanol/oleic acid dispersion. Since these peaks do not arise when NiO is dispersed in 2-butanol without oleic acid, the peaks must come from the oleic acid moiety. The differences between the neat oleic acid (**Figure 1C**) and the oleic acid moiety adsorbed on the NiO provide insight into the mechanism of adsorption. Involvement of the C=C bond in the adsorbate/particle binding interaction is improbable because the C-H stretch region (~2,800 cm^{-1} to 3,200 cm^{-1}) is undisturbed. Notably, the vinylic C-H stretch is in the same position for adsorbed and neat oleic acid. On the other hand, the C=O stretch corresponding to the carboxylic acid functionality (1,708 cm^{-1}) is strong and present for neat oleic acid, but absent for adsorbed oleic acid. Similarly, the out of plane OH deformation mode of the oleic acid (γ(OH), ~ 940 cm^{-1}) disappears upon dispersion with NiO. The disappearance of the carbonyl stretching mode and the OH deformation mode, is accompanied by the appearance of a ν_a(COO) peak (1,547 cm^{-1}) suggesting that the oleic acid bonds to the NiO through both oxygens in an η_2 configuration[21]. The proposed η_2 species may be chelating (both oxygens bonding through a single Ni surface center) or bridging (the oxygens bonding to the surface through adjacent Ni centers) (**Figure 2**). Distinguishing between these options would require the ability to resolve the ν_s (COO) and ν_{as} (COO) modes, as has been established through previous infrared and X-ray crystallographic studies of acetate compounds[23].

Diffuse reflectance infrared spectroscopy data is sensitive to sample preparation (efficacy of sample/KBr mixing and KBr/sample particle size) and to the extent to which the infrared spectroscopic source is properly warmed up. **Figure 3** provides an example of a U-shaped baseline and wider peaks. While the spectrum in **Figure 3** provides similar qualitative information about the nature of the oleic acid/NiO bond, the peak widths impede resolution of spectral features, particularly in the regions below 1,250 cm^{-1} and above 3,000 cm^{-1}. Further, the U-shaped baseline exaggerates the intensity of the spectral features with increasing distortion on either end of the wavenumber scale.

Finally, transformation of the diffuse reflectance infrared spectroscopic data via application of the Kubelka Munk equations provides a mechanism by which the intensity of scattered radiation can be quantitatively related to concentration[24]. These transformation algorithms are available on many commercially available software packages (for example, Shimadzu's IR Solution software). However, attempts to extract quantitative information from diffuse reflectance infrared spectroscopy should be undertaken carefully because relative intensities of bands vary with particle size. Further, the relationship between concentration and scattered radiation intensity becomes nonlinear at high sample concentrations[24].

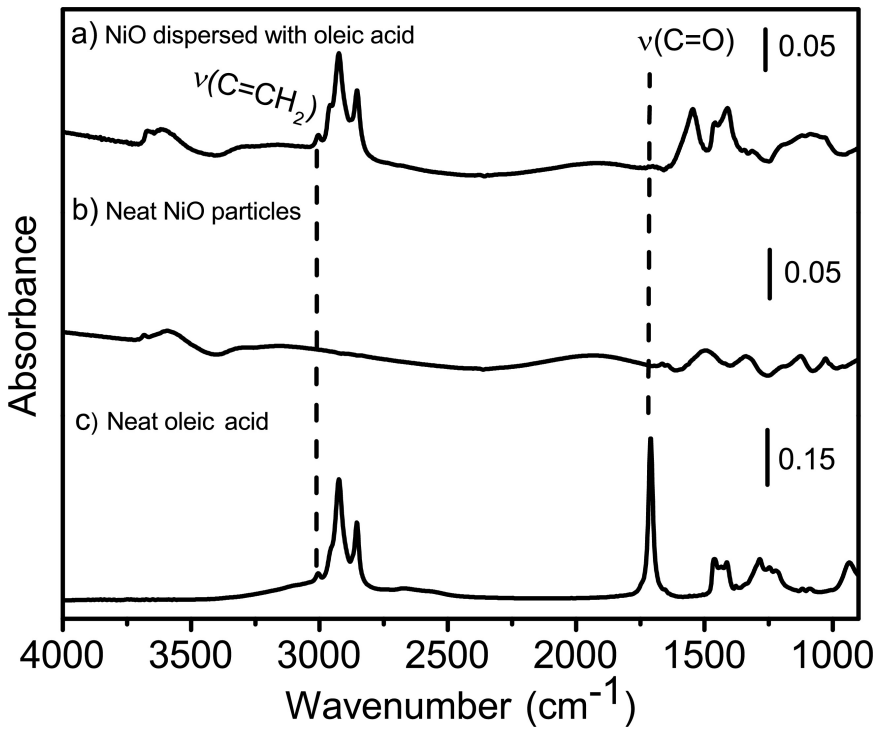

Figure 1. Raw infrared spectroscopic data. Diffuse reflectance infrared spectroscopic data corresponding to **(A)** NiO particles obtained from a NiO/oleic acid/2-butanol dispersion, as compared to **(B)** NiO particles alone, as compared to **(C)** attenuated total reflectance infrared spectroscopic data from neat oleic acid.

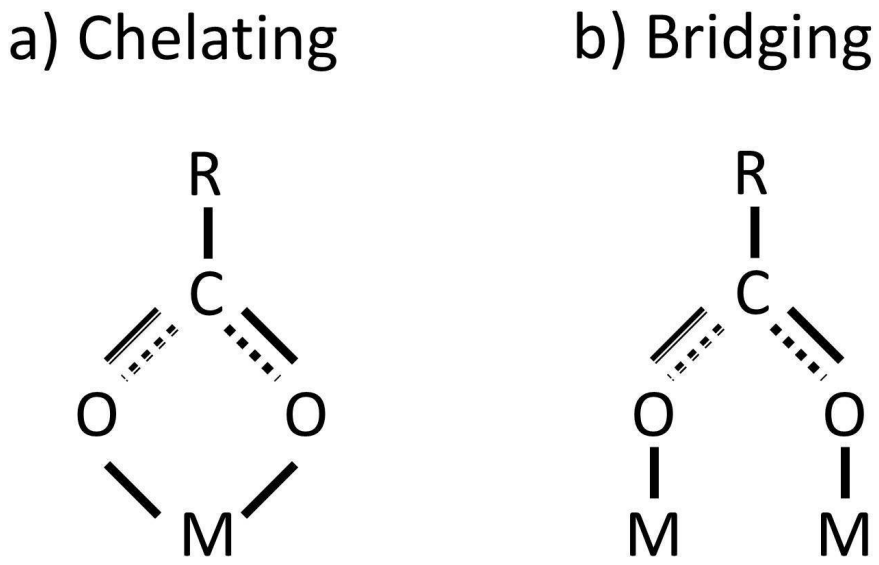

Figure 2. Possible η_2 configurations for oleic acid bonding to NiO. Possible configurations include: **(A)** chelating, and **(B)** bridging. These options for adsorption are based on typical structures observed in inorganic complexes[23]. Bond lengths and bond angles are not drawn to scale.

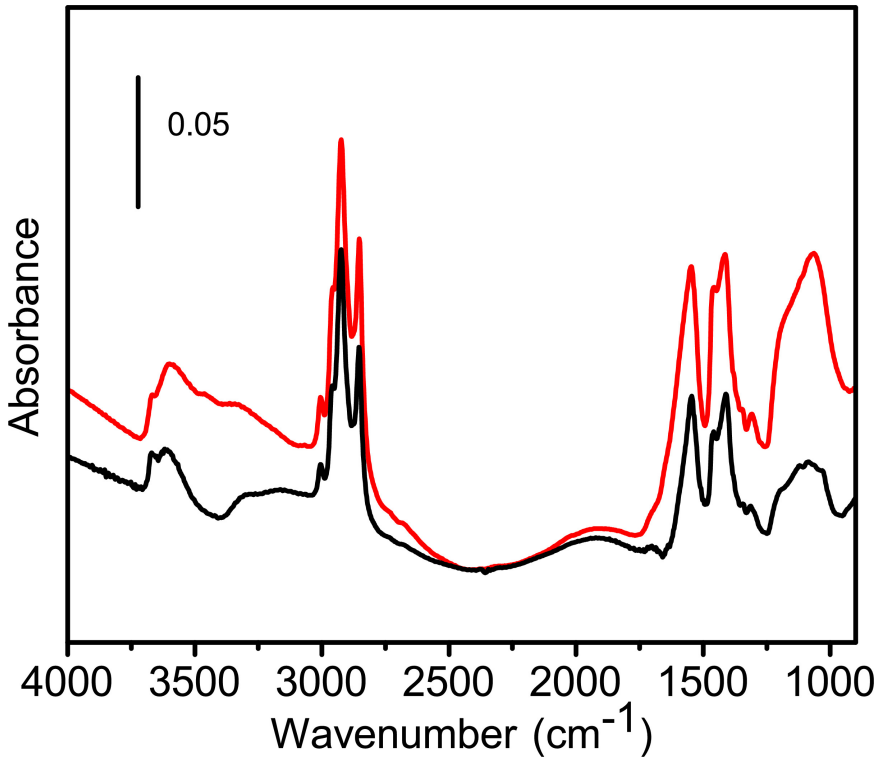

Figure 3. Raw infrared spectroscopic data. Diffuse reflectance infrared spectroscopic data corresponding to NiO particles obtained from a NiO/oleic acid/2-butanol dispersion. The red trace illustrates the U-shaped baseline and increased peak widths characteristic of inadequate warm up of the IR source and inadequate mixing and grinding of the sample and KBr powders. For the data in this figure, the IR source of the Shimadzu IR Prestige-21 instrument was powered on approximately 1 hr prior to measurement. For the Shimadzu IR Prestige-21 instrument, improved data was typically obtained when the IR source was powered on for twelve or more hours prior to measurement. For the red trace in this figure, mixing and grinding was performed for less than one minute and inhomogeneity in the size of grains in the sample was visually evident.

Discussion

The two critical factors for generating high quality infrared spectra using this procedure are: 1) minimizing the absolute quantity of water contamination and the differences in the quantity of water contamination between the sample and reference cups; and 2) creating sample and reference cups with uniform flat layers and similar KBr grain sizes. Both of these factors are achieved by paying particular attention to the sample preparation procedures outlined in section 2.3.

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In order minimize the overall quantity of water contamination and to keep the water contamination the same in the reference and sample, it is necessary to minimize the amount of time that the hygroscopic KBr is exposed to water vapor in the atmosphere and to keep the reference and sample KBr exposed to the atmosphere for approximately the same amounts of time. To minimize the amount of time that KBr is exposed to water vapor in the atmosphere during sample preparation, the ink particle sample should be weighed before the KBr packets are opened (or KBr powder is weighed). Also, the infrared sample compartment should be kept under a continuous purge of clean, dry air (or nitrogen gas) so that no water adsorption occurs during measurement. To minimize the difference in water contamination between the sample and reference cups, a new KBr reference cup should be created and measured each time a new sample is created and measured. Further, the KBr used for the sample cup should be open and exposed to the air with minimal delay after the reference KBr is ground.

To create sample and reference cups with uniform flat layers and similar KBr grain sizes, the samples should be ground for the same amount of time and with the same vigor. With practice, manual grinding is quite effective, although mechanical grinding and blending accessories are commercially available. Once a proper powder has been achieved, the sample and reference cups must be packed so that the top layer is flat and uniform. One simple way to do this is to fill the cup with powder, lightly press the powder with the pestle, then top off the cup with additional powder. This top layer of powder is then leveled by running the side of a razor blade along the surface. Once created, the sample and reference cups must then be transported into the diffuse reflectance apparatus without disturbing the flat surfaces. To do this, all care must be taken not to shake the cups.

When performing the diffuse reflectance sampling for ink particles, the most common challenges encountered are baseline irregularity, excessive peak width, and inadequate signal to noise ratio. The most frequent baseline irregularity is a pronounced U-shape in which the high and low wavenumber regions have exaggerated increases in absorbance. This may be an artifact of inadequate sample mixing[24]. Alternatively, this may be indicative that the infrared radiation source in the spectrometer is not sufficiently warmed up. In comparison to other infrared sampling in other modes, the diffuse reflectance measurement appears highly sensitive to spectrometer warm up time. Similarly, peak width is quite sensitive to sample preparation, in particular to the particle size of the ground KBr. Large particle sizes result in broader peaks[24]. Therefore, if the peak width is too large to resolve the desired spectral features, it may be useful to switch KBr suppliers, extend manual grinding times, or switch to mechanical grinding. Since the present technique focuses on detection of surface adsorbates, inadequate signal to noise ratio is also sometimes encountered. If a MCT-A detector is available, it may be useful to switch from the default DLaTGS detector to the more sensitive MCT-A. Signal to noise ratio is also improved by increasing the number of scans and decreasing the spectral region over which the scans are performed.

Even when all care is taken in sample preparation and measurement, there are some inherent limitations to the application of diffuse reflectance infrared spectroscopy to the analysis of adsorbate bonding in functional inks. First, the density and sizes of the functional particles must be in a range that can be separated from the ink vehicle via centrifugation. The greater the density difference between the ink vehicle and particles, and the larger the particle sizes, the easier the separation. This information is summarized by Stokes Law (eq. 1):

$$V_s = \frac{2}{9}\frac{(\rho_p - \rho_f)}{\mu} g R^2 \quad [1]$$

where *Vs* is the settling velocity of a particle with density ρ_p and radius *R*. The fluid density and viscosity are ρ_f and μ, respectively, and the acceleration due to gravity is *g*. Organic pigments or other carbon-based materials in the range of less than 100 nm may require high g forces, and hence high centrifugation speeds to separate. Even when separable, organic pigments or other carbon based particles may be difficult to measure because of the strong and broad absorbance of carbon in the infrared region. In practice, decreasing the sample concentration of the carbon-based material (*i.e.*, increasing the dilution with KBr) sometimes helps improve the detectability of adsorbates, but the signal still tends to be low. The final limitation of this technique is that it is an *ex-situ* measurement. Care must be taken to ensure that during the drying process, the adsorbed species does not decompose nor change significantly its interaction with the functional ink particle. One way to check this is to perform attenuated total reflectance infrared spectroscopy (ATR-IR) on a small amount of the still wet sediment immediately after centrifugation. The ATR-IR spectra can be collected periodically as the sample dries on the ATR plate. The bands observed will thus show the adsorbate plus the decreasing amounts of solvent as a function of time. If the adsorbate bands generated through this ATR-IR experiment agree with the adsorbate bands generated during the diffuse reflectance measurement, then there is evidence that the drying process does not significantly change the nature of the adsorbate/particle interaction. We note here that while the ATR-IR performed in this manner generates useful information, the diffuse reflectance measurement is preferred because the ATR-IR measurement thus performed requires that the sample remain in the chamber for an amount of time sufficient to evaporate the solvent. Data acquired during these long experimental times may suffer from significant water bands (even when the compartment is vigorously purged by clean dry air). Confirmation experiments can also be performed using ATR-IR experiments on the unseparated ink[9], but proper baseline subtraction is non-trivial in such a situation, and it may be impossible to distinguish between physisorbed polymer and polymer in solution.

The above described diffuse reflectance infrared spectroscopy protocol provides valuable insight into the nature of the interaction between adsorbates and the functional particles in ceramic, metal oxide, and metal inks. In turn, this insight can inform the rational formulation of functional inks. As the printing of ceramic, metal oxide, and metal devices transitions from academic research to commercial manufacturing, this diffuse reflectance infrared spectroscopy technique will be useful to industrial formulation laboratories. Instead of relying on indirect evidence of particle/adsorbate interaction (rheology, particle size, zeta potential), formulators will have direct evidence of which molecules most effectively bond to and stabilize a given particle.

Disclosures

The authors have nothing to disclose.

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