

Scalable gas phase nanoparticle treatment methods required for large-scale nanofluid and nanocomposite synthesis

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ABSTRACT

Photo-induced chemical vapor deposition (photoCVD), referred to as UV polymerization under certain conditions, shows promise as a scalable method for nanoparticle surface treatment. PhotoCVD does not require the use of exotic reagents such as those required by many gas phase reaction techniques. Much like plasma, it relies on photon bombardment to form radicals from a wide variety of organic precursors, selected on the basis of the desired surface properties. Most of the work in the field of photoCVD has stemmed from the semi-conductor industry, where the focus has been high deposition rates [1]. As a result, investigations have focused on high cost, short wavelength UV sources for the polymerization to take place [2]. In the case of nanoparticle functionalization for incorporation into other media, coating thickness is not a particular concern – thus photoCVD can be made readily scalable through the use of cheap UV sources. This talk will present an overview of scalable gas phase methods and focus on the use of photoCVD for the low-cost treatment of nanoparticles required for nanofluid and nanocomposite synthesis.

Keywords: nanoparticles, functionalization, coating, scale-up, photoCVD.

1 INTRODUCTION

Recent work by Buongiorno et al. [3] has demonstrated that while nanofluids do indeed exhibit increased heat transfer properties (namely, thermal conductivity) with respect to the base fluid, there is no abnormal enhancement as had been claimed by early proponents of nanofluids. Similar conclusions with respect to the mechanical properties of polymer nanocomposites have also been reached. However, this lack of abnormal enhancement of material properties does not discount the usefulness of incorporating nanoparticles into liquid or polymer matrices, but it does challenge us to decrease the currently high cost of nanoparticle synthesis and treatment methods. Indeed, nanoparticles cost anywhere from 150\$ to 2000\$ per kilogram (metals and metal oxides - exotic materials excluded) [4]. While particle loadings required may be relatively low (typical values range from 0.5% to 5% for nanofluids), this cost is still quite prohibitive to allow for

the incorporation of nanoparticles in materials on a large scale.

Further, these prices only represent the cost to synthesize nanoparticles and do not take into account the cost of nanoparticle treatment prior to dispersion into another medium. The traditional, low-cost approach employed to prevent nanoparticle agglomeration and facilitate dispersion has been to use surfactants. However, these surface-active compounds have been demonstrated to exhibit significant shortcomings, particularly with respect to their thermal stability [5]. Thermal stability is necessary to widen the temperature range in which nanofluids can be used and to prevent agglomeration prior to dispersion into polymer matrices (high temperature melts). Surface functionalization, which allows for the formation of a chemical bond between the nanoparticle surface and the desired functional groups, can currently be accomplished through a variety of methods, ranging from solvent-based chemistry [6] to electrochemical methods [7] to gas and plasma-based techniques [8, 9]. The latter have shown a high degree of success in allowing for the synthesis of a thermally stable particle coating (see Figure 1), but the cost of implementing plasma-based techniques is quite high (low pressure requirements, power supplies, etc.). This talk will present an overview of scalable gas phase methods and focus on the use of photoCVD for the low-cost treatment of nanoparticles required for nanofluid and nanocomposite synthesis.



Figure 1: A thermally stable nanofluid synthesized via a plasma-based method (taken from [10]).

2 CHEMICAL VAPOUR DEPOSITION (CVD) FOR COATING APPLICATIONS

2.1 What is CVD ?

By definition, CVD is the action of depositing a stable solid product formed from a gas-phase reaction. CVD processes are typically operated under highly active/energetic environments (e.g.: high temperature, plasma, light stimulation), since chemically stable gases are normally preferred as precursors. Depending on the application, the reaction can be conducted either in the gas phase or onto the surface of a substrate. In coating processes, it is preferable to promote reaction directly on the substrate. A reaction conducted in gas phase typically leads to the formation of fine particulates that can form a coating, but adherence will be poor [11]. For this reason, the emphasis will be kept on substrate-surface reactions. Substrates can take on many different geometries and, while CVD typically refers to deposition on planar surfaces (such as shown in Figure 2), for the purposes of this work, it will be applied to powder surfaces (used interchangeably with the term “particle functionalisation”).

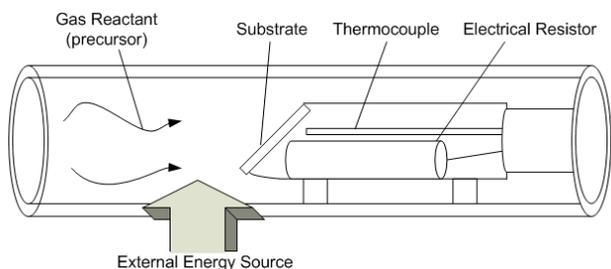


Figure 2: Example of a simple CVD setup with substrate holder for coating application

2.2 Reactive Vapour Generation

First, the reactive vapour has to be generated. This vapour can be composed of one or several components and its original form can be either liquid or gaseous. When the precursor is originally in liquid form, its flow rate can be easily monitored, but a heating element is necessary in order to evaporate the flow. In such a case, a carrier gas is typically used to help transport the precursor. At this point, the gas mixture is preferably chemically stable in order to prevent the occurrence of unwanted reactions outside of the CVD reactor.

2.3 Gas Dissociation

This step consists of exposing the gas to an active environment in order to make it chemically reactive by forming radicals. The active environment can be caused simply by high temperature or by more sophisticated means

like plasma or UV radiation. The gas will usually dissociate into intermediate species or directly react. In the case of CVD applied to substrate coating, including particle functionalization, it is desired that the reaction not occur in the gas phase; rather, it is preferable if the intermediate species are stable enough to last until they reach the heated substrate where the kinetics should be significantly favoured (as illustrated in Figure 2).

2.4 Absorption Onto the Heated Substrate

The product of the reaction is a solid that grows at the surface by polymerization and sometimes a gaseous by-product. In the case of functionalization of particles, absorption represents the main challenge for the scalability. In fact, the potential large scale reactor will have to promote gas-solid contact effectively on the entire surface of the particle. Following the reaction, unreacted species and gaseous by-products are expelled by flow.

3 DIFFERENT TYPES OF CVD

The three main types of coating methods by CVD are the thermally activated CVD, the plasma enhanced CVD (PECVD) and the photo-induced CVD (photoCVD).

3.1 Thermally Activated CVD

Thermal CVD has the main advantage of being simple. The effect of temperature on reaction kinetics is well known and the cost of heating equipment is very cheap. In order to be cost-effective in terms of energy use, the reactants used in thermal CVD should react at relatively low temperatures. However, the use of such compounds may be prohibitive due to their high reactivity and, often, high toxicity [12]. Further, the extent of chemical reactions achievable is somewhat limited given that the only source of activation energy is heat. This last restriction is critical given that a wide range of CVD processes require either a polymerization reaction with a significant activation energy or use of heat-sensitive reagents. In the case of particle functionalization with organic monomers, this last disadvantage suggests thermal CVD should be rejected as a viable option. On the other hand, one can still combine the activation by heat with other stimuli in order to compensate for this flaw.

3.2 Plasma-Enhanced CVD (PECVD)

PECVD uses the electron ionization and UV irradiation resulting from the plasma to provide the activation energy required to promote the desired chemical reactions. It allows reasonable deposition rate at low temperature. Unfortunately, plasma enhanced reactors need to operate at low pressure and require specialized power supplies to generate the glow discharge, both of which translate into significant equipment cost. Moreover, the relationships

between the deposition reactions and the plasma parameters are challenging to develop [13]. Many papers have been published about particle functionalization by PECVD [10, 14, 15], but this technology seems to have only found interest in laboratory scale facilities due its fairly low scalability.

3.3 Photo-Induced CVD (PhotoCVD)

The main advantage of photoCVD is that reactions requiring high activation energy can be conducted at low temperature, similar to PECVD. The UV radiation, provided that it is supplied at the appropriate wavelength, is used to break bonds in the gas reactants. As with other methods, the substrate can be heated to concentrate the reaction on its surface in order to produce the desired coating layer. The main disadvantage of the photoCVD is that the possible reactions are limited compared to PECVD due to the restricted energy distribution range.

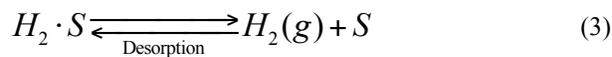
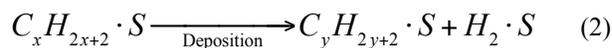
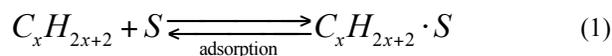
On the other hand, photoCVD offers a better control over film properties compared to other techniques and can readily be scaled up to industrial levels. This latter fact, combined with an appropriate radiation power level, makes photoCVD an interesting candidate for use at larger scales. Moreover, for many coating reactions, cheap and ubiquitous mercury-discharge lamps are sufficient to achieve the desired results, thus further increasing the scalability potential. The semiconductor industry, for example, has already proven the scalability of photoCVD [1]. However, that industry focuses on considerable deposition rates [2] which we posit are far from being critical for the surface functionalization where coating thickness required is minimalistic. In this case, the focus will be the formation of a uniform monolayer on the particle surface.

4 CRITICAL PARAMETERS

CVD is a chemically complex process that includes chemisorption, desorption, gas phase and substrate surface chemical reactions, parameters that are driven by reaction kinetics and mass transport limitations. These parameters will dictate the criteria for precursor selection and operating conditions.

4.1 Kinetic Considerations

In the case of particle functionalization, the desired reaction consist of a polymerization process. This means that the precursor gas must contain carbon. Equations 1 to 4 describe a proposed general mechanism of the UV polymerization on the particle from a hydrocarbon precursor based on CVD surface reaction mechanisms [16], where S represents the surface of the catalyst.



$$r_{C_x H_{2x+2}}'' = \frac{k_1 P_{C_y H_{2y+2}}^\alpha}{1 + K_1 P_{H_2}^\beta + K_2 P_{C_y H_{2y+2}}^\chi} \quad (4)$$

Indeed, in the previous equations, y represents a larger value than x since it is a polymerization mechanism.

4.2 Thermodynamic Considerations

For many CVD application, it is necessary to determine if the proposed reaction pattern is possible. A preliminary verification includes the Gibbs energy of reaction approach. If the Gibbs energy difference between the products and the reactants is negative, it means that the reaction might not occur. It is possible to calculate the equilibrium constant for the reaction and if it tends to 0, this confirms that the reaction will not occur. However, in the case of polymerization, it is public knowledge that the reaction exist.

Another interesting thermodynamic consideration might be the energy necessary to break the bonds between the reactant atoms. In the case of PhotoCVD, by the use of UV radiation, the reactants can be excited and dissociated. This excitation is dependant of the absorption spectrum and the energy necessary to break the bond (e.g. Energy=348eV; length=154pm for C-C). By choosing the right frequency and the right intensity, the intermediate species (radicals) desired for the reaction can be created.

4.3 Mass Transport Considerations

The mass transport rate depends strongly on the surface porosity. Depending of the nature of the particle to be functionalized, the porosity of the particle will vary. Indeed, metal oxides tend to be more porous than pure metals. This is the main reason why many heterogeneous reactions are diffusion limited since a typical catalyst is supported by a metal oxide. This consideration is usually also true for nanoparticles, exepted for the ones that have been synthesized by vaporisation [17]. The following table, adapted from Fogler [16] summarizes the variation of reaction rate and their dependence with velocity, particle size and temperature in function of the limitation. By following this table, one should be able to make sure that the reaction is not mass transport limited.

Table 1: Reaction rate dependences with velocity, particle size and temperature as function of the limitation.

Limitation	Velocity	Particle Size	Temperature
External Diffusion	$U^{1/2}$	$D_p^{-3/2}$	Linear
Internal Diffusion	Independent	D_p^{-1}	Exponential
Surface Reaction	Independent	Independent	Exponential

5 DESIGN CRITERIA

5.1 Precursor Selection

For the purpose of particle surface functionalization and to allow for its scalability, the precursor must be cheap, stable at room temperature, sensitive to UV radiation and available at relatively high purity. Even if contaminants are not critical for functionalization application, it is always preferable to be able to predict how the precursor will behave in the active environment. If liquid, it is usually desirable to have high saturation pressure and be very volatile to facilitate the vaporisation and, thus, reduce the cost of vaporization. If gaseous, the vaporisation step can be avoided which further reduces the energy costs. Ideally, the precursor should have low toxicity and flammability since it is critical for large scale process safety and economics.

5.2 Reactor Design Criteria

A large-scale reactor implementing photoCVD must:

- Maximize the contact between the nanoparticles and the reacted precursor;
- Have its particles preheated prior to their entrance in the coating process;
- Excite the reactant gas by UV before/during the contact with particles;
- Be designed in consideration of the life expectancy of the radicals resulting from the UV treatment.

6 CONCLUSION

It must be kept in mind that nanofluids are still a field of interest for the industry and that their use as heat transfer fluids requires that thermally-stable surface treatments be applied. PhotoCVD is a promising low-cost technology for surface functionalization, especially for large-scale nanofluid synthesis since it can be operated under ambient to near-ambient conditions. Moreover, since coating thickness is not a particular concern for nanoparticle functionalization, photoCVD can be made readily scalable through the use of cheap UV sources and very common precursors. The main challenges will be to accommodate the criteria mentioned previously (5.2).

REFERENCES

- [1] Zhang, B., Liao, Y.-C., Girshick, S., and Roberts, J., Journal of Nanoparticle Research, 2008. **10**(1): p. 173-178.
- [2] Truica-Marasescu, F., Pham, S., and Wertheimer, M., Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 2007. 265(1): p. 31-36.
- [3] Buongiorno, J., Venerus, D.C., Prabhat, N., et al., Journal of Applied Physics, 2009. 106(9): p. 094312-14.
- [4] NanoAmor. Nanostructured and Amorphous Materials Inc. 2011; Available from: <http://www.nanoamor.com/>.
- [5] Wen, D. and Ding, Y., Journal of Thermophysics and Heat Transfer, 2004. 18(4): p. 481-485.
- [6] Bao, H., Chumanov, G., Czerw, R., et al., Colloid & Polymer Science, 2005. 283(6): p. 653-661.
- [7] Feil, F., Furbeth, W., and Schutze, M., Surface Engineering, 2008. 24(3): p. 198-203.
- [8] Tavares, J., Swanson, E.J., and Coulombe S., Plasma Processes and Polymers, 2008. 5(8): p. 759-769.
- [9] Leparoux, M., Leconte, Y., Wirth, A., and Buehler, T., Plasma Chemistry and Plasma Processing, 2010. 30(6): p. 779-793.
- [10] Tavares, J. and Coulombe, S., Powder Technology, 2011. 210(2): p. 132-142.
- [11] Choy, K.L. In: Nalwa H.S., editor. Handbook of nanostructured materials and nanotechnology, vol. 1: synthesis and processing. San Diego (CA): Academic Press; 2000. p. 533.
- [12] Choy, K.L., Progress in Materials Science 48 (2003) 57-170.
- [13] Catherine, Y. In: Mathad, G.S., Schwartz, G.C., Smolinsky, G., editors. Plasma processing. Pennington: Electrical Society, 1985, p. 317.
- [14] Qin, C., Coulombe, S., Materials Letters 60 (2006) 1973-1976.
- [15] Kouprine, A., Gitzhofer, F., Boulos, M. and Fridman, A., Plasma Chemistry and Plasma Processing, Vol. 24, No. 2, June 2004.
- [16] Fogler, H.S., "Elements of Chemical Reaction Engineering", 3rd Ed., Prentice-Hall International, Inc, New York, 1999, p 849-852 & Professional reference shelf p. 854-855.
- [17] Tekna Advanced Materials Inc. Spherical and Densified Silica powder, Available from: <http://www.tekna.com/powder/spherical-powder/silica.html>