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AN INDUSTRIAL METHOD FOR NANOPARTICLE SYNTHESIS WITH A WIDE RANGE OF COMPOSITIONS

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Abstract. The Direct Nanoparticle Deposition process is based on combustion of gaseous and atomised liquid raw materials in an atmospheric oxy-hydrogen flame. The method produces nanosize metal oxides, noble metals and their combinations. Raw materials with very different vapour pressures can be used. Efficient mixing of materials ensures homogeneous multicomponent-nanoparticle composition. Rapid quenching and a short residence time produce monodisperse particles. The DND process is currently in industrial use in the production of ultrapure, doped optical fibres and in glass colouring. Due to the versatility of the method it can be used in various applications where multicomponent materials with well scalable production is required.

1. INTRODUCTION

Flame processes are by far the most widely used for the manufacture of commercial quantities on nanoparticles. An example of the process is the Outside Vapour Deposition (OVD) process used by Corning Inc. for the production of telecommunication optical fibres. The annual production volume is about 1500 tons of silica/Ge-doped silica. The purity of the material is extremely pure as the optical fibre requirements are so strict that only ppb-levels of impurities are allowed. Although the primary particles in the process are nanosize, they are largely agglomerated and sintered due to the extended residence time at high temperature.

Optimising nanoparticle production is not an easy task. Primary requirements for the nanoparticle properties affect the optimal production method and the following properties should be considered when designing the production method and raw materials:

- Multicomponent: the functionality of nanomaterials can be considerably increased by doping the base material. The production method used needs to be able to handle raw materials with very different vapour pressures. The formation of the nanoparticle needs to be controlled.
- Ultrapure (when required): vaporized halides should be used whenever possible or otherwise the procedure used for preparing the ultrapure liquid raw materials (like for doped fibre production) should be followed.
- Spherical: as gas-to-particle route and particle growth by condensation readily produces spherical particles, it is the evident formation method.
- Monodisperse: A uniform thermal reactor and homogeneous particle formation route needs to be secured to achieve monodisperse particles. The high temperature and high cooling rate requirement are best achieved by using a hydrogen-oxygen, well-mixing flame. The geometry of the burner system needs to be symmetric.
- Unagglomerated nanoparticles: a very short exposure time to the combustion is required and if necessary, nanoparticle encapsulation should be provided.

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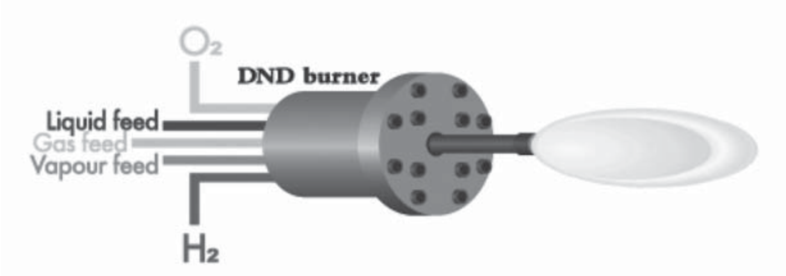

Fig. 1. Direct Nanoparticle Deposition (DND) is based on the combustion of gaseous and atomised liquid raw materials in an atmospheric oxy-hydrogen flame. The system accepts raw materials with very different vapour pressures – gases, vapours and liquids (solutions). Efficient mixing of the raw materials ensures homogeneous nanoparticle composition.

- Scalability: the real challenge arises when the nanoproduct (nanopowder, nanostructured coating, etc.) has to be produced in commercially relevant quantities. The scalability of the production process is a key issue in ensuring a smooth commercialisation. The flame processes are generally well scalable.

2. MEETING THE NANOPARTICLE PRODUCTION REQUIREMENTS BY DIRECT NANOPARTICLE DEPOSITION

Direct Nanoparticle Deposition (DND) is based on the combustion of gaseous and atomised liquid raw materials in an atmospheric oxy-hydrogen flame. The method produces metal oxides, noble metal nanoparticles and their combinations. The flexibility in raw material feeding gives the freedom of incorporating raw materials with very different vapour pressures. High-purity materials can be produced by integrating vapor-delivered and liquid-delivered materials. Efficient mixing of the raw materials is one basic requirement for homogeneous nanoparticle composition – especially with multicomponent materials. In addition to this, rapid quenching and a short residence time produce small particle size and a narrow particle-size distribution, i.e. monodisperse particles, and also ensure the homogeneity of multicomponent particles. Although the causality leading to small unagglomerated spherical particles and excellent homogeneity is not straightforward, it is the key element of the DND-process (Fig. 1).

One of the critical elements of the DND process is the formation of micron-sized liquid droplets in the burner. Such droplets can be produced using various atomizers, such as an ultrasonic atomizer, centrifugal atomizer, single-fluid atomizer and two-fluid atomizer [1]. With high production rates, the atomisation needs to be situated as close to the point-of-use of the fine droplets as possible, because otherwise the droplets tend to agglomerate to larger droplets.

The formation of a nanoparticle from a micron droplet is a complicated process. Various parameters affect the formation process, e.g. the vapour pressure of the metals, temperature of the flame, gas velocities, the droplet route through the flame and the Gibbs free energy of the raw materials.

It is usually very tedious to study experimentally the different formation mechanisms in the DND flame. Qualitative feedback can be obtained from the particle size distribution curve: with a single formation route, like evaporation-condensation, the particle size distribution should be single-peaked and show a small mean particle size distribution. A typical particle size distribution for Palladium nanoparticles produced by DND is shown in Fig. 2a [2], showing a nice single-peaked size distribution.

In order to tune the DND process into producing single-peaked or wider-peaked nanoparticles, the following criteria must be considered:

- the flame temperature has to be sufficiently high – typically in the DND process the maximum flame temperature is about 3000K;
- the micro-droplet has to remain a sufficient time in the hot zone so that complete solvent and metal evaporation can take place;
- the metal must have a sufficient vapour pressure at the flame temperature;

Palladium's vapour pressure is about 100 mm Hg at 3000K, and as seen, it can be tuned to form particles through the evaporation-condensation

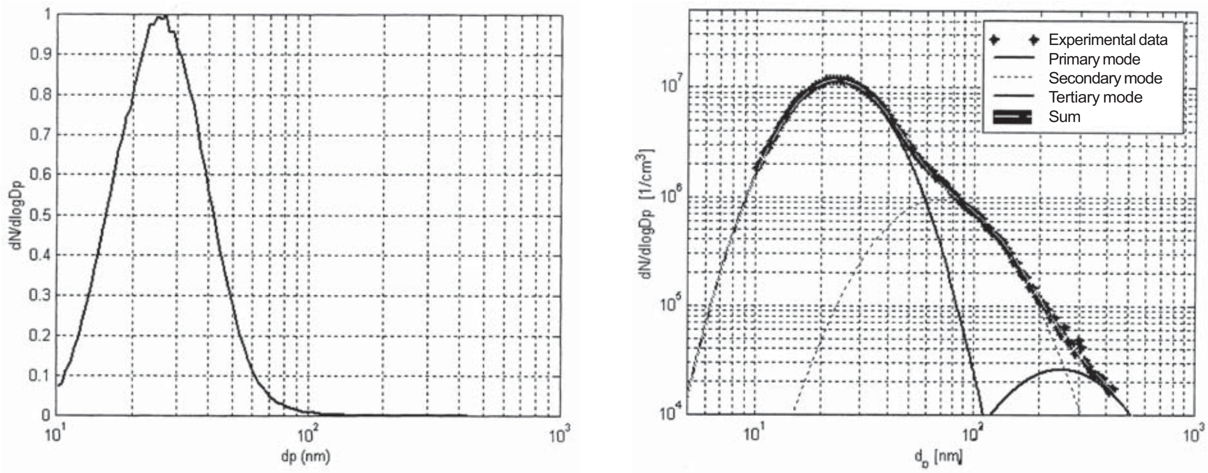

Fig. 2. (a) Particle size distribution of Palladium nanoparticles produced by DND (b) Particle size distribution of Lanthanum nanoparticles produced by DND. The distribution can be approximated to form from three different single-peaked distributions, each showing different routes for particle formation.

route. Lanthanum (La) has a vapour pressure of a few tens of mm Hg at 3000K and the particle size distribution shown in Fig. 2b is not single-peaked, thus providing qualitative information that the particle formation is following several different routes.

The size of the nanoparticles produced by the DND process depends mainly on the mass feed rate. The shape of the particle size distribution curve remains fairly constant, but the mean diameter increases with increasing mass feed rate. This increase and the mean particle size are quite independent of the material produced.

Both CFD-modelling and experimental results show that the DND process is well scalable and it can be used from 1 mg/min to several tons/year production volumes.

3. DOPED OPTICAL FIBRE MANUFACTURING BY DND

Erbium-doped-fibre amplifier (EDFA) is an excellent solution to amplify light in optical telecommunication lines. The production of Erbium-doped fibres with high performance parameters has two major challenges: 1) the homogeneity of the Erbium-doped core area and 2) avoiding the Erbium clustering (or phase separation) [3].

Outside deposition is generally superior in fibre perform manufacturing, because it provides better possibilities for the homogeneous control of the concentration profile and more degrees-of-freedom in the process than inside deposition processes [3].

Although the outside vapour deposition (OVD) process is in principle well suitable for in-situ doping, two major problems exist when using erbium. The first one is related to a practical engineering problem in feeding the precursors into the OVD burner. The second problem is related to the material-formation reactions.

The traditional OVD-burner feeds the pre-cursors to the flame in vaporized form, and thus high-vapour-pressure precursors are needed to realize the process with practical process equipments. However, the rare earths and certain co-dopants, as aluminium, have no high-vapour-pressure precursor in low temperatures. This is a technical problem that need complex solutions, but can be somehow solved. There have been a lot of trials to overcome this problem, [4], but in spite of this, there is no published data of successful results. One plausible reason for unsatisfactory results is the second drawback relating the material synthesis process. The oxidizing reactions of these dopants tend to occur in different circumstances, and thus, in different locations in the flame. In addition to this, the oxidized products of these dopants have highly different vapour pressures than those of silica and germania. It is unsure, if the dopants at all exist in the same particles after this flame synthesis process. Even if they do, they are anyhow located in separate shells each [3]. This leads to a situation, where the dopants are not soluted into the silica matrix. Because the equilibrium favours the phase separation, the phase separation (i.e. erbium clustering) tends to be per-

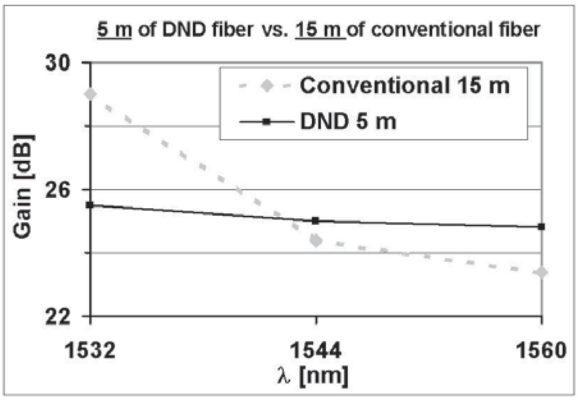

Fig. 3. Comparison between DND-fiber and conventional fiber showing that the same signal gain can be obtained by using 5 m of DND fiber vs. 15 m of conventional fiber. The figure also shows that in the DND-fiber the signal gain is very uniform at different wavelengths (λ).

manent through all the preform fabricating and fibre drawing steps. For this the most used techniques are based on certain kind of 'dipping processes' in liquid solutions (so-called MCVD-process) This process is extremely fabrication unfriendly, has bad yield and leads to unsatisfactory final quality and performance parameters.

The flexible material feeding system of DND enables the combination of high-vapour pressure materials (like $SiCl_4$) to low vapour-pressure materials (like Er-salts). The second challenge, the Erbium clustering is avoided by the specific reaction circumstances. As a result the produced fibre has superior homogeneity and can be doped by times higher Er- concentrations than those fabricated by the conventional MCVD process (Fig. 3).

4. GLASS COLOURING BY DND

Glass can be coloured by solution colours or colloidal colours. Solution colouring ions are normally added to the glass raw materials at concentrations of 0.5 – 5 wt.%. The amount of colloidal colorant can be as low as 0.01 wt.% for gold and 0.05 wt.% for silver. Colouring of glass is usually made in separate furnaces, where the glass composition is fixed. One furnace is required for each colour produced – obviously increasing the capital investment required and making colour changes difficult [5].

The DND technique has successfully been applied to glass colouring [6] and is currently used in the production of tableware glass in Finland. In the DND process solutions containing the colouring ions are atomised and sprayed either as vapour or as metal oxide nanoparticles on the hot glass surface. The colouring agents then diffuse into glass and react with the glass matrix producing a characteristic colour. No separate colour-glass furnaces are required and the material consumption is very low.

Cobalt colour in soda-lime silicate glass is most often intensive blue [7]. In such cases, cobalt is in a divalent (Co^{2+}) form in the glass structure. In the DND process, cobalt is brought onto the glass surface in the form of cobalt oxide, with the raw material being cobalt nitrate. The particle size is not important in the produced colouring effect. If the thermal reactor (flame) or the substrate glass surface are not hot enough, cobalt oxide will remain on the glass surface as cobalt oxide instead of dissolving into the glass structure. A hot flame and hot substrate produces a homogenous blue colour with a wide particle size distribution. In cobalt colouring, high feed rate and thus large particle size and high particle concentration is preferred to produce a good intensive blue.

In colloidal colouring, high feed rates of concentrated silver nitrate solutions produce a white colour. However, low feed rate of concentrated solution or higher feed rate of diluted solution produces a transparent yellow colour. The number mean diameter of the produced silver nanoparticles is four times larger than the maximum diameter for a yellow colour producing particle and thus the collected particle size must somehow change in the glass or close to the glass surface to a yellow colour producing size. Diffusion of silver out of the collected particle into the hot glass substrate after collection is supported by the produced concentration gradient and a high self diffusion coefficient of silver ions in soda-lime silicate glass [8]. In the cooling of the glass, dissolved silver either precipitates onto a surface of an existing particle or forms new silver nuclei in the glass or both. Dissolution of the silver particle is not complete since yellow in this case is produced in a single step process, without striking.

5. IMPROVED PHOTOCATALYSIS BY DND

TiO_2 photocatalysis is the most promising heterogeneous photocatalysis reaction for air or water purification. The concept of heterogeneous photocatalytic degradation is simple: the use under irradiation of a stable solid semiconductor for stimulating a reaction at the solid/solution interface. By definition, the solid can be recovered unchanged after many turnovers of the redox system.

When TiO_2 is irradiated by uv light with the wavelength less than 390 nm, an electron-hole pair is generated. The oxidation potential of the system is higher than oxidation potential of hydroxide and thus – when in contact with water and oxygen – irradiated TiO_2 is able to form a hydroxyl radical. Hydroxyl radical is highly reactive – much more reactive than e.g. ozone, hydrogen peroxide or chlorine gas – and can chemically decompose a pollutant into harmless end-products [9].

The important issue governing the efficiency of photocatalytic oxidative degradation is minimizing electron-hole recombination by maximizing the rate of interfacial electron transfer to capture the photogenerated electron and/or hole. The addition of noble metals to a semiconductor could modify the photocatalytic process by changing the semiconductor surface properties. Practically this should be done by partially coating the TiO_2 nanoparticle with noble metal, like Ag, Au, Pt or Pd. After excitation, the electron migrates to the metal where it becomes trapped and e^-/h^+ recombination is avoided. The hole is then free to migrate to the surface where oxidation of the organics can occur [10].

The DND process can be used to produce TiO_2 particles with various different crystalline phase compositions (i.e. the 70% anatase, 30% rutile composition found in Degussa P25, which has become an industrial standard for comparing photocatalytic TiO_2). DND can also – within the same single-step process – produce TiO_2 particles covered with nanosize noble metal particles.

6. CONCLUSIONS

The requirement for nanomaterial production and nanoparticle characteristics is becoming more stringent when the nanoparticles are propagating from research laboratories into practical industrial use. Especially the manufacturing methods need to be capable of producing multicomponent nanomaterials in scalable production quantities.

Direct Nanoparticle Deposition (DND) is based on the combustion of gaseous and atomised liquid raw materials in an atmospheric oxy-hydrogen flame. The method produces metal oxides, noble metal nanoparticles and their combinations. The flexibility in raw material feeding gives the freedom of incorporating raw materials with very different vapour pressures. Efficient mixing of the raw materials in connection with rapid quenching and a short residence time ensures homogeneous multicomponent-nanoparticle composition, small and monodisperse particles.

The DND process is currently in industrial use in the production of ultrapure, doped optical fibres and in high-volume glass colouring. Due to the versatility of the method it can be used in various applications where multicomponent materials with well scalable production is required.

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