Coating of Glass Surfaces with Nanoparticles of different Materials Synthesized in Microemulsions

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ABSTRACT

In this paper, a new method is presented to coat glass substrates with nanoparticles of different materials such as manganese perovskite ($Sr_{0.5}Ca_{0.5}MnO_3$), zirconium oxide (ZrO_2), yttrium iron garnet ($Y_3Fe_5O_{12}$) and palladium (Pd). The particles were synthesized using w/o-microemulsions, which were also employed to coat the surfaces. The laboratory-scale method involved five basic steps (surface cleaning, synthesis of the nanoparticles, coating, drying and calcination). Finally, the coated substrates were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

Keywords: coating, microemulsions, nanoparticles

1 INTRODUCTION

Nanostructured coating on solid substrates has a significant importance due to the possibility to synthesize materials with specific physical-chemical properties such as magnetic, catalytic, electronic, mechanical, etc. These properties are attractive for several industrial applications. However, they depend strongly on the size and morphology of the particles. Therefore, the control of the parameters of the particles provides a way to enhance the features of the coated surfaces.

The following section delineates the procedure for coating glass substrates with nanoparticles of different materials. The laboratory-scale method involved five basic steps (surface cleaning, synthesis of the nanoparticles, coating, drying and calcination).

Reverse micelles have been successfully used to synthesize nanoparticles with a good control of size and morphology. Microemulsions form spontaneously and present behaviors that change systematically with temperature. With these properties, microemulsions represent a suitable medium for the deposition of particles on cleaned surfaces to yield thin films. The advantage of this method over other processes, which involve solution deposition (e.g. sol-gel [1]), is the wide variety of compounds that are possible to synthesize employing microemulsions, as well as the possibility to change the composition of the microemulsions in order to favor the deposition. Additionally, the use of reverse micelles for coating the surfaces is inexpensive and does not require special equipment.

2 EXPERIMENTAL PART

The method to coat the surfaces with nanoparticles is a five-steps procedure; cleaning the glass surfaces, synthesis of the nanoparticles, coating, drying and calcination. The chemicals employed to carried out the experimental part were supplied by Fluka and were used without further purifications.

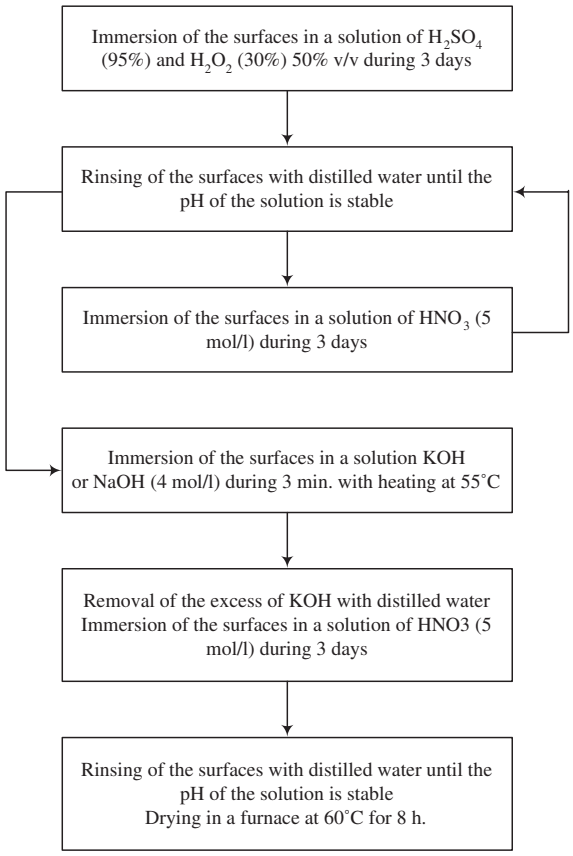

Figure 1: Diagram of the surface cleaning process.

2.1 Surfaces Cleaning

Glass surfaces were supplied by Mezel-Glaser. The surfaces were cleaned employing the process described in [2].

This process is based on cleaning the surface with different acid-basic solutions, followed by rinsing the surfaces with sufficient amount of distilled water untill the pH of the solution is stable. Afterwards, a dry process in a furnace for eight hours takes place. An Scheme of the cleaning process is giving in figure 1. Well cleaned surfaces exhibit contact angles of 0^o between the surface and distilled water.

2.2 Particle Synthesis

Particles of palladium, zirconium oxide, yttrium iron garned and perovskite $Ca_{0.5}Sr_{0.5}MnO_3$ were synthesized in microemulsions according to synthesis proposed in [3], [4], [5] and [6], respectively.

The syntheses of the different materials were carried out in a semi-batch reactor at constant stirring rate, feed rate, and temperature. In general, the synthesis in reverse micelles is achieved by preparing two microemulsions with identical composition (W_o, α and γ) but with different aqueous phases. Microemulsion "A" contains the solutions with the salts while microemulsion "B" contains the appropriated precipiting agent. For example, if the reaction occurs via oxidation the aqueous phase is a solution with the oxidizing agent. These microemulsions are mixed in the reactor. A four pitched blade turbine impeller was used as agitator. The feed input was located near the agitator and above the liquid level. The stirring rate, feed rate and temperature were constant. These conditions were chosen according to the microemulsion feature for each synthesis and following the procedure described in [7].

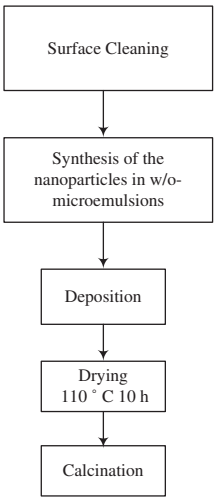

Figure 2: Diagram of the coating process.

2.3 Coating and Drying Process

The microemulsion containing the particles was directly dripped onto the cleaned glass surfaces. Two processes further followed. In the first one, surfaces were sloped at 45^o and the microemulsion was spread from the top to the bottom of the surfaces. In the second process, the glass surfaces were coated with a defined volume of the microemulsion without sloping the surfaces. Afterwards, the surfaces were dried in a furnace at 110^oC for 10 hours. Finally, some surfaces coated in the last way were briefly immersed in a mixture of water-methanol $(3:1)$ to remove the excess of particles.

2.4 Calcination Process and Characterization of the Samples

Dried surfaces were calcinated to pyrolyze the surfactants as well as to obtain the desired crystall structure of the materials. The heat treatment did not exceed 600^oC, except for the yttrium iron garnet. YIG required a higher temperature for crystallization to the desired phase. The samples were characterized by XRD using an X-ray diffractometer Siemens D500 with Cu anode (radiation $K_{\alpha 1}$ of $\lambda = 0.154\ nm$) and by scanning electron microscopy (SEM) using a Hitachi S-520. Figure 2 resumes the steps of the employed method.

3 RESULTS AND DISCUSSIONS

Figure 3 shows the X-ray patterns for the different coated surface. The results were compared with the patterns in "EVA" program to identify the correct structure. The average crystall size D_{hkl} was calculated using the Debye-Scherrer's equation 1 with the full width at the half maximum β (in rad.) of the x-ray diffraction peak.

$$D_{hkl} = \frac{K\,\lambda}{\beta\,Cos\theta} \tag{1}$$

Where K is a constant (often taken as 1), λ represents the X-ray wavelength, β and θ are the full width at the half maximum (in rad.) and the Bragg angle, respectively.

The results calculated using Debye-Scherrer's equation are in good agreement with those obtained by SEM. Table 1 summarized the particle size obtained by XRD and by SEM as well as the thickness of the films for the surfaces coated without slope (second procedure).

Table 1: Particle diameters obtained by $^*XRD$ (D_{hkl}), $^\ddagger SEM$ (D_p) and †thickness of the film (D_F) in nanometers.

Material	$^*D_{hkl}$	$^\ddagger D_p$	$^\dagger D_F$
Pd	30	32	112
ZrO_2	27	30	300
$(Y_3Fe_5O_{12})$	20	22	450
$(Sr_{0.5}Ca_{0.5}MnO_3)$	44	46	470

The SEM analysis shown that surfaces coated by spreading the microemulsion on the sloped surfaces (first procedure) were not homogeneous and the films presented several fissures. In contrast to this behavior, surfaces coated in the second procedure (without slope) were homogeneous films.

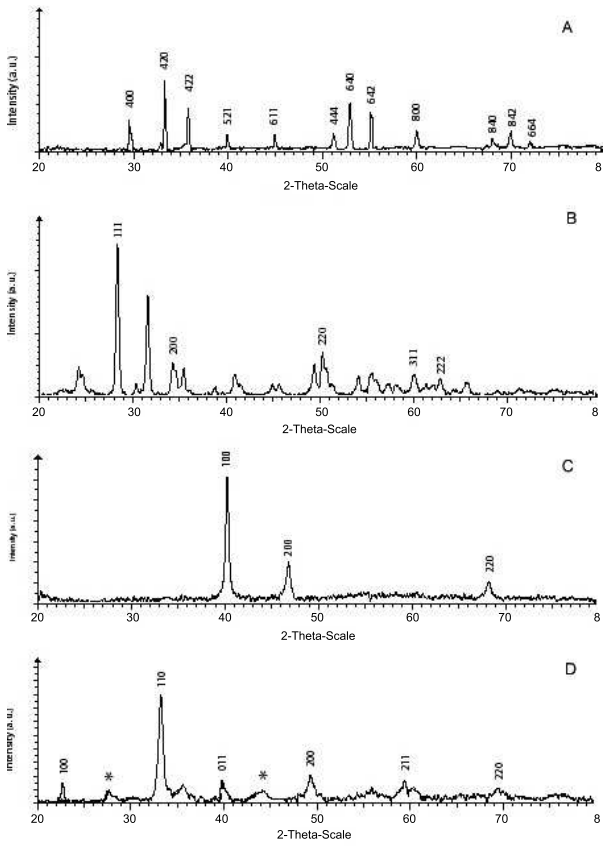

Figure 3: XRD patterns of (A) YIG, (B) $ZrO2$, (C) Pd and (D) Perovskite layers at glass surfaces.

Figure 4 shows the surface topography of the glass coated with yttrium iron garnet and the thickness of the film. Additionally, a relationship between the employed volume of the microemulsion and the final thickness of the film was found. Table 2 compares the employed microemulsion volume and the thickness of the film for the surfaces coated with perovskite.

Table 2: Volume of employed microemulsion and the thickness of the perovskite film (D_F).

Volume (ml)	D_F (nm)
0.2	140
0.4	246
0.6	470

Coated surfaces obtained by the second procedure (without slope) and treated with methanol-water yield homogeneous dispersions of nanoparticles. Figure 5 presents a glass surface coated with palladium nanoparticles and treated in this way.

The particle sizes were significantly smaller than those found normally when the microemulsion is removed and the precipitated particles calcined, probably because the particles

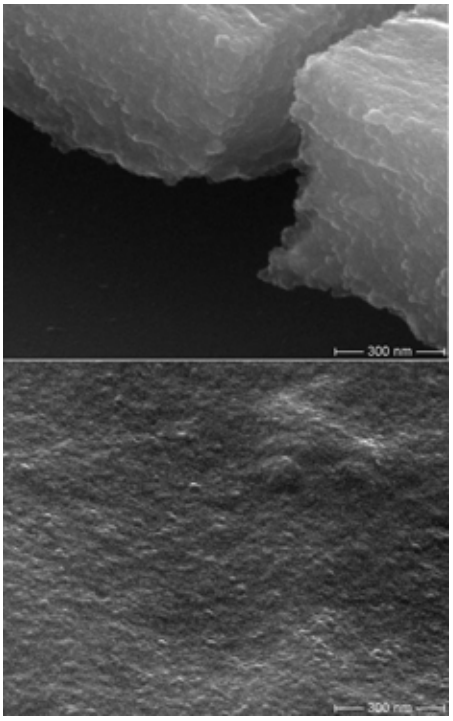

Figure 4: SEM of YIG nanoparticles attached to a glass surface.

are fixed to the substrate before removing the surfactant. Figure 6 shows the possible release of the particles on the substrate by using microemulsions for precipitation and coating.

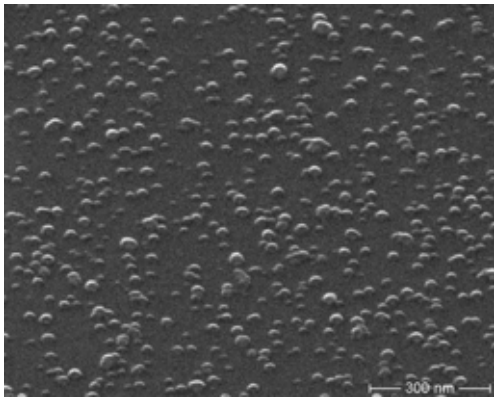

Figure 5: SEM of Pd nanoparticles attached to a glass surface.

The advantage of this method over other processes, which involve solution deposition (e.g. sol-gel [1]), is the wide variety of compounds that are possible to be synthesized, as well as the possibility to change the composition of the microemulsions in order to favor the deposition. This method is inexpensive and does not require special equipment.

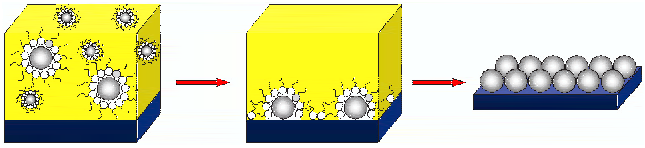

Figure 6: Diagram showing the possible release of the particles on the substrate.

4 CONCLUSIONS

A five-step method for coating of glass surfaces with nanoparticles of different materials was presented. Microemulsions containing the particles were a suitable medium for the deposition. The films were homogeneous and the thickness depended on the volume of employed microemulsion. The method presents some advantages. For example, the wide variety of compounds that can be synthesized in reverse micelles as well as the possibility to change the composition of the microemulsion in order to control the deposition. In addition to these advantage, the method is inexpensive and does not require special equipment.

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