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# Gravure printing for thin film ceramics manufacturing from nanoparticles

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ABSTRACT

Printing technologies can offer high potential for the thin film deposition of functional materials. Among the printing techniques, the gravure is considered one of the most promising, although to date it is still little employed, especially for the inorganic functional materials. In this work, the study of the gravure printing process for the metal oxides thin film production on flexible polymer substrate is reported. For this purpose, zinc oxide (ZnO) was chosen due to its versatile properties and nanosize effects, which make it suitable for many high technology areas. The gravure printing was made using low viscosity inks of ZnO nanoparticles. The characteristics of the printed thin films were examined and discussed. Thanks to the understanding of the physics underlying the film forming during the printing process combined to the knowledge on such specific material, uniform, compact, very transparent and smooth films were obtained in different nanometric thicknesses. Moreover, the possibility of fabricating ceramic nanocomposite films directly through this printing technique is also presented. Thanks to its scientific approach, this work makes available to the world of ceramics an industrial versatile and low-cost production technique which can allow to study and develop high-quality thin film ceramics with technologically interesting properties as well as nanoparticles behavior and their treatments in order to develop and use their fascinating nanosize properties.

## 1. Introduction

In the recent years, a growing interest in nanomaterials was observed due to their size-dependent properties that yield a wide variety of novel applications in many areas [1–3]. Among these materials, metal oxide nanoparticles are extremely appealing for future technological applications in electronics, optics, biomedical [4] where such materials are mostly employed as thin films or patterns. One of the main and current challenges of nanotechnology is to research methods for reliably assembling them into appropriate functional materials. Therefore, the choice of a proper deposition technique becomes as important as the material itself [5].

Typically, nanoparticles are used as colloidal solutions [6] representing a key potential advantage for their solution processing even for film production by industrial low-cost printing techniques [7,8]. In fact, in contrast to the traditional expensive and lab-confined methods, printing is one-step, all-additive, large area technology that enables direct deposition and patterning of materials under ambient conditions with minimum energy, time and materials wastes [6,9]. In addition, printing is typically performed by high speed roll-to-roll press allowing high throughput processing of flexible substrates [5]. Among the roll-to-roll industrial printing techniques, the gravure is the most widely used in the field of newspapers, magazines, currency and packaging and is particularly promising because it combines high printing speed (over hundreds of meters per minute), high resolution patterning and high registration accuracy [5,9–15].

Despite of its many advantages, to date, the use of the gravure printing for the deposition of thin functional film, especially based on oxide nanoparticles, is very limited mainly due to the lack of knowledge. The few explorative attempts in literature include the production of transparent electrodes [5,9,13] and layers for thin film transistors [4,8,11], photocatalyst [16], rectenna [17], organic photovoltaic cells [18,19]. One of the main limit of this printing technique is represented by the difficulties in the formulation of low viscosity inks able to form layers with appropriate characteristics. In fact, the use of any additives or binder in the ink formulation for improving the printability as well as the possibility of contaminants deriving by the atmospheric conditions can reduce the material functionality in the film form. Furthermore, most of such materials would require a thermal sintering step after printing for achieving adequate properties, not compatible with low

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temperatures required for the plastic substrates. Nevertheless, acquiring a deep knowledge of the physical aspects involved in the different stages of this process applied to such materials, the gravure printing can become a thin film leading technology for the nanomaterials on flexible substrates providing low-cost and good quality at the same time.

Therefore, the aim of this work is the systematical study of the gravure printing applied to the metal oxide nanoparticles: thanks to the understanding of the fundamental physical mechanisms underlying the film forming process, the investigation and control of the defects formation can be possible, thus promoting the gravure printing for their industrial production. To this purpose, zinc oxide (ZnO) nanoparticles were chosen as reference material. Thanks to its unique properties, such as high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and high photostability, non-toxicity and low cost [2,20], ZnO can be used in many high technology industrial areas such as light emitting diodes, photodetectors, photodiodes, photocatalyst, optical modulator waveguides, chemical and bio sensors, varistors, energy harvesting devices [21–25]. The appeal of ZnO is also increased by the possibility to obtain it in thin film form, typically converting a precursor layer to ZnO by heating or depositing nanoparticles from a suspension [26,27]. While the first method requires annealing temperatures over 200 °C and/or long processing times, the second approach uses low temperature compatible with an industrial roll-to-roll process on flexible substrate [19,28]. ZnO as thin film can be used in the field of solid state device including electronics, opto-electronics, sensors, dielectric and optical coating [29]. Nevertheless, the preparation of high quality ZnO thin films is still the subject of continuous research, demanding for controlled design, large area surface-pattern and periodicity [20,29]. Therefore, this study focus on gravure printing of ZnO layers on polymer substrate as cost-effective high quality patterned ceramic thin film manufacturing technology, even working as seed layers for growing nanostructures. Coupling the comprehension of the process technology with the physics related to specific materials opens the possibility to use this technique in many different fields.

For further promoting the gravure printing as production method of thin film ceramic materials, nanocomposites films of ZnO-$Al_2O_3$ were also prepared.

The optical and morphological properties of the as-printed layers were examined and discussed. Here, the evaluation of the barrier properties is also proposed as a complementary tool for assessing the effective quality (including defects) of the printed layer.

## 2. Materials and methods

All the prints were performed in air at room temperature onto the chemically pretreated side of a 125 μm thick polyethylenenaphthalate (PEN) substrate (DuPont Teijin Films/Teonex® Q65FA).

Commercial undoped ZnO and $Al_2O_3$ colloidal suspensions (supplied by Sigma-Aldrich Co.), consisting of nanoparticles having respectively size < 130 nm and < 50 nm, were used as starting materials. Ethanol was used as process solvent to dilute such starting materials and prepare printable inks having different mass loading producing different film thicknesses. Before printing, the inks were sonicated (by using Sonica 2200 EP ultrasonicator) at 50 °C for 10 min and then filtered using a PTFE syringe filter having 0,45 μm pore size for preventing the aggregation and further disaggregate the present nanoparticles.

Viscosity of the obtained inks were measured by a viscosimeter (A& D SV-10) at 30 Hz constant frequency and 25 °C.

All the printing experiments were carried out at a printing speed of 60 m/min by using a commercial lab-scale IGT G1–5 printer equipped with a cylinder having line density of 70 lines/cm, stylus angle of 120°, screen angle of 53° and different cell depths (30, 35, 40, 45 μm). After several preliminary tests, the conditions reported in Table 1 were selected as the optimal ones for film formation without naked-eye-visible defects. After printed, the samples were dried at three different temperatures (25, 70 and 140 °C) for one hour before characterization, in order to study the effect of the solvent evaporation on the quality of the printed layers.

The thickness and surface roughness of the printed samples reported in Table 1 were investigated by interferometry-based optical profilometer (Talysurf CCI HD, Taylor Hobson). The root mean square surface roughness was obtained according to the ISO 25178 standard.

The printed films were optical and morphological characterized by performing UV–visible transmission measurements (Lambda 900, Perkin Elmer) and by scanning electron microscopy (LEO 1530 Elektronenmikroskopie), respectively.

Finally, to characterize the quality of the produced layers, the water vapor transmission rate (WVTR) of the printed samples was also evaluated by means of electrical calcium corrosion test. This method allows to estimate indirectly the WVTR of a film by monitoring the change in electrical conductance of a thin evaporated Calcium layer on it that reacts with permeating water vapor over time [30]. The sensor samples were prepared as reported elsewhere [31]. The resistance change of the calcium layer was measured at different temperature and at fixed relative humidity (RH) of 90%. WVTR was calculated as reported elsewhere [32].

All the reported values are the average results of the performed measurements.

## 3. Results and discussion

### 3.1. Overview of the gravure printing process

Gravure printing is characterized by the direct transfer of low viscosity ink solutions from separate micro-engraved cells of a chromed cylinder onto a substrate by the pressure of a rubber cylinder, as depicted in Fig. 1. Several parameters control the quality of the printed products: the physical ones, of the ink (viscosity, rheological behavior, surface tension, solvent evaporation rate) and of the substrate (surface energy, porosity, smoothness), and those of the process (cells geometry and density, impression pressure and speed).

Although it may appear a relatively simple process, gravure printing has a complex multi-physical nature involving several coupled non-linear fluid mechanical phenomena [33]. In particular, the gravure printing process can be considered as a series of sub-processes (inking, doctoring, transfer, spreading, drying), each with its ideal operating regime, concurring to determine the final quality of the printed product [34]. Few works are dedicated to the detailed comprehension of the physics of all the stages of the gravure process and, in most cases, they are limited to the polymer solutions. Therefore, in order to obtain high quality gravure printed films of inorganic materials from nanoparticles suspension, it is necessary to understand the effects of the resultant of the different forces acting on the sol during each stages. Since different physical quantities are involved, dimensional analysis can be used for describing the physical system in each stage of the complex problem of the gravure printing. Essentially, at the microscopic level, the fluid dynamic of the gravure printing process is governed by the balance between viscous and surface tension forces: while the former impede the flow, the latter are the driving forces [11]. Their balance can be represented at a particular printing speed (U) by the dimensionless capillary number $Ca = \eta U/\gamma$, where $\eta$ and $\gamma$ are the viscosity and the surface tension of the ink, respectively [13,34]. The different sub-processes of the gravure printing can have different dependencies on Ca, thus generating different regimes. To this regard, the approach used for the study of the different stages takes significant inspiration from the one proposed by Grau et al. [34] here applied to the case of the ZnO nanoparticles.