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Invited review

Recent advances in inkjet printing synthesis of functional metal oxides

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ABSTRACT

Inkjet printing (IJP) synthesis has emerged as a useful technique for the fabrication of functional metal oxides in the fields of nanotechnology and materials science. In this paper, we will review the fundamental state-of-the-art principles of the special ink formulations used for IJP synthesis of functional metal oxides and the applications of these oxides.

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Introduction

Metal oxides, and particularly multi-component metal oxides, have been studied as promising solid-state materials for a wide variety of applications in the fields of nanotechnology (Brosseau, Youssef, Talbot, & Konn, 2003; Devan, Patil, Lin, & Ma, 2012) and materials science (Bisquert et al., 2008; Jiang et al., 2012) because of their unique chemical, physical and mechanical properties. These

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oxides have been widely used, not only as supporting or active species in catalysis (Fan, Liu, & Huang, 2013; Jackson & Hargreaves, 2009; Li & Shen, 2012; Wachs, 2005), but also as a basis for the fabrication of electronic devices (Lokhande, Dubal, & Joo, 2011; Meyer et al., 2012; Sun, Thompson, & Nishida, 2007), solar cells (Jose, Thavasi, & Ramakrishna, 2009), and chemical sensors (Sun et al., 2012; Wang, Yin, Zhang, Xiang, & Gao, 2010). Because of the specific characteristics or properties of metal oxides, such as particle sizes, structures, and compositional variables, that are required for different applications, a high-yield and reproducible synthesis method for the production of these metal oxides is required. Inkjet printing (IJP) is regarded as one of the most promising techniques for the creation of functional metal oxides on various substrates because it has an automatically controlled printing scheme with precise and flexible droplet volumes, it provides a homogeneous mix at the molecular level in the liquid state, and it offers rapid mass production.

In 1997, Schultz and co-workers reported the first example of use of an inkjet delivery system to form a library of phosphors based on rare-earth-activated metal oxides (de Gans & Schubert, 2003). Since then, the research interest in IJP fabrication of metal oxides has increased significantly, as clearly demonstrated by more than 200 scientific publications on the subject over the past decade. These publications mainly focus on two aspects: (1) formation of uniform thin films for electronic devices, energy storage and gas sensor applications, and (2) high-throughput fabrication of a complex metal oxide library for the optimization and discovery of new functional materials. The aim of this review is to introduce the IJP technique to recent graduates or researchers who are not familiar with this technique. We will therefore not offer in-depth explanations of the following inkjet printing fundamentals here: (1) drop generation, (2) drop interaction with the substrate, and (3) drying of the drops to form a solid. These processes are obviously very important to the fabrication of high-quality ceramic, polymer, and metal components, and several excellent reviews are available that cover these aspects (Calvert, 2001; Derby, 2011; Singh & Sariciftci, 2006; Singh, Haverinen, Dhagat, & Jabbour, 2010; Tekin, Smith, & Schubert, 2008).

This review summarizes the major advances in nano-ink formulations for the generation of new solid-state materials during the period from 2008 to 2013, including progress made in the combinatorial discovery and optimization of inorganic and heterogeneous catalysts, the development of sensors, and other applications of these materials. The vast majority of industrial IJP equipment is designed for use with inks for graphics applications and is not compatible with metal oxide inks. For the aforementioned electronic applications, the formulation of jettable inks, which are composed of a liquid carrier medium, metal oxide precursors and other additives, is the most critical step. These jettable functional inks are designed to have chemical and physical properties that are similar to those of standard inkjet inks to further enhance the compatibility of these inks with the print-head system and the drop ejection morphology when using a stable system.

Inkjet functional ink properties requirements

We begin with a brief introduction to IJP technology. Inkjet printers operate in either continuous or drop-on-demand (DOD) modes. In the continuous mode (Fig. 1(a)), the ink is pumped through a nozzle to form a liquid jet. Uniformly spaced and sized droplets are obtained by periodic perturbation of the jet, leading to surface tension-driven jet break-up. Continuous IJP has been widely used in the industrial coding, marking and labeling markets, where speed is essential. Compared with the continuous mode, the DOD mode offers smaller drop sizes, greater accuracy and fewer restrictions on the properties of the ink. The DOD mode is the dominant technique for the fabrication of functional materials. An acoustic pulse that is generated thermally or piezoelectrically ejects the ink droplets from a reservoir through a nozzle. In a thermal DOD inkjet printer or a bubble jet (Fig. 1(b)), a heat resistor is applied to raise the ink temperature to the bubble nucleation temperature, which then produces a vapor bubble and forces an ink droplet out of the nozzle. However, control of the variable ink temperature presents a major challenge to the stability of the ink formulation, particularly for a chemical solution system. In addition, thermal DOD is largely restricted to aqueous systems and therefore imposes severe restrictions on the selection of the metal oxide precursors. Piezoelectric DOD IJP (Fig. 1(c)), however, relies on the deformation of a piezoelectric membrane to generate an acoustic pulse. Without the need for temperature variation, piezoelectric DOD is in principle suitable for use with a wider variety of solvents, and is thus the best option for combinatorial purposes.

In the printing process, to avoid the agglomeration of ink components that would clog the print head reservoir, the inkjet solutions used for the fabrication of functional metal oxide materials should have properties such as particle size, viscosity, surface tension, and density that are equivalent to those of standard inkjet printer inks. The general property requirements for fluids to be used in inkjet printers are listed in Table 1 (Blazdell, Evans, Edirisinghe, Shaw, & Binstead, 1995; Dong, Carr, & Morris, 2006; Mott, Song, & Evans, 1999; Oezkol, Ebert, & Telle, 2010). Among these properties, the viscosity and the surface tension must be carefully controlled and adjusted, because they strongly affect the fluid dynamics of the droplets. Inks with high viscosity reduce the droplet ejection speed, leading to aggregation and agglomeration of the inks in the print head channels. However, high surface tension makes drop generation difficult and it becomes easy to form satellite droplets rather than a single drop of ideal size. If the surface tension of the ink is too low, it can lead to pollution of the droplets that makes liquid ink drip toward the substrate at random during the printing process. Several excellent reviews have been published in recent years that can help readers to better understand the principles of ink formulation (Derby, 2010; Duineveld et al., 2002; Sun et al., 1997).

The fluid rheological requirements for printable inks are determined by the physics and the fluid mechanics of the drop generation process (Maier, Stöwe, & Sieg, 2007; Martin, Hoath, & Hutchings, 2008). The behavior of fluids can be represented by the Reynolds, Weber, and Ohnesorge numbers (*Re*, *We*, *Oh*):

$$Re = \frac{v\rho\alpha}{\eta}, \tag{1a}$$

$$We = \frac{v^2\rho\alpha}{\gamma}, \tag{1b}$$

$$Oh = \frac{\sqrt{We}}{Re} = \frac{\eta}{(\gamma\rho\alpha)^{1/2}}. \tag{1c}$$

Here, ρ, η, and γ are the density, dynamic viscosity and surface tension of the fluid, respectively, v is the velocity, and α is a characteristic length. Another useful parameter is the Z number, which is the inverse of the Ohnesorge number (*Oh*), is independent of the fluid velocity and can be used to evaluate the printability of an inkjet ink. The equation for the Z number is as follows:

$$Z = \frac{1}{Oh}. \tag{1d}$$

Fromm (1984) defined the parameter based on a simple model of fluid flow in a drop generator with simplified geometry and proposed $Z > 2$ as the best condition for formation of stable droplets.