The Influence of Synthesized TiO$_2$-Nanoparticles on the Performance of Inks Utilized in Printing Documents

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Summary: Titanium dioxide is also called titania and occurs in nature in anatase and rutile forms. It is widely used as a white pigment, catalyst support, and photocatalyst. Nano-TiO$_2$ pigments in pure crystallographic anatase phases have been successfully synthesized via sol-gel method. Nano-TiO$_2$ material has been characterized by various techniques such as XRD, TEM, and XPS. The prepared nano-TiO$_2$ was mixed with two different offset inks (falcon and jobbing) to upgrade the physical and optical properties of the offset inks and compared with Degussa TiO$_2$ before and after the application was tracking and measured. Generally, requiring a small amount of modification is better to avoid any ink malfunction, nano ink requires 0.1 % is because of the photoactive anatase structure of TiO$_2$, while Degussa requires 1 % because it has a 15% rutile structure, which considered a photonactive phase structure of TiO$_2$.

Keywords: Offset ink, pigment nanoparticles, Dispersion, optical density, ink film thickness, TiO$_2$-nano particles.

Introduction

Titanium oxide (TiO$_2$) or titania is the naturally occurring substance of oxides [1]. TiO$_2$ (titania) nanocatalysts have a demonstrated potential to treat “difficult-to-remove” pollutants and subsequently are relied upon to assume a significant part in the remediation of environmental and contamination challenges [2]. It has various range of applications and is mainly used as a pigment including painting and food coloring [3]. It is also considered as a quintessential photocatalyst and among the diverse TiO$_2$ polymorphs, pure anatase is considered the most encouraging polymorph for photocatalytic applications as it offers lower dielectric constant, higher electron mobility and lower density contrasted with the rutile and brookite phase [4, 5]. Additionally, TiO$_2$ materials have the added advantage of offering enormous brightness, which also improves the quality of the final product in terms of appearance [6, 7].

TiO$_2$-nanostructures in various forms, among the remarkable characteristics of nanomaterials, are acquiring broader utilization due to their size-related characteristics [8]. For nanometer-scale, the energy band of TiO$_2$ structure becomes discrete owing to adjusting the optical and textural properties [9-11]. Thus, several works have focused on nanocrystalline TiO$_2$ syntheses with an enormous surface area and TiO$_2$ nanostructures have attracted much consideration and are projected to show a significant role in serving to determine several contaminations and environmental problems and so utilization of TiO$_2$ for hydrogen production and photo-assisted water-splitting apparatus offers a way for clean and low-price production of hydrogen by solar energy [12, 13]. Traditional ink owning harmful components has caused many problems and electronic devices emulate bio functionalities such as synaptic plasticity presents a promising route versatile and energy-efficient computing systems as the demand for rapid prototyping and environmentally friendly fabrication of such devices rise, there are obvious incentives toward finding solutions for low-cost materials and flexible deposition techniques [14].

In this paper, we synthesized TiO$_2$ nanoparticles as reported in the literature [15]. The prepared nano-TiO$_2$ was characterized by N$_2$ adsorption-desorption isotherm (BET), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), and x-ray photoelectron spectroscopy (XPS), tracking its effects on comparison with commercial ones and measuring the optical and physical properties of the treatment before and after application using two different offset inks (Falcon and Jobbing).

Experimental

Materials

Titanium tetrachloride (TiCl$_4$, 98%) was purchased from organochem. Company, India.
Ammonium hydroxide (NH$_2$OH, 35%), and ethanol (C$_2$H$_5$OH, 99%) were purchased from Adwic pharmaceutical and chemicals company Egypt. Titanium dioxide (TiO$_2$, 98%) was purchased from Alpha Chemika India. Falcon and jobbing inks were purchased from Bakin Company Egypt.

**Preparation of TiO$_2$ nanoparticles**

By the hydrolysis method of titanium tetrachloride [16], 4 ml solution of TiCl$_4$ was dropped into 400 ml of a mixture of ethanol and distilled water (4:1) volume ratio. The mixture was heated at 80 °C with stirring. White suspension of TiO$_2$ nanoparticles was formed. After about 120 min of heating at 80 °C and then the process was continued for 120 min after formation of the nanoparticles to reduce most of the chloride ions as HCl gas. The precipitant nanoparticles were separated and collected by centrifugation at 5300 rpm for 30 min the precipitate was filtrated and washed several times with water until pH reaches 7 for removing any impurities. Eventually, TiO$_2$ particles were dried in a drying oven at 50 °C and calcinated at 400 °C for 4 h to obtain a white powder of TiO$_2$ nanoparticles.

**Preparation of the modified inks**

Modified inks mixtures were prepared by mixing of synthesized and commercial Degussa TiO$_2$ with offset inks (falcon and jobbing) with weight ratios (0.1, 0.15, 1, 3) %. So, falcon offset ink (F) has 4 samples with each TiO$_2$ sample FNx, and FDx, and so jobbing offset ink (J) JNx, and JDx, where N refers to nano TiO$_2$ modification, D is commercial Degussa modification, and x is the ratio of modified TiO$_2$ either nano and Degussa, where x = (0.1, 0.15, 1, 3).

**Characterization**

Herein, all prepared samples were characterized by various techniques. The crystal structure of samples was analyzed as a powder by X-ray diffraction (XRD) with a Philips X’Pert Pro Super diffractometer operating in transmission mode with CuKα radiation ($\lambda = 0.15418$ nm). The FT-IR spectrum of the samples was characterized by an IR spectrometer (Thermo Scientific Nicolet iS10) by utilizing KBr as a dispersant, which ranged from 450-4000 cm$^{-1}$. The morphology of the materials was monitored by using a scanning electron microscope (SEM) (JEOL-JSM-6510 LV). The particle size of the materials was determined by using a transmission electron microscope (TEM) (JEOL-TSM-7950 LV). The textural properties of the prepared samples were determined by N$_2$ sorption isotherms at 77° K (Quantachrome NOVA Automated). X-ray Photoelectron Spectroscopy was performed using a KRATOS XSAM-800, which ranged from 0 to 1300 eV.

**Ink Characterizations**

After preparation of materials and mixing them with the 2 different offset inks (falcon and jobbing), the physical properties (morphological and rheological) were measured to analyze whether the modified offset ink make suffice on its role or not. Viscosity and yield value were measured using Laray viscometer (France). Tack property was measured using an electronic digital inko-meter (USA). The ink flow property was measured using a glass flowmeter, and gloss was measured by using zehtner gloss, Germany.

**Results and Discussion**

**Characterization of the synthesized nano-titanium dioxide**

XRD was undergone to examine the crystallinity and structured feature of the investigated nano and Degussa TiO$_2$. The XRD patterns of nano and Degussa TiO$_2$ are shown in Fig 1. All diffraction peaks of the nano TiO$_2$ sample show the complete organization of the anatase phase relating to the diffraction peaks at 2θ= 20, 25.33°, 38.03°, 48.02°, 53.04°, 53.2° and 63.04° corresponding to lattice planes (101), (004), (200), (105), (211) and (204) for anatase structure, respectively, (JCPDS card No. 84-1286) [17]. On the other hand, XRD analysis of the Degussa TiO$_2$ exhibited the presence of two phases; Anatase “tetragonal” and rutile “tetragonal” at 2θ= 27.68°, 36.32°, and 41.28°, which related to (110), (011), and (111), respectively (JCPDS card no. 21-1272) [18].

The crystallite size of the pure and doped-TiO$_2$ samples (D) were computed using Scherrer eq. (1) [19].

$$D = \frac{k\lambda}{\beta \cos \theta}$$  

where D is average crystallite size in angstrom unit (Å), k$^2$ is shape factor and 0.9 is used, β is line width at half maximum intensity (FWHM) in radians, λ is the wavelength of incident x-ray radiation equal to 1.54 Å for Cu target Kα radiation, θ is Bragg’s angle is the half diffraction angle.

The lattice constant values of all the samples were evaluated by using the eq. (2) [19].
\[ d^2 = \frac{a^2}{h^2 + k^2} + \frac{c^2}{l^2} \] (2)

In which (hkl) are the Miller indices, \( d_{hkl} \) is lattice space, (a) and (c) are lattice dimensions. The results obtained are listed in Table S1.

FT-IR spectra analysis was performed to determine the structure and functional groups of the prepared samples. Fig 2 display the FT-IR spectra of all the investigated samples, which show a strong absorbance band exhibited in the range of 450–700 cm\(^{-1}\). This band is attributed to the stretching vibration of Ti-O-Ti bond alluding to the creation of TiO\(_2\). The shift observed in this band elucidates the incorporation of the TiO\(_2\) lattice. Another vibration band ranged from 1622 cm\(^{-1}\) to 1696 cm\(^{-1}\) corresponding to the O-H bending vibration was also observed. This might be attributed to the presence of H\(_2\)O molecules adsorbed on the surface of TiO\(_2\). The vibration band located at \( \sim 3400 \) cm\(^{-1}\) can be assigned for adsorbed H\(_2\)O molecules [20]. The main observed FT-IR bands are shown in Table S2.

SEM images have displayed the shape of both nano and Degussa TiO\(_2\) samples. Moreover, in the 2 images, small spherical particles can be seen. The global and uniform particles shown in images are intelligible together. An extra significant result is that the crystal sizes of nano samples are clearly decreased and the accumulations of them are also increased as shown in (Fig 3 a, b).

The TEM of the nano and Degussa TiO\(_2\) samples are represented in (Fig 3 c, d). It exhibits that nanoparticles have an almost spherical shape corroborating with the SEM images. The mean size-resolved from the width of arbitrarily chosen nanoparticles is like nanoparticles sizes as determined from the XRD results.

\( \text{N}_2 \) adsorption/desorption isotherms for the nano and Degussa TiO\(_2\) samples are shown in Fig 4. All materials show type IV isotherms, which is a typical characteristic of mesoporous materials. This is indicative of porosity between particles as opposed to the individual particles [21, 22]. The shape and the position of the hysteresis loop are observed to be dependent. This means that the surface textural properties have been changed by the crystalline size of TiO\(_2\). The textural properties (surface area, pore volume \( V_p \) and pore diameter) were estimated and the obtained results are summarized in Table S3.

To confirm the surface composition and oxidation states of TiO\(_2\), X-ray photoelectron spectroscopic study (XPS) was done, and the results are exhibited in Fig 5. The surface oxygen (O 1s spectrum) belongsto O\(^2\) species in TiO\(_2\) (B.E.= 529.8 eV), a small peak appears at 531.1 eV and is relegated to OH (surface hydroxyl) [23, 24]. The binding energies of Ti 2p\(_{3/2}\) and Ti 2p\(_{1/2}\) are noticed approximately at 458.8 and 464.5 eV, respectively [25]. The ratio of the areas of the two peaks \( A(\text{Ti } 2p_{3/2})/A(\text{Ti } 2p_{1/2}) \) is equal to 0.5 and the binding energy difference owing to the spin-orbital coupling, \( \Delta E_b = E_b(\text{Ti } 2p_{1/2}) - E_b(\text{Ti } 2p_{3/2}) \) is 5.7 eV in great concurrence with the expected and reported value [26, 27]. These two peaks are the attributes of Ti\(^{4+}\).

**Physical characterization of offset inks**

We study the influence of the addition of nano and Degussa TiO\(_2\) to 2 different offset inks (falcon and jobbing), with 4 different ratios (0.1, 0.15, 1, 3) % and then compared the morphological and rheological properties of 2 inks before and after modification with TiO\(_2\).

**The influence of TiO\(_2\) addition on the morphological properties of inks**

SEM of the 2 offset inks pure and with modified one with different ratio of TiO\(_2\) are displayed in Fig 6. Fig (6 a, 1a) shows the pure offset inks falcon and jobbing, respectively at 2 different magnifying views. Fig 6 are for the modified offset inks falcon and jobbing, respectively at 2 different magnifying views. Fig 6 are for the modified offset inks falcon and jobbing, respectively at 2 different magnifying views (highest ratio (3%), and lowest ratio (0.1%)), and for TiO\(_2\) samples. There's no such a significant difference even at high magnification zoom under the SEM, which refers to the high homogeneity of TiO\(_2\) additives in the offset ink matrix [28, 29].

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Fig. 1: XRD patterns of (a) nano TiO$_2$ (b) Degussa TiO$_2$

Fig. 2: FT-IR of TiO$_2$ samples.
Fig. 3: SEM images of a) Degussa TiO$_2$, and b) nano TiO$_2$ samples and TEM images of c) Degussa TiO$_2$, d) nano TiO$_2$, both e) and h) show the particle distribution of Degussa and nano TiO$_2$ samples respectively.
Fig. 4: N₂ adsorption/desorption isotherm of a) Degussa TiO₂, and b) nano TiO₂ samples.

Fig. 5: XPS peaks for nano TiO₂ sample; (a) for O 1s and (b) for Ti 2p.

Fig. 6: SEM of falcon ink at a) high zoom pure, b) 0.1% Degussa TiO₂, c) 3% Degussa TiO₂, d) low zoom pure, e) 0.1% nano TiO₂, f) 3% nano TiO₂, SEM of jobbing ink at 1a) high zoom pure, 1b) 0.1% Degussa TiO₂, 1c) 3% Degussa TiO₂, 1d) low zoom pure, 1e) 0.1% nano TiO₂, 1f) 3% nano TiO₂
The influence of TiO$_2$ addition on the rheological properties of inks

We study the rheological properties of the modified ink with its different ratio to assure that the modification with TiO$_2$ does not demolish the rheological properties of the ink.

**Viscosity and wettability**

*To the best of our knowledge*, the fundamental constituents of ink are pigment, added substance, and solvent. Little changes in the composition or unclear raw materials bring about various chemical and physical properties of the ink that might contrarily influence the printing process [30]. Additionally, the viscosity and density of the ink are of great importance for ink producers because these physical properties give significant information on the quality and utility of the raw material and the final product [30, 31]. We study the viscosity of offset inks (Falcon and jobbing ink) after adding TiO$_2$ with Four different ratio (0.1, 0.15, 1, 3%) as shown in Fig 7 and then compared the results with the standard data of the pure offset inks as listed in Table S4.

Interestingly, in the case of falcon modified ink with Degussa TiO$_2$ (FD), and with nano TiO$_2$ (FN) as shown in Fig (7 a). It is noticed that the addition of TiO$_2$ either nano or Degussa leads to increase viscosity, that is because of the high density of solid TiO$_2$ in comparison with falcon ink [22]. While, in the case of jobbing modified ink with Degussa TiO$_2$ (JD), and with nano TiO$_2$ (JN) as shown in Fig (7 b). It is noticed that the addition of nano TiO$_2$ leads to increase viscosity, that is because of the high density of solid TiO$_2$ in comparison with falcon ink, while JD viscosity decreases with Degussa TiO$_2$, due to hydrophilicity of Degussa TiO$_2$, besides the hydrogen bond between TiO$_2$, and oxygenated groups in jobbing offset ink, which make Degussa a good mixture with jobbing offset ink, and decrease viscosity [29, 32].

Water contact angles were measured with the sessile drop method by using CAST V2.6 (Solon Tech. Shanghai Co., Ltd., China). The volume of a water droplet was fixed at 3.0 µL, and the contact angle was estimated at 30 s after attachment to the material’s surface (glass substrate coated with ink samples) [33, 34]. Fig 8 shows the contact angle of modified ink with Degussa and with nano TiO$_2$ decreased compared to the original ink this may be attributed to the TiO$_2$ particles was decreased the surface tension of ink by altering the pH of ink [35]. Thus, the contact angle was decreased from 37.2° to 21.4° and 25.6° in the case of nano TiO$_2$ and Degussa TiO$_2$ as displayed in Fig 8.

![Fig. 7: Viscosity change in falcon offset ink (a) and jobbing offset ink (b) with modification of TiO$_2$.](image-url)
Fig. 8: Comparing the contact angle original ink with modified one with TiO$_2$ using the sessile drop method.

Yield value

The yield value (commonly called “yield point”) is the resistance to initial flow or represents the stress needed to start the fluid movement. This resistance is owing to the electrical charges located on or close to the surfaces of the particles. The values of the yield point and thixotropy are estimated of the same fluid properties under dynamic and static states.

We study the effect of adding nano and Degussa TiO$_2$ to 2 different offset inks (falcon and jobbing), with 4 different ratios (0.1, 0.15, 1, and 3%) on the yield value as shown in Fig 9 and then compared the results with the standard data of the pure offset inks as presented in Table S5.

In general, the falcon modified ink with Degussa TiO$_2$ (FD), and with nano TiO$_2$ (FN) as exhibited in Fig 9. It is noticed that the addition of TiO$_2$ either nano or Degussa leads to increase yield value. The yield value is highly increased with increasing nano TiO$_2$ ratio in FN due to high dispersion between TiO$_2$ nanoparticles, while the yield value is slowly increased with increasing Degussa TiO$_2$ ratio in FD due to low dispersion between TiO$_2$ particles [32, 36], and the high density of TiO$_2$ solid [36-38]. While the jobbing modified ink with Degussa TiO$_2$ (JD), and with nano TiO$_2$ (JN) as shown in (Fig 9 b). It is noticed that the addition of Degussa/nano TiO$_2$ leads to decrease yield value, that’s because of the high density of solid TiO$_2$ in comparison with jobbing ink, besides the hydrogen bond between TiO$_2$, and oxygenated groups in jobbing offset ink, which make TiO$_2$ gives a good mixture with jobbing offset ink and decreasing the yield value [39, 40].

Fig. 9: Yield value change in offset inks with modification of TiO$_2$ a) falcon and b) jobbing.
Tack and Flow

A property of printing inks that portrays the cohesion that exists between particles of the ink film, the force needs to split an ink film, or in other words, its stickiness. Ink with a high degree of tack (or a tacky ink) claims more force to split than does a less tacky film. Hence, the effect of adding Degussa/nano TiO$_2$ to 2 different offset inks (falcon and jobbing), with 4 different ratios (0.1, 0.15, 1, and 3%) has been studied as shown in Fig 9. Furthermore, the obtained results are compared with the standard data of the pure offset inks as exhibited in Table S6.

In both cases of offset inks (falcon and jobbing) which modified with Degussa TiO$_2$, and with nano TiO$_2$ as shown in Fig (10 a, b). It is noticed that the addition of TiO$_2$ either nano or Degussa leads to decrease tack value in both offset inks. The tack value is highly decreased with increasing nano TiO$_2$ with small ratios (0.1 and 0.15%) due to high dispersion between TiO$_2$ nanoparticles and slightly decreased at high ratios (1 and 3%), due to the high density of solid TiO$_2$ in comparison with offset inks alone, which lead to increasing ink viscosity [41, 42]. While in the case of the modification with Degussa TiO$_2$ the tack value decreased with falcon ink at all ratio due to increasing viscosity with increasing density. On contrary, the tack value of jobbing ink was increased by increasing Degussa TiO$_2$ due to the hydrogen bond between TiO$_2$, and oxygenated groups in jobbing offset ink, which make Degussa gives a good mixture with jobbing offset ink, and increase tack value, due to viscosity decrement [43].

The influence of TiO$_2$ addition on the optical properties of inks

Improving the optical properties of ink like print density, gloss, and accelerated aging and color spacing that were reflected the quality of ink in the printing process. So, we have measured the optical properties of offset inks (falcon and jobbing) after the modification with Degussa/nanoTiO$_2$ with four different ratios (0.1, 0.15, 1, and 3%) and then compared the obtained results with the standard data of pure offset ink.

Print density

Print density is the estimation of light reflected off the substrate, or how dark the print seems after each press stroke. Hence, Fig 11 display the effect of TiO$_2$ addition on the print density of offset inks (falcon and jobbing). In the case of the falcon modified ink with Degussa TiO$_2$ (FD), and with nano TiO$_2$ (FN) as shown in (Fig 11 a, b). It is noticed that the addition of Degussa/nano TiO$_2$ leads to making sinusoidal relation between average print density (Avg. $\rho$), and TiO$_2$ ratio. The highest Avg. $\rho$ acquired in nano ratio was FN$_{0.15}$, while in Degussa was FD$_1$ (Table 1). Also, Fig (S1) shows that the addition of TiO$_2$ either nano or Degussa leads to make sinusoidal relation between statistical standard deviation of print density (st. $\rho$), and TiO$_2$ ratio (either nano or Degussa). The highest st. $\rho$ acquired in nano ratio was FN$_{0.15}$, while in Degussa was FD$_1$ (Table 1), that is because of
the high density of solid TiO$_2$ in comparison with falcon ink [36, 38].

However, in the case of the jobbing modified ink with Degussa TiO$_2$ (JD), and with nano TiO$_2$ (JN) as shown in (Fig 10 b) that the addition of TiO$_2$ either nano or Degussa leads to make sinusoidal relation between Avg. $\mu$, and TiO$_2$ ratio (either nano or Degussa). The highest Avg. $\mu$ acquired in nano ratio was JN$_{0.15}$ and JD$_{0.15}$ (Table 1). The highest st. $\mu$ acquired in was JN$_{0.1}$, JD$_{0.1}$ as shown in Fig S1 due to the hydrophilicity of TiO$_2$, besides the hydrogen bond between TiO$_2$, and oxygenated groups in jobbing offset ink [32]. From the above results, we can conclude that the modification with a small amount of TiO$_2$ is better than a high amount to avoid any ink malfunction. Apparently, offset inks were modified with nano TiO$_2$ require 0.1 % is because of the photoactive anatase structure of TiO$_2$, while Degussa requires 1 % because it has 15% rutile structure (as shown in XRD patterns), which considered as photoinactive phase structure of TiO$_2$ [44, 45].

**Gloss**

Interestingly, High gloss inks accomplish their best outcomes when utilized on paper (typically coated paper) that permits a high degree of ink resistance or does not allow rapid penetration of the ink vehicle into the paper surface. Rapid drainage of the fluid vehicle hampers oxidation and increments the printed gloss. The application of heat to facilitate ink drying also attempts to lessen printed gloss. High-gloss inks are made for use in both letterpresses and offset lithographic printing processes [46]. Hence, the addition of nano and Degussa TiO$_2$ to 2 different offset inks (falcon and jobbing), with 4 different ratios (0.1, 0.15, 1, 3%) as shown in Fig 12 for falcon and jobbing, respectively; the effect of TiO$_2$ modifications to the offset inks, and the comparison to standard data of the pure offset inks are listed at Table S7.

The falcon modified ink with Degussa TiO$_2$ (FD), and with nano TiO$_2$ (FN) as shown in (Fig 12 a). It is noticed in (Fig 12 a) that the addition of TiO$_2$ either nano or Degussa leads to making sinusoidal relation between average gloss (Avg. $g$), and TiO$_2$ ratio (either nano or Degussa). The highest Avg. $g$ acquired in nano ratio was FN$_{0.1}$, while in Degussa was FD$_1$. (Fig S2, a) shows that the addition of TiO$_2$ either nano or Degussa also leads to make sinusoidal relation between the statistical standard deviation of gloss (st. $g$), and TiO$_2$ ratio either nano or Degussa. The highest st. $g$ acquired in nano ratio was FN$_{3}$, while in Degussa was FD$_3$, that is because of the high photoactivity of solid TiO$_2$ either nano or Degussa owing to major anatase structure in TiO$_2$ with falcon ink [41, 47, 48].

**Table 1:** Average and standard deviation of print density for modified falcon (F) AND jobbing (J) inks.

<table>
<thead>
<tr>
<th>TiO$_2$ ratio (%)</th>
<th>Average print density</th>
<th>St. deviation</th>
<th>Average print density</th>
<th>St. deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FN</td>
<td>FD</td>
<td>FN</td>
<td>FD</td>
</tr>
<tr>
<td>0.1</td>
<td>2.282</td>
<td>2.326</td>
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<td>0.076</td>
</tr>
<tr>
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<td>2.241</td>
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</tr>
<tr>
<td>1</td>
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<td>2.342</td>
<td>0.056</td>
<td>0.028</td>
</tr>
<tr>
<td>3</td>
<td>2.194</td>
<td>2.191</td>
<td>0.051</td>
<td>0.065</td>
</tr>
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</table>
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Requiring a small amount of modification is better to avoid any ink malfunction, nano ink requires 0.1 % is because of the photoactive anatase structure of TiO$_2$, while Degussa requires 1 % because it has 15% rutile structure (as shown in XRD patterns), which considered as photoinactive phase structure of TiO$_2$[44, 45]

**Conclusion**

In this spired, TiO$_2$ nanostructures were prepared by the sol-gel method as enhanced platforms in the ink technology. Briefly, we modified two ink systems (falcon and Jobbing) with two TiO$_2$ (nano, and Degussa), including four ratios (0.1, 0.15, 1, and 3 %), then we compared the rheological properties (viscosity, yield value, flow, tack), as well as the optical properties (print density, gloss, accelerated aging, color spacing) of the two offset inks before and after addition of TiO$_2$. Several characterization techniques were applied to characterize and confirm the initial, intermediate, or final obtained structures. In particular, XRD confirmed that the prepared TiO$_2$ was nanostructured with anatase allotropy, while Degussa had 85% anatase and 15% rutile. In addition, XPS showed that the prepared TiO$_2$ was pure without any impurities. Furthermore, the addition of TiO$_2$ didn’t change the morphology of the two used offset inks, according to SEM. Most importantly, the rheological of the two offset inks were improved by TiO$_2$ modification (whether nano or Degussa), while the optical properties were better with the addition of a small ratio of the nano TiO$_2$, due to the high photoactivity of anatase phase structure. This promising strategy of designing ink systems containing two types of TiO$_2$ can inspire the engineering of advanced nanomaterials and find extensive applications in ink technology, specifically for mixing other inorganic materials with different commercial inks.

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