 doi.org/10.52568/001331/JCSP/45.05.2023

The Influence of Synthesized TiO_2-Nanoparticles on the Performance of Inks Utilized in Printing Documents

[1]Sayeda S. Ali, [1]Mohammad Hegazy, [1]Yasser K. Abdel-Monem, [1,2]Ahmed S. Abou- Elyazed
[1]*Chemistry Department, Faculty of Science, Menoufia University, Shebin El-Kom, Egypt.*
[2]*MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, 150001, China.*
Ahmedphysical90@gmail.com*

(Received on 9th August 2021, accepted in revised form 21st August 2023)

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 photoinactive 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 andJobbing).

Experimental

Materials

Titanium tetrachloride ($TiCl_4$, 98%) was purchased from organochem. Company, India.

*To whom all correspondence should be addressed.

Ammonium hydroxide (NH_4OH, 35%), and ethanol (C_2H_5OH, 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 (λ= 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 zehnter 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, 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].

$$D = \frac{k^{\circ}\ \lambda}{\beta\ cos\ \theta} \qquad (1)$$

where D is average crystallite size in angstrom unit (Å), k° 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].

$$d^2 = \frac{a^2}{h^2 + k^2} + \frac{c^2}{l^2} \quad (2)$$

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_2O molecules adsorbed on the surface of TiO_2. The vibration band located at ~ 3400 cm^{-1} can be assigned for adsorbed H_2O 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.

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(Ti $2p_{1/2}$)/A(Ti $2p_{3/2}$) 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 ratios (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]

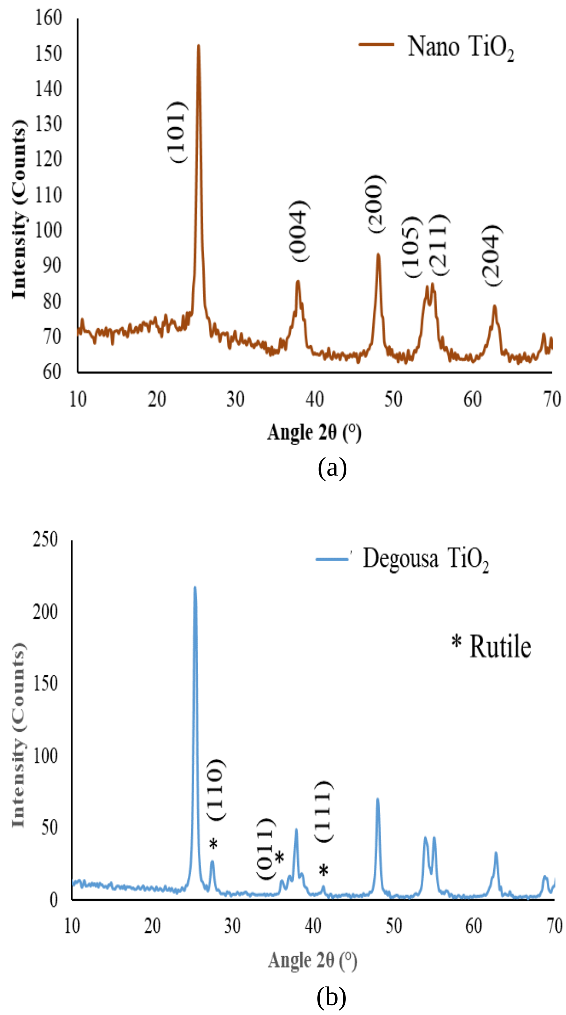


Fig.1: XRD patterns of (a) nano TiO2 (b) Degussa TiO2

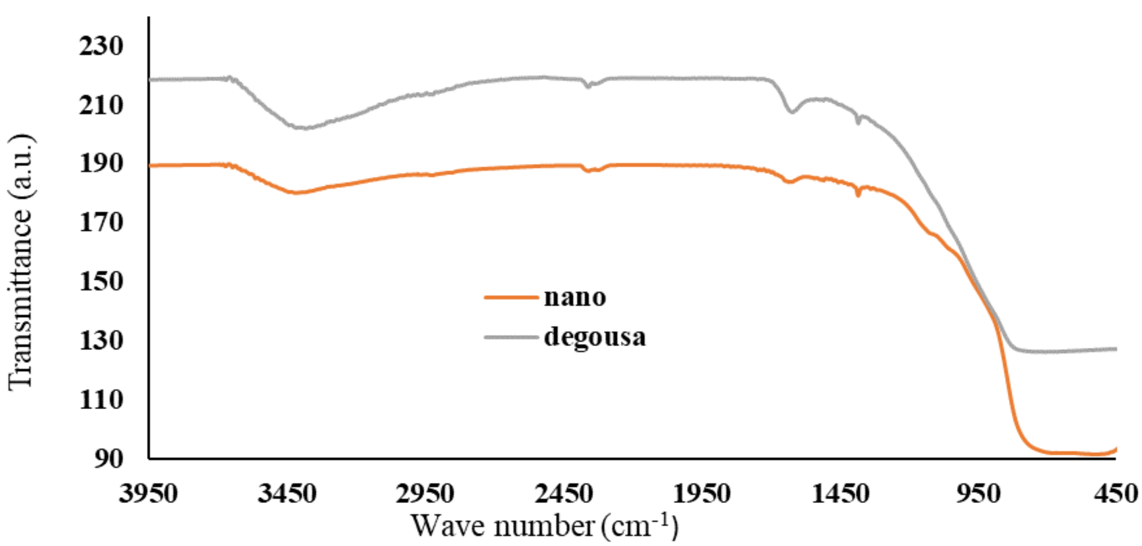


Fig. 2: FT-IR of TiO_2 samples.

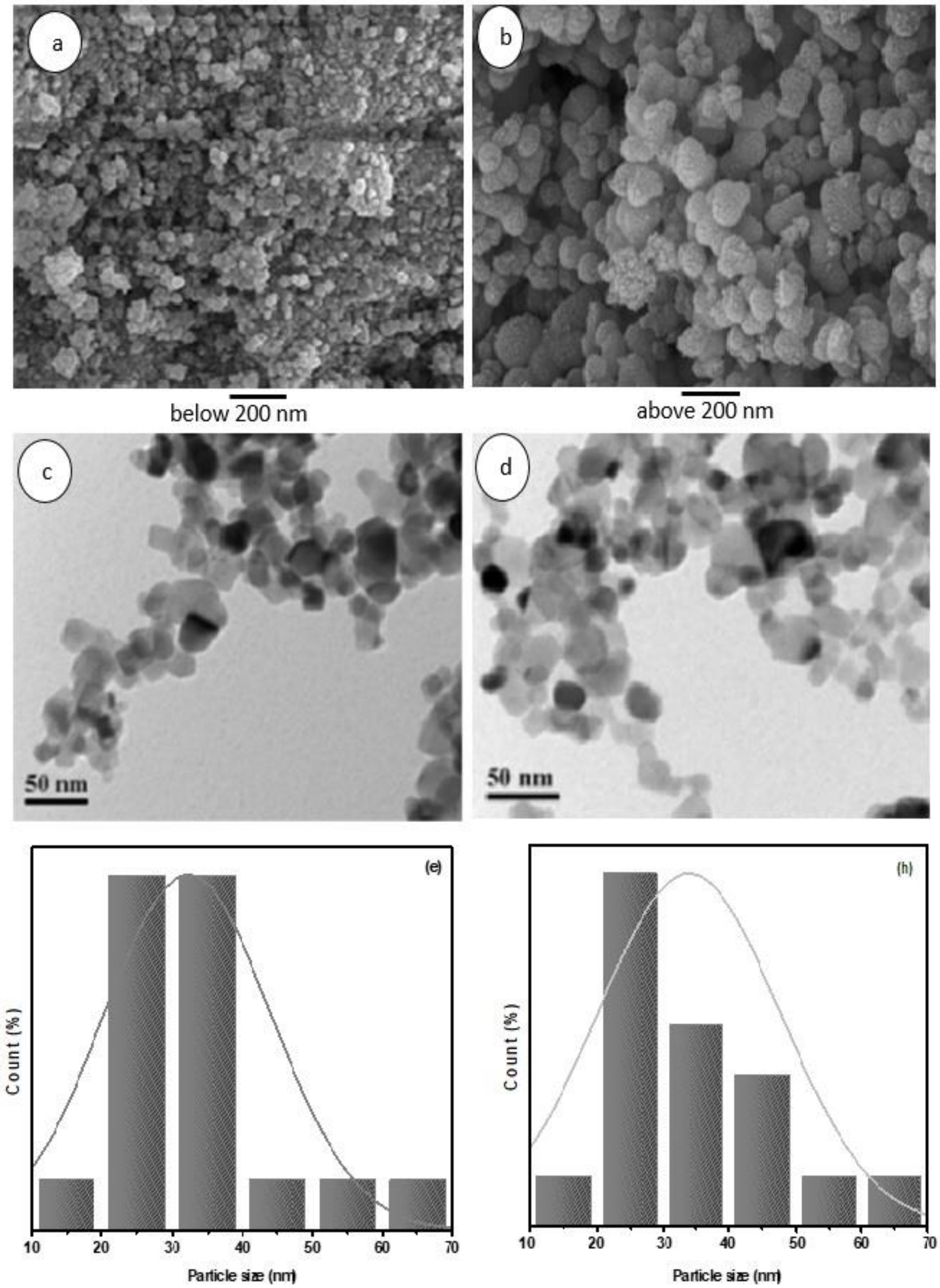


Fig. 3: SEM images of a) Degussa TiO_2, and b) nano TiO_2 samples and TEM images of c) Degussa TiO_2, d) nano TiO_2 , both e) and h) show the particle distribution of Degussa and nano TiO_2 samples respectively.

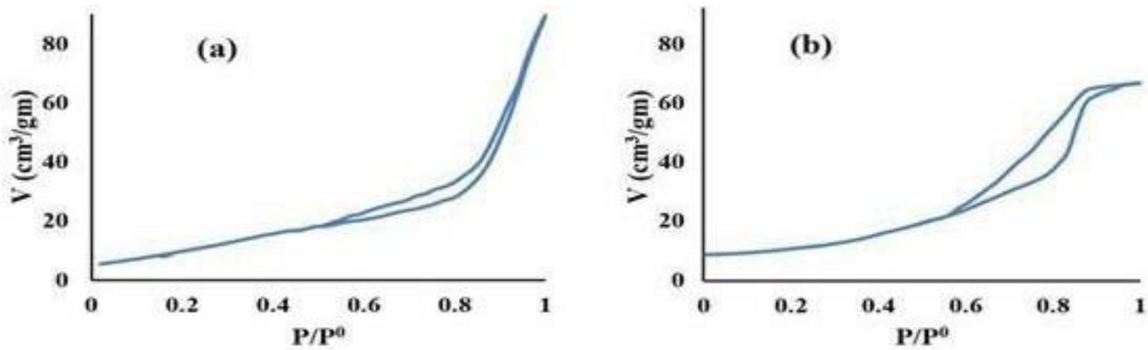


Fig. 4: N_2 adsorption/desorption isotherm of a) Degussa TiO_2, and b) nano TiO_2 samples.

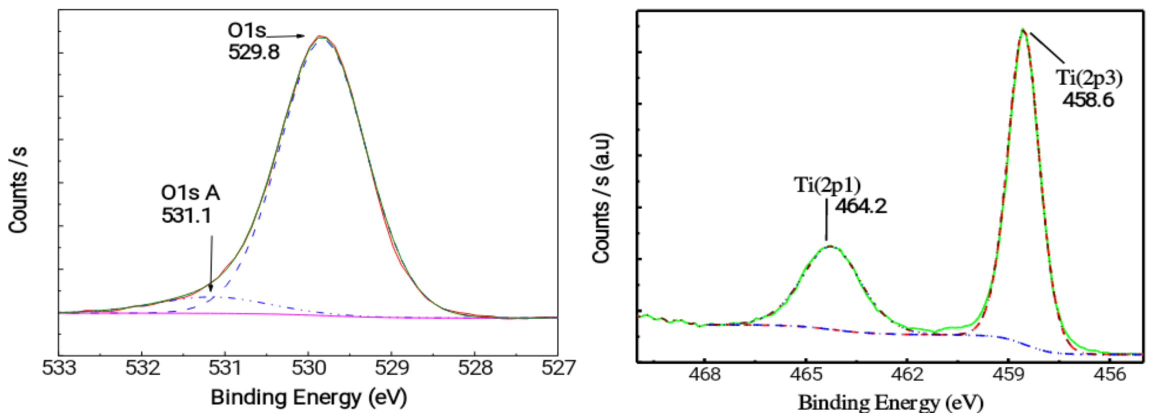


Fig. 5: XPS peaks for nano TiO_2 sample; (a) for O 1s and (b) for Ti 2p.

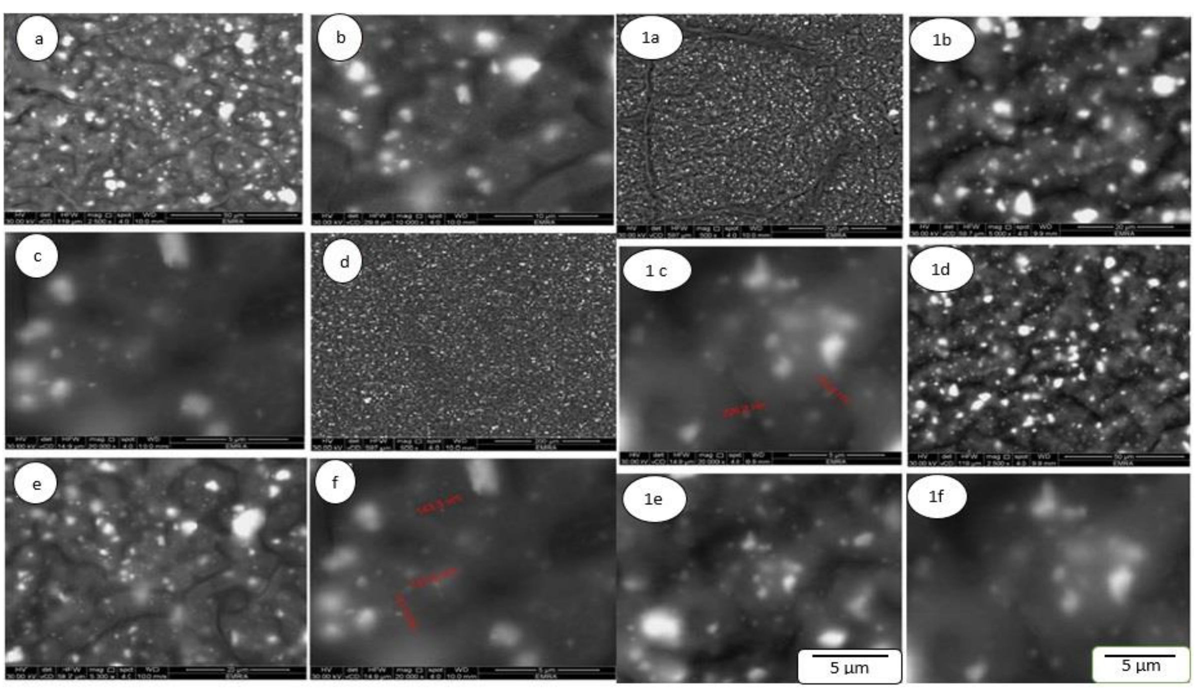


Fig. 6: SEM of falcon ink at a) high zoom pure, b) 0.1% Degussa TiO_2, c) 3% Degussa TiO_2, d) low zoom pure, e) 0.1% nano TiO_2, f) 3% nano TiO_2, SEM of jobbing ink at 1a) high zoom pure, 1b) 0.1% Degussa TiO_2, 1c) 3% Degussa TiO_2, 1d) low zoom pure, 1e) 0.1% nano TiO_2, 1f) 3% nano TiO_2

The influence of TiO_2 addition on the rheological properties of inks

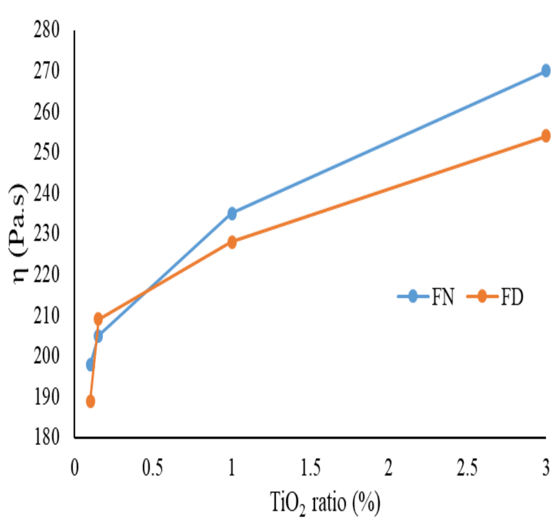
We study the rheological properties of the modified ink with its different ratio to assure that the modification with TiO_2 does not demolish the rheological properties of the ink.

Viscosity and wettability

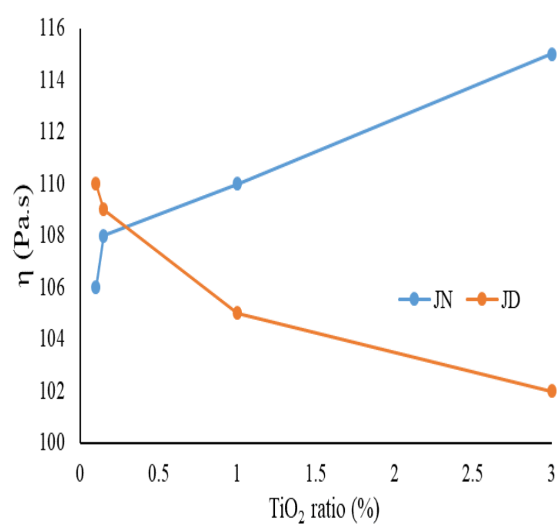
To the best of our knowledge, the fundamental constituents of ink are pigment, added substance, and solvent. Little changes in the composition or unclear raw materials bring about various chemical and physical properties of the ink that might contrarily influence the printing process [30]. Additionally, 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



(A)



(B)

Fig. 7: Viscosity change in falcon offset ink (a) and jobbing offset ink (b) with modification of TiO_2.

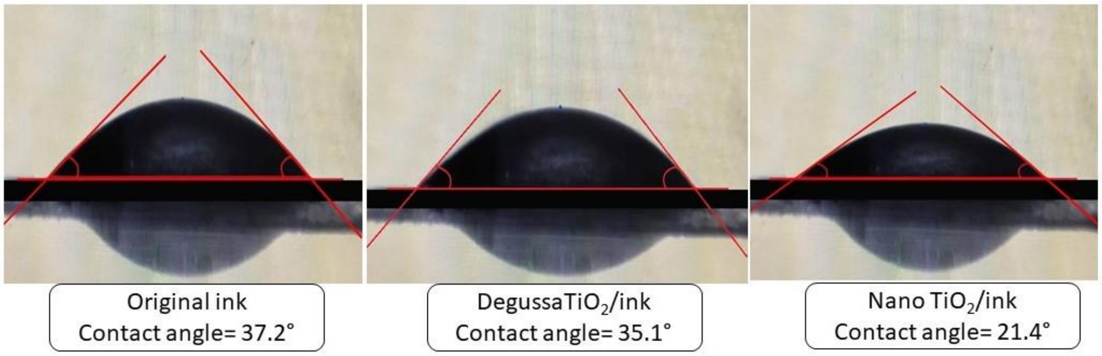


Fig. 8: Comparing the contact angle original ink with modified one with TiO_2 using the sessile drop method.

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].

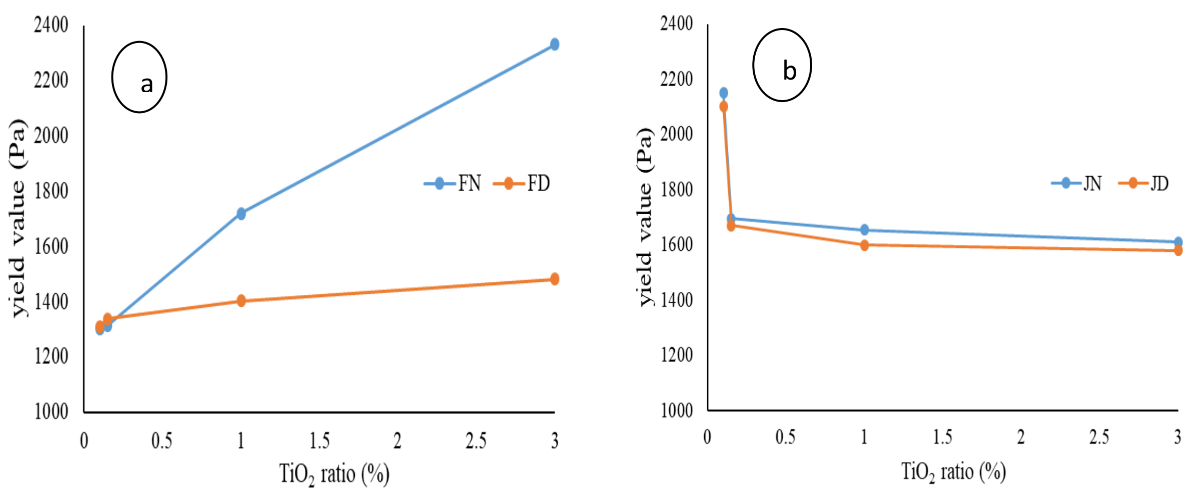


Fig. 9: Yield value change in offset inks with modification of TiO_2 a) falcon and b) jobbing.

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 (falconand 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 (falconand 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.

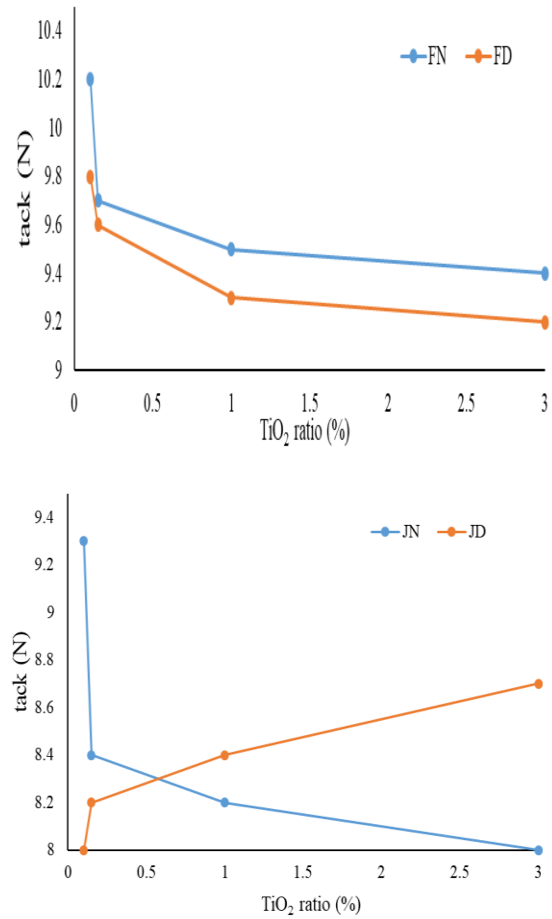


Fig. 10: Tack value change in falcon offset ink (a) and jobbing offset ink (b) with modification of TiO_2.

Print density

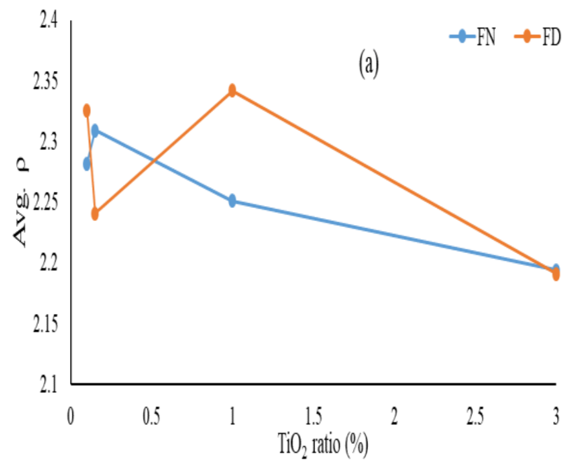
Print density is the estimation of light reflected off the substrate, or how dark the print seems after each press stroke. Hence, Fig 11 display the effect of TiO_2 addition on the print density of offset inks (falconand jobbing). In the case of the falcon modified ink with Degussa TiO_2 (FD), and with 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. ρ), and TiO_2 ratio. The highest Avg. ρ 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. ρ), and TiO_2 ratio (either nano or Degussa). The highest st. ρ 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. ρ, and TiO_2 ratio (either nano or Degussa). The highest Avg. ρ acquired in nano ratio was $JN_{0.15}$ and $JD_{0.15}$ (Table 1). The highest st. ρ 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].



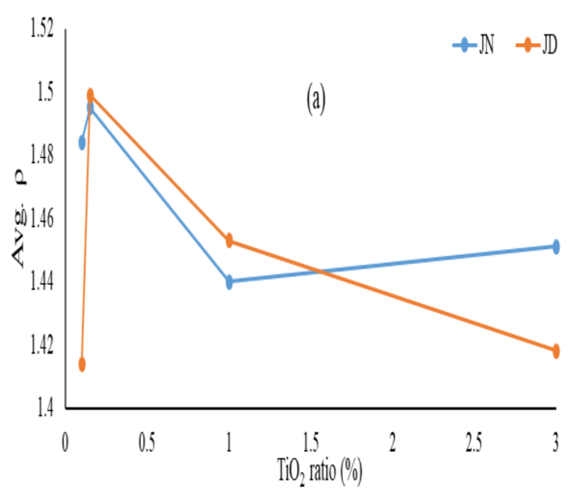


Fig 11: The relation between average print density and TiO_2 ratio for both offset inks; falcon ink (a), jobbing ink (b)

.

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

TiO_2 ratio (%)	Average print density		St. deviation		Average print Density		St. deviation	
	FN	FD	FN	FD	JN	JD	JN	JD
0.1	2.282	2.326	0.055	0.076	1.484	1.414	0.078	0.061
0.15	2.309	2.241	0.041	0.098	1.495	1.499	0.025	0.034
1	2.251	2.342	0.056	0.028	1.44	1.453	0.031	0.031
3	2.194	2.191	0.051	0.065	1.451	1.418	0.042	0.051

The jobbing modified ink with Degussa TiO_2 (JD), and with nano TiO_2 (JN) as shown in (Fig 12b) that addition of TiO_2 either nano or Degussa leads to make sinusoidal relation between Avg. g, and TiO_2 ratio (either nano or Degussa). The highest Avg. g acquired in nano ratio was $JN_{0.1}$, and $JD_{0.1}$, respectively. The highest st. ρ acquired in was $JN_{0.1}$, $JD_{0.1.5}$ (Fig S2, b), due to hydrophilicity of TiO_2, besides the hydrogen bond between TiO_2, beside the low flow of jobbing ink requires low percent of TiO_2 either nano or Degussa to increase gloss value to obtain high values of gloss units (GU) [31].

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].

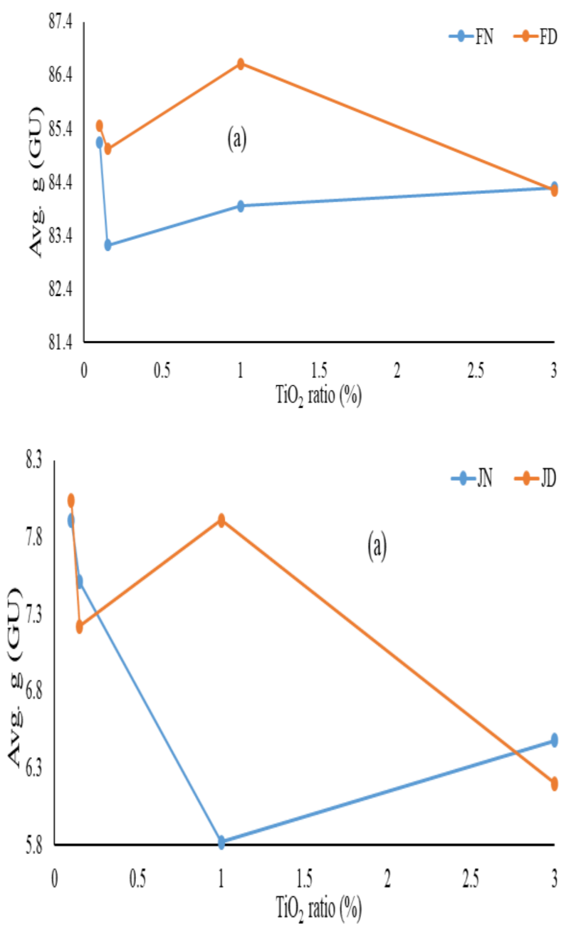


Fig. 12: The relation between average gloss and TiO_2 ratio for both offset inks; (a) Falcon ink, (b) Jobbing ink.

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.

Acknowledgment

The authors acknowledge the financial support Faculty of Science, Menufia University.

References

1. H. Shi, R. Magaye, V. Castranova, and J. Zhao, "Titanium dioxide nanoparticles: a review of current toxicological data, *Part Fibre Toxicol*, **10**, 15 (2013).
2. X. Zhang, X. Zhang, B. Xi, and M. Zhang, Advanced nanomaterials for catalysis: synthesis, characterization, and application, *J Nanomater*, 2015 (2015).
3. M. J. Gázquez, J. P. Bolívar, R. Garcia-Tenorio, and F. Vaca, A review of the production cycle of titanium dioxide pigment, *Mater Sci and Appl*, 2014 (2014).
4. E. Berardo and M. A. Zwijnenburg, Modeling the water splitting activity of a TiO2 rutile nanoparticle, *J Phys Chem* ***C***, **119**, 13384 (2015).

5. A. E. Shalan, M. M. Rashad, Y. Yu, M. Lira-Cantú, and M.S.A. Abdel-Mottaleb, Controlling the microstructure and properties of titania nanopowders for high efficiency dye sensitized solar cells. *Electrochimica Acta*, **89**, 469 (2013).
6. M. A. Hubbe, J. J. Pawlak, and A. A. Koukoulas, Paper's appearance: A review, *Bioresources*, **3**, 627 (2008).
7. S. Naseem, Microstructural, Optical, Electrical and Magnetic Properties of Pristine/Doped TiO2 Nanostructures and their Photocatalytic Applications, Aligarh Muslim University, (2019).
8. M. M. Rashad, E. M. Elsayed, M. S. Al-Kotb, and A. E. Shalan, The structural, optical, magnetic and photocatalytic properties of transition metal ions doped TiO2 nanoparticles. *Journal of Alloys and Compounds*, **581**, 71 (2013).
9. D. G. Mieritz, A. l. Renaud, and D.-K. Seo, Unusual changes in electronic band-edge energies of the nanostructured transparent n-type semiconductor Zr-Doped anatase TiO2 (Ti1–x Zr x O2; x< 0.3), *Inorg Chem*, **55**, 6574 (2016).
10. A. E. Shalan, S. Narra, T. Oshikiri, K. Ueno, X. Shi, H. P. Wu, M. M. Elshanawany, E. W. G. Diau, and H. Misawa, Optimization of a compact layer of TiO 2 via atomic-layer deposition for high-performance perovskite solar cells. *Sustainable Energy and Fuels*, **1**,1533 (2017).
11. M. M. Rashad, A. E. Shalan, Surfactant-assisted hydrothermal synthesis of titania nanoparticles for solar cell applications. *J. Mate. Sci.: Mate. in Electronics*, **24**, 3189 (2013).
12. I. Ali, M. Suhail, Z. A. Alothman, and A. Alwarthan, Recent advances in syntheses, properties and applications of TiO2 nanostructures, *RSC Adv*, **8**, 30125 (2018).
13. A. M. Elseman, A. H. Zaki, A. E. Shalan, M. M. Rashad, and Q. L. Song, TiO_2 nanotubes: an advanced electron transport material for enhancing the efficiency and stability of Perovskite solar cells. *Industrial and Engineering Chemistry Research*, ***59***, 18549 (2020).
14. S. Nishimoto, A. Kubo, K. Nohara, X. Zhang, N. Taneichi, T. Okui, *et al.*, TiO2-based superhydrophobic–superhydrophilic patterns: Fabrication via an ink-jet technique and application in offset printing, *Appl Surf Sci*, **255**, 6221 (2009).
15. W. Li and T. Zeng, "Preparation of TiO2 anatase nanocrystals by TiCl4 hydrolysis with additive H2SO4, *PloS one*, **6**, e21082 (2011).
16. G. Lusvardi, C. Barani, F. Giubertoni, and G. Paganelli, Synthesis and characterization of TiO2 nanoparticles for the reduction of water pollutants, *Mater*,**10**, 1208 (2017).
17. E. M. Rockafellow, L. K. Stewart, and W. S. Jenks, Is sulfur-doped TiO2 an effective visible light photocatalyst for remediation?, *Appl Catal B*, **91**, 554 (2009).
18. C. W. Dunnill, Z. A. Aiken, A. Kafizas, J. Pratten, M. Wilson, D. J. Morgan, *et al.*, White light induced photocatalytic activity of sulfur-doped TiO 2 thin films and their potential for antibacterial application, *J Mater Chem*, **19**, 8747 (2009).
19. N. Ahmed, M. Ramadan, W. M. El Rouby, A. A. Farghali, and N. K. Allam, Non-precious co-catalysts boost the performance of TiO2 hierarchical hollow mesoporous spheres in solar fuel cells, *Int J Hydrogen Energy*, **43**, 21219 (2018).
20. X. Li, D. Wang, Q. Luo, J. An, Y. Wang, and G. Cheng, Surface modification of titanium dioxide nanoparticles by polyaniline via an in situ method, *J Chem Technol Biotechnol*, **83**, 1558 (2008).
21. S. Brunauer, P. H. Emmett, and E. Teller, Adsorption of gases in multimolecular layers, *JACS*, **60**, 309 (1938).
22. M. Khalfaoui, S. Knani, M. Hachicha, and A. B. Lamine, New theoretical expressions for the five adsorption type isotherms classified by BET based on statistical physics treatment, *J Colloid Interface Sci*, **263**, 350 (2003).
23. Y. K. Abdel-Monem, Efficient nanophotocatalyt of hydrothermally synthesized Anatase TiO2 nanoparticles from its analogue metal coordinated precursor, *J Mater Sci: Mater Electron*, **27**, 5723 (2016).
24. E. Al-Hetlani, M. O. Amin, and M. Madkour, Detachable photocatalysts of anatase TiO2 nanoparticles: Annulling surface charge for immediate photocatalyst separation, *Appl Surf Sci*, **411**, 355 (2017).
25. A. Bumajdad, M. Madkour, Y. Abdel-Moneam, and M. El-Kemary, Nanostructured mesoporous Au/TiO2 for photocatalytic degradation of a textile dye: the effect of size similarity of the deposited Au with that of TiO2 pores, *J Mater Sci* , **49**, 1743 (2014).
26. F. Azeez, E. Al-Hetlani, M. Arafa, Y. Abdelmonem, A. A. Nazeer, M. O. Amin, and M. Madkour, The effect of surface charge on photocatalytic degradation of methylene blue dye using chargeable titania nanoparticles. *Scientific reports*, ***8***, 1 (2018).
27. J. G. Kang, and Y. Sohn, Interfacial nature of Ag nanoparticles supported on TiO 2 photocatalysts. *J. Mate. Sci.*, **47**, 824 (2012).
28. M. Von Bahr, F. Tiberg, and V. Yaminsky, Spreading dynamics of liquids and surfactant solutions on partially wettable hydrophobic

substrates, *Colloids Surf A Physicochem Eng Asp,* **193**, 85 (2001).
29. E. Dolezel-Horwath, W. Carinthian, and E. Zikulnig-Rusch, Evaluation of the compatibility between low pressure melamine (LPM) film printing substrates and inkjet inks, *Eur J Wood Wood Prod,* **70**, 5 (2012).
30. H. Kipphan, Springer Science and Business Media, *Handbook of print media: technologies and production methods*, Springer-Verlag Berlin Heidelberg, Switzerland, (2001).
31. R. Leach, *The printing ink manual*: Springer Science and Business Media, p.245 (2012).
32. T. Blake and J. Haynes, Kinetics of liquidliquid displacement, *J Colloid Interface Sci,* **30**, 421 (1969).
33. A. S. Abou-Elyazed, Y. Sun, A. M. El-Nahas and A. M. Yousif, A green approach for enhancing the hydrophobicity of UiO-66 (Zr) catalysts for biodiesel production at 298 K. *RSC Advances*, **10**, 41283 (2020).
34. A. V. Vinogradov, V. V. Vinogradov, Effect of acidic peptization on formation of highly photoactive TiO_2 films prepared without heat treatment. *J. American Ceramic Soc.*, **97**, 290 (2014).
35. D. Bugakova, V. Slabov, E. Sergeeva, M. Zhukov, and A. V. Vinogradov, Comprehensive characterization of TiO_2 inks and their application for inkjet printing of microstructures. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **586**, 124146 (2020).
36. R. Bollström, D. Tobjörk, P. Dolietis, A. Määttänen, P. Ihalainen, J. Peltonen, *et al.*, Towards Paper Electronics–Printing Transistors on Paper in a Roll-to-Roll Process, in *NIP and Digital Fabrication Conference,* **636** (2011).
37. C. Clair, *A history of European printing*, Academic Press Inc, New York, (1976).
38. D. Desjumaux, D. Bousfield, T. Glatter, D. Donigian, and J. Ishley, Influence of pigment size on wet ink gloss development, *JPPS*, **24**, 150 (1998).
39. J. Drelich and D. Chibowska, Spreading kinetics of water drops on self-assembled monolayers of thiols: Significance of inertial effects, *Langmuir,* **21**, 7733 (2005).
40. V. Bonfrate, D. Manno, A. Buccolieri, S. K. Padmanabhan, A. Licciulli, A. Serra, *et al.*, Design and Synthesis of Iron-Doped Nanostructured TiO2 and Its Potential Use in the Photodegration of Hazardous Materials Present in Personal Care Products, *Chemistry Select,* **2**, 5095 (2017).
41. H. Koivula, Painosalama Oy, Studies in offset ink setting, Åbo Akademi University (2012).
42. J. Fetsko and A. Zettlemoyer, Factors affecting print gloss and uniformity, *TAPPI J,* **45**, 667 (1962).
43. B. Fouchet, P.-A. Noirot, D. Desjumaux, and R. Van Gilder, Absorption dynamics of offset ink components in thin latex films of different structures and compositions, *JPPS,* **32**, 123 (2006).
44. S. Reda, M. Khairy, and M. Mousa, Photocatalytic activity of nitrogen and copper doped TiO2 nanoparticles prepared by microwave-assisted sol-gel process, *Arab. J. Chem*, **13**, 86 (2020).
45. C.-Y. Tsai, H.-C. Hsi, T.-H. Kuo, Y.-M. Chang, and J.-H. Liou, Preparation of Cu-doped TiO2 photocatalyst with thermal plasma torch for low-concentration mercury removal, *Aerosol Air Qual Res,* **13**, 639 (2012).
46. S. Rousu, J. Gustafsson, J. Preston, and P. Heard, Interactions between UV curing, hybrid-UV and sheetfed offset inks and coated paper–commercial print trials, *TAGA J,* **2**, 174 (2006).
47. K. Chockalingam, A. Ganapathy, G. Paramasivan, M. Govindasamy, and A. Viswanathan, NiO/TiO2 nanoparticles for photocatalytic disinfection of bacteria under visible light, *J Am Ceram Soc,* **94**, 2499 (2011).
48. P. Pongwan, K. Wetchakun, S. Phanichphant, and N. Wetchakun, Enhancement of visible-light photocatalytic activity of Cu-doped TiO2 nanoparticles, *Res. Chem. Intermed,* **42**, 2815 (2016).