Photocatalytic Degradation of Paraquat Herbicide and Printing Tie Dye under UV/Sunlight by Graphene Oxide-TiO_2 Nanocomposites

A thesis

Submitted in the partial fulfilment of the requirements for the award of degree of

MASTER OF SCIENCE
in
CHEMISTRY

Submitted by
Dimple
(Roll No. 301602017)

Under the supervision of

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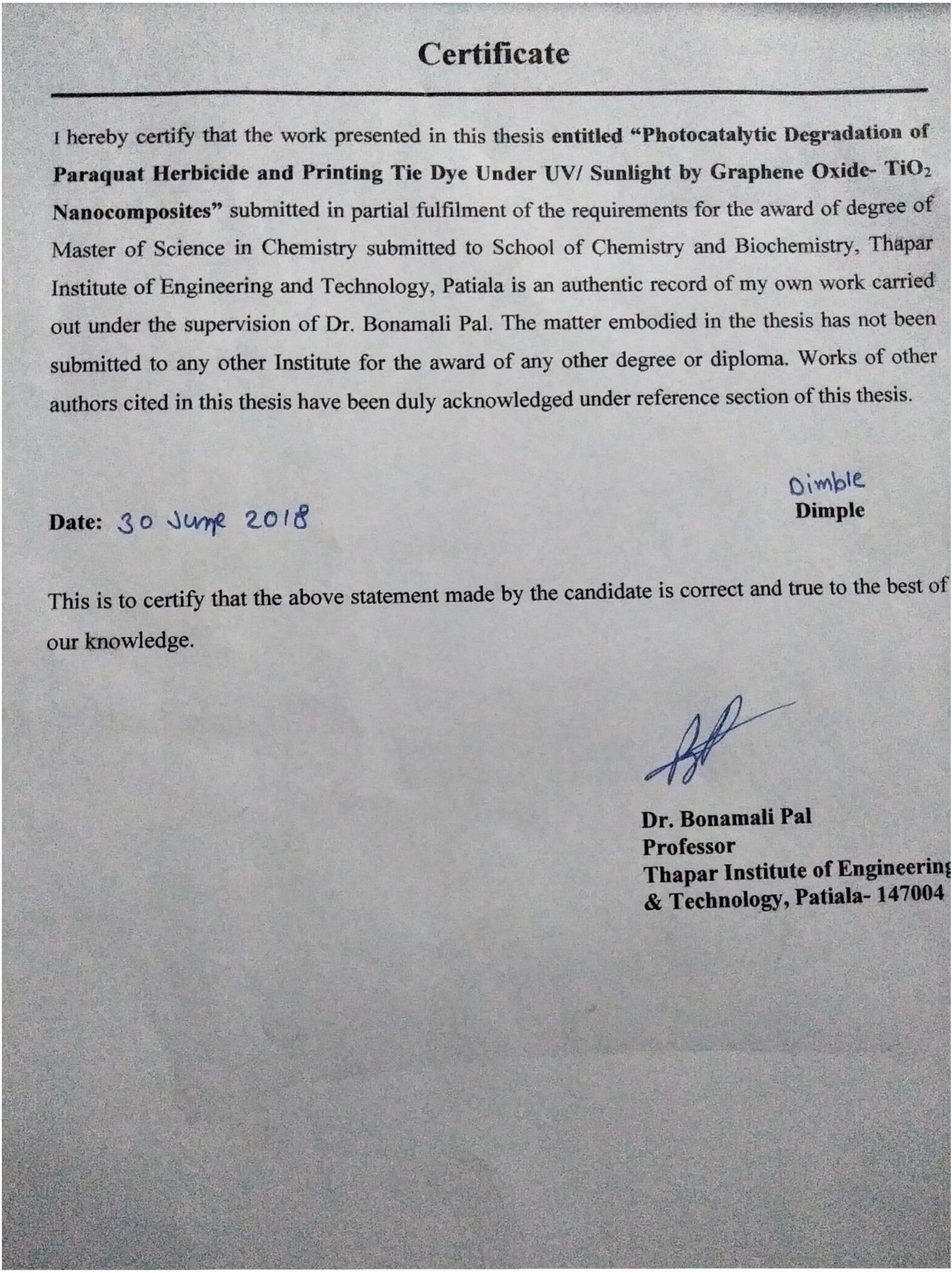
June, 2018

Dedicated to

My family

&

Teachers



Certificate

I hereby certify that the work presented in this thesis **entitled "Photocatalytic Degradation of Paraquat Herbicide and Printing Tie Dye Under UV/ Sunlight by Graphene Oxide- TiO_2 Nanocomposites"** submitted in partial fulfilment of the requirements for the award of degree of Master of Science in Chemistry submitted to School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala is an authentic record of my own work carried out under the supervision of Dr. Bonamali Pal. The matter embodied in the thesis has not been submitted to any other Institute for the award of any other degree or diploma. Works of other authors cited in this thesis have been duly acknowledged under reference section of this thesis.

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List of Abbreviations

NPs	Nanoparticles
CB	Conductance band
VB	Valence band
UV	Ultraviolet
SEM	Scanning electron microscope
GO	Graphene Oxide
DI	Deionized water
NC	Nanocomposite

List of Symbols

º C	Degree Celsius
%	Percent
G	Grams
Mg	Milligram
CB	Conduction band
VB	Valance band
µ	Micro
mM	Millimeter
SEM	Scanning electron microscope
Ppm	Particles per million

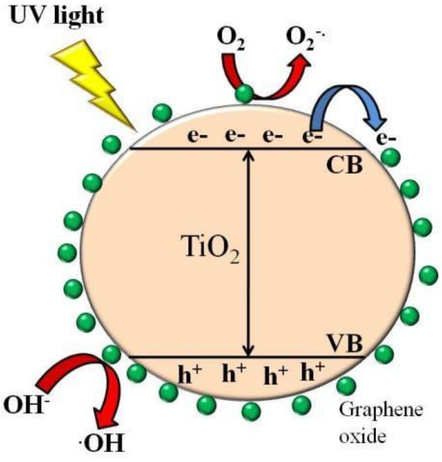
Abstract

Graphene oxide was prepared by hummer's method through oxidation of graphite. Graphene was used in combination with TiO_2 because of non- toxic, large surface area and excellent conductivity for the preparation of graphene oxide (GO)-TiO_2 nanocomposite. Surface modification with GO enhances photocatalytic activity of TiO_2. The prepared nanocomposite was then characterized by XRD, SEM, and FTIR. Herbicides are used to destroy or inhibit the growth of unwanted vegetation such as weed killers. GO-TiO_2 was used for the degradation of herbicide paraquat (1, 1`-dimethyl-4, 4`-bipyridinium dichloride) and cotton tie dye in the presence of UV and Sunlight irradiation. Degradation at different time intervals was measured by UV absorption at λ_{max} 257 nm for paraquat. While tie dye was studied at λ_{max} 400 nm. Graphene loaded TiO_2 shows best catalytic activity for the degradation of paraquat herbicide and cotton tie dye. Almost complete degradation of paraquat herbicide was achieved as absorbance decreased from 1.509-0.314 a.u after 90 minutes under UV light irradiation. Similarly, very fast degradation of the tie dye was obtained, absorbance decreased from 0.998-0.298 a.u under sunlight irradiation of 120 minutes. The degradation speeded up because graphene prevents the recombination of electron-hole pair. Due to this GO-TiO_2 shows better catalytic activity as compare to TiO_2 both in UV irradiation and Sunlight. It was seen to follows zero order kinetics. k- $36*10^{-4}Ms^{-1}$ for paraquat herbicide and k- $61*10^{-2}Ms^{-2}$ was achieved. High photocatalytic activity for the degradation of paraquat (79 %) and cotton tie dye (86%) was obtained.

1. Introduction

Titanium dioxide (TiO_2) based heterogeneous photocatalysis has gained a lot of importance in environmental applications such as water purification and degradation of pollutants [1]. This significance can be attributed to the lower toxicity, exceptional chemical and physical stability and higher efficiency as well as lower cost of TiO_2 [2-4]. Particle size, surface area and crystal structure greatly affect the efficiency of TiO_2. Although highly efficient photocatalyst however, applications of TiO_2 are restricted mainly due to increased recombination rate of light induced (e^- -h^+) pairs [5] and decreased light absorption due to wide band gaps [6,7]. Several modifications with carbonaceous materials like activated carbon powder (ACP), carbon nanotubes (CNTs), graphene and graphene oxide (GO) [8-13] can be done to improve its photocatalytic efficiency.

Among these GO has received vivid attention in recent years because transfer of electrons can take place from conduction band of TiO_2 to surface of GO as reported by *Kamat et al.*[14]. As graphenes have high electron mobility, it leads to generation of Ti-O-C bonds extending the absorption towards region of higher wavelength [15]. GO-TiO_2 nanocomposite is considered a better photo catalyst than TiO_2 since graphene fulfils the condition for perfect sensitizer as it has zero band-gap. The photo-induced e^-s between GO and TiO_2 quickly transports to π- π e^-s for coupling which helps to suppress photo-generated (e^--h^+) pairs of TiO_2 [16]. Scheme 1 demonstrates that under the presence of UV light irradiations the e^-s absorbs energy and gets excited to conduction band (CB), while holes are produced in valence bands (VB).



Scheme 1: Schematic representation showing transfer of electrons from CB to VB.

Organic dyes, herbicides, pesticides are all considered as pollutants which possess threat to environment as these are toxic and have carcinogenic effects. In order to remove and degrade them GO-TiO_2 nanocomposite works as a good photocatalyst. This light induced degradation leads to decolourisation and hence photo oxidation of the pollutants. Paraquat (1, 1`-dimethyl-4, 4`-bipyridinium dichloride) is a kind of herbicide also known as methyl viologen dichloride. It has toxic effects on humans as well as animals because of its redox properties which creates superoxide ions. Also it has been related to induce Parkinson's disease.

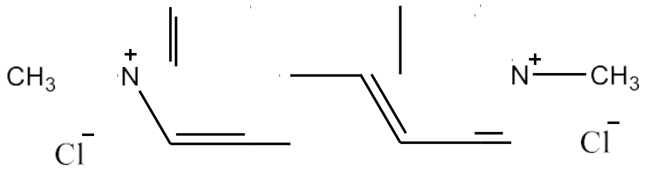


Fig. 1: Structure of Paraquat herbicide.

Similarly, the industrial tie dye (Procion) is also considered as a pollutant as it also contributes to air and water pollution needs to be degraded [17]. Previous studies revealed that GO-TiO_2 nanocomposite had better activity than pure TiO_2 for degradation of methylene blue dye as reported by *Tang et al.* [18] in 2011. *Kuen-Jo et al.* reported the photo degradation of aromatic pollutants using GO-TiO_2 as well as P25 TiO_2 and found superior activity of GO-TiO_2 in 2013 [19]. Also, *Zeng et al.* in 2012 reported the use of GO-TiO_2-Fe_3O_4 nanocomposite for the degradation of pollutants in waste water treatment [20]. In 2012, *Yoo et al.* reported the use of $GO_{reduced}$-TiO_2 for the photo degradation of model rhodamine B dye [21]. In 2012, *Fan et al.* compared the effect of GO-TiO_2 nano wires and nanoparticles for reduction of pollutant dyes and found GO-TiO_2 nano wires to be more efficient [22]. In addition *Pal et al.* in 2016 analysed the effects of Au-TiO_2-GO for H_2 production from water splitting [23].

2. Objectives

- Preparation and characterization of graphene oxide (GO) and GO-TiO_2 nanocomposite.
- To study the photocatalytic efficacy of GO-TiO_2 nanocomposite for degradation of Paraquat and Tie dye under UV and sunlight irradiation.

3. Experimental Section

3.1. Chemical Reagents

Graphite, Sodium nitrate ($NaNO_3$), Potassium permanganate ($KMnO_4$), Hydrogen peroxide (H_2O_2 30%) and Paraquat were purchased from SD Fine Chemicals, India. Sulphuric acid (H_2SO_4), Hydrochloric acid (HCl), Ethanol and Methanol were purchased from Loba Chemie India. Tie dye was purchased from Trident Ltd, Barnala, Punjab. All chemicals were used without any further purification. Commercially available TiO_2 (P25; 70% Anatase + 30% Rutile phase) was received as a gift from Degussa corporation Germany. Deionized water (DI) was obtained from ultra-filtration system (milli-Q, Millipore) with measured conductivity of 35 mho cm^{-1} at 25°C.

3.2. Methods

3.2.1. Preparation of graphene oxide (GO)

Graphene oxide was prepared by Hummers method as reported previously [24]. 0.5g graphite and 0.5g $NaNO_3$ were mixed in 25ml of H_2SO_4 with continuous stirring under ice bath for 4 h. $KMnO_4$ (3g) was added slowly to the above mixture while keeping the temperature lower than 15ºC. After complete addition of $KMnO_4$ the mixture was heated at 35ºC for 1 h with continuous stirring till it completely gets brownish in colour. 46ml of distilled water was further added to the mixture and temperature was increase to 95ºC. Turn off heater and add 100 ml of distilled water under stirring for 1hr. Then the solution is treated with 10 ml of 30% H_2O_2 till the appearance of yellow colour is seen. The mixture was then centrifuged and washed with 10% HCl and deionized water several times. Finally the solution was dried at 60°C for 24 h to obtain graphene oxide powder.

3.2.2. Preparation of GO-TiO_2 nanocomposite

Firstly, GO (25.2 mg) powder was dispersed in 30 mL deionized water and sonicated for 30 minutes. This suspension was diluted with 200 mL of deionized water, and then it was mixed with 50 mg of TiO_2 dispersed in deionized water. Mixture was sonicated for 1.5 h and stirred for 12 h at room temperature. The solution was centrifuge for 5 min at 5000rpm and dried at 60ºC for 4h.

3.2.3. Characterization techniques

Various techniques are used to characterize GO-TiO_2 NCs. The technical details of these techniques are given below:

Ultraviolet-Visible (UV-Vis) Spectrophotometeric analysis: The optical properties of GO-TiO_2 were analyzed by UV-Vis (Specord 205) spectrophotometer. 5 mg of each prepared 30, 60, 90 min photo deposited GO-TiO_2 catalyst was diluted by 2 mL of de-ionized water and their UV–Vis absorption spectra were obtained.

Fourier-Transform Infrared (FTIR) Spectroscopy: FT-IR spectroscopy was used to obtain information about the composite. All the FT-IR analysis of the samples was carried out on FT-IR, Agilent Cary 630 spectrometer. The electromagnetic spectrum range was 400 nm to 4000 nm at the time of measurement.

Powder X-Ray Diffraction (P-XRD): This technique is primarily used for identification of phase, composition and crystal system of the materials; it can also give information on unit cell dimensions. For the identification of crystal system, phase, composition and crystallinity of the materials this technique was used. PANalytica X' pert PRO X-ray diffractometer with Cu Kα ($\lambda = 1.54$ Å) radiation was used for XRD pattern analysis. A smooth plain surface paper was used to press the powder samples into a sample holder. The XRD study was done from Sophisticated Analysis Instrumentation Laboratory (SAIF Lab), Panjab University, Chandigarh, India.

Scanning electron microscope (SEM) analysis: For SEM and elemental examinations, a single drop (10 μL) of the solution of the GO-TiO_2 NPs were placed on a 300 mesh copper grid coated with a carbon film. The grid was left to dry at room temperature. SEM analysis was carried out using JSM-6510LV, electron microscope working at 30 kV.

3.2.4. Photocatalytic activity of GO-TiO_2 nanocomposite

Photocatalytic activity of prepared GO-TiO_2 and pure TiO_2 catalyst was used for the degradation of paraquat herbicide by taking 8mg of catalyst added to paraquat sample (10 ml, 10ppm) with constant stirring under UV and sunlight irradiation. Similarly, cotton tie dye are degraded by adding 8 mg catalyst to a tie dye (10 ml, 0.2 mM) with constant stirring under UV and sunlight irradiation. UV-Visible spectra of these samples were observed to determine the photocatalytic activity of GO-TiO_2 after different time interval.

4. Results and Discussion

4.1. Optical and Structural Analysis

Figure 2 shows the FTIR spectrum of bare graphene oxide and GO-TiO_2. Strong C-O absorption band at 1170 cm^{-1} for carboxyl groups was observed for GO. The bands at 1562cm^{-1} and 3424 cm^{-1} arise mainly due to C=C aromatic bond and O-H vibrations respectively [25].

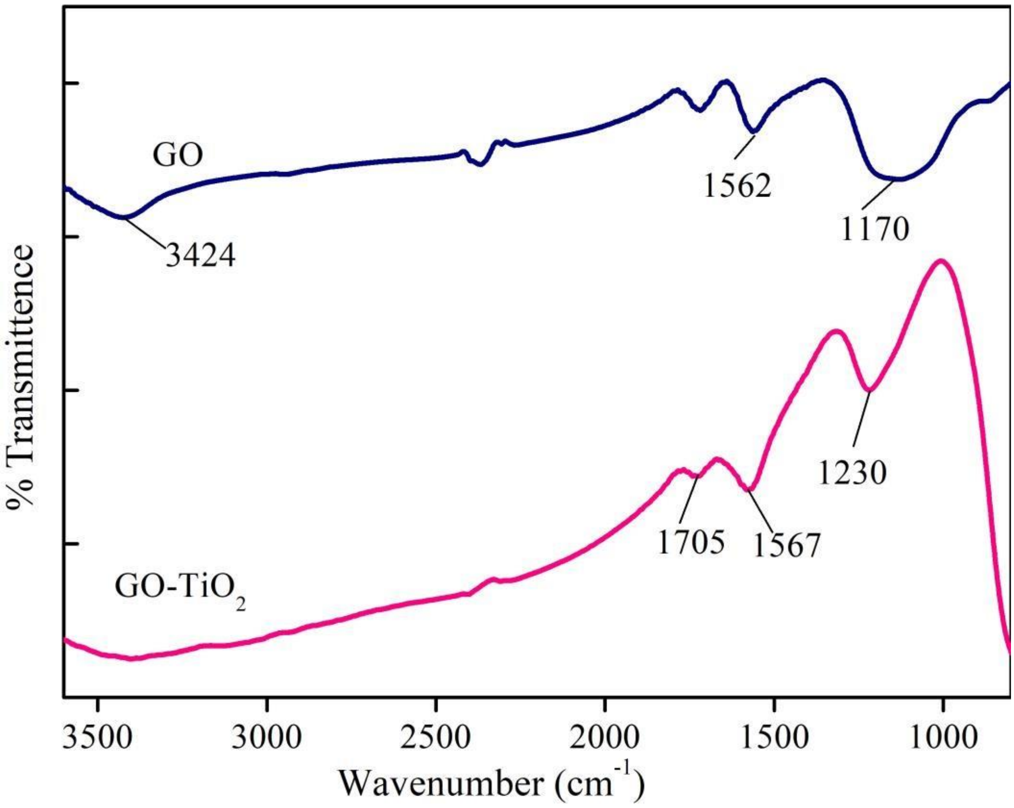


Fig.2: FTIR spectrum of GO and GO-TiO_2.

Bands associated with oxygen containing functional groups disappeared indicating complete reduction of GO in spectrum if GO-TiO_2. The band appearing at 1230 cm^{-1} is ascribed to Ti-O-C bonding indicating the complete formation of GO-TiO_2 nanocomposite. Also, the bands at 1567 cm^{-1} and 1705 cm^{-1} arises due toTiO_2-GO OH stretching and bonding [26,27].

Figure 3 shows the XRD spectra of GO-TiO_2. The diffraction peaks at 2 ϴ positions 25.32º, 37.84º, 48.74º, 53.95º, 55.05º, 62.75º having planes (101), (004), (200), (105), (211), (204) were observed. All the peaks are identified through standard JCPDS card 01-084-1286. Correlating with literature it was observed that the peak at 25.32º corresponds to anatase phase. *Nguyen-Phan et al.* reported these peaks for pure P 25 TiO_2 particles [28] while a distinct peak at 2ϴ- 10º was reported for GO [29]. No GO related peak appeared in the spectra of GO-TiO_2 mainly as the amount of GO was low as well as the low diffraction intensity which is below the detection limits of the instrument.

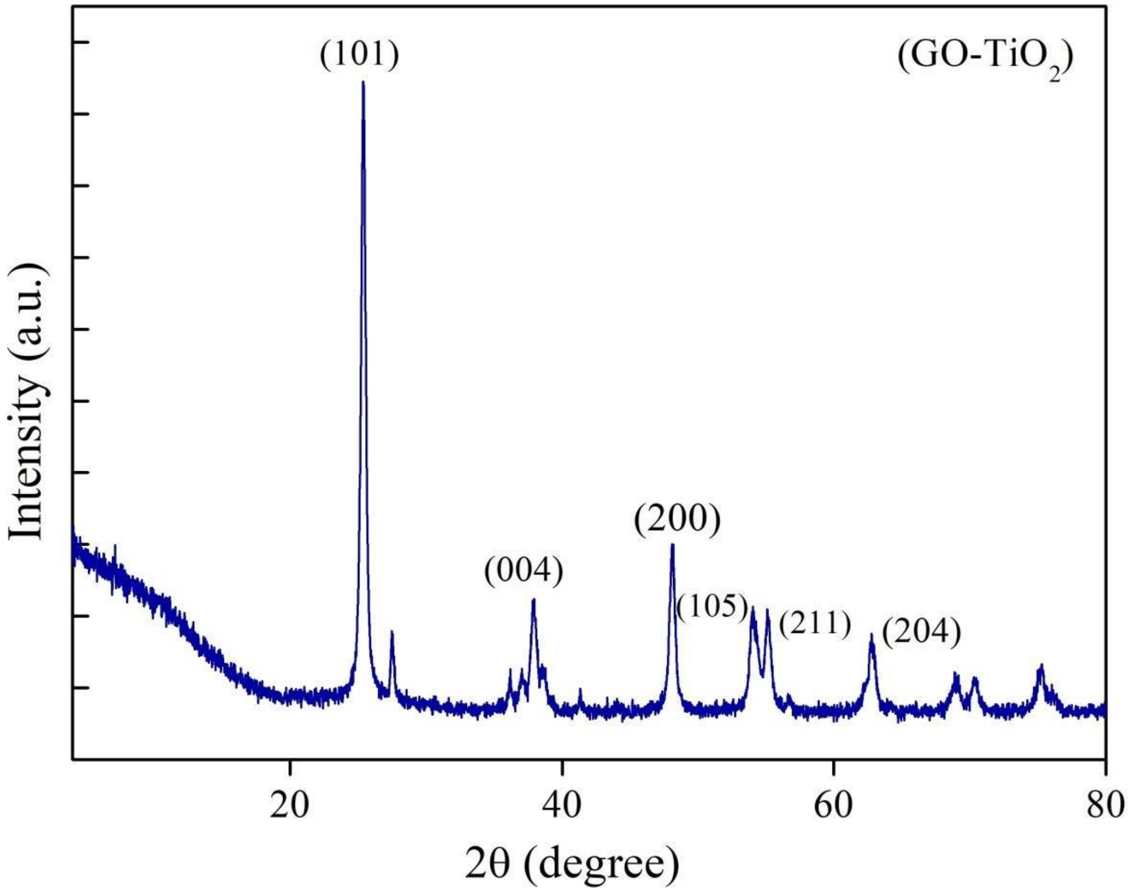


Fig.3: XRD spectra of GO-TiO_2.

Morphological properties of GO-TiO_2 NC were studied by SEM (figure 4). Although the images were not very clear, it was assumed from the images that the particles were spherical in shape.

Fig.4: SEM studies of (a) GO and (b) GO-TiO$_2$.

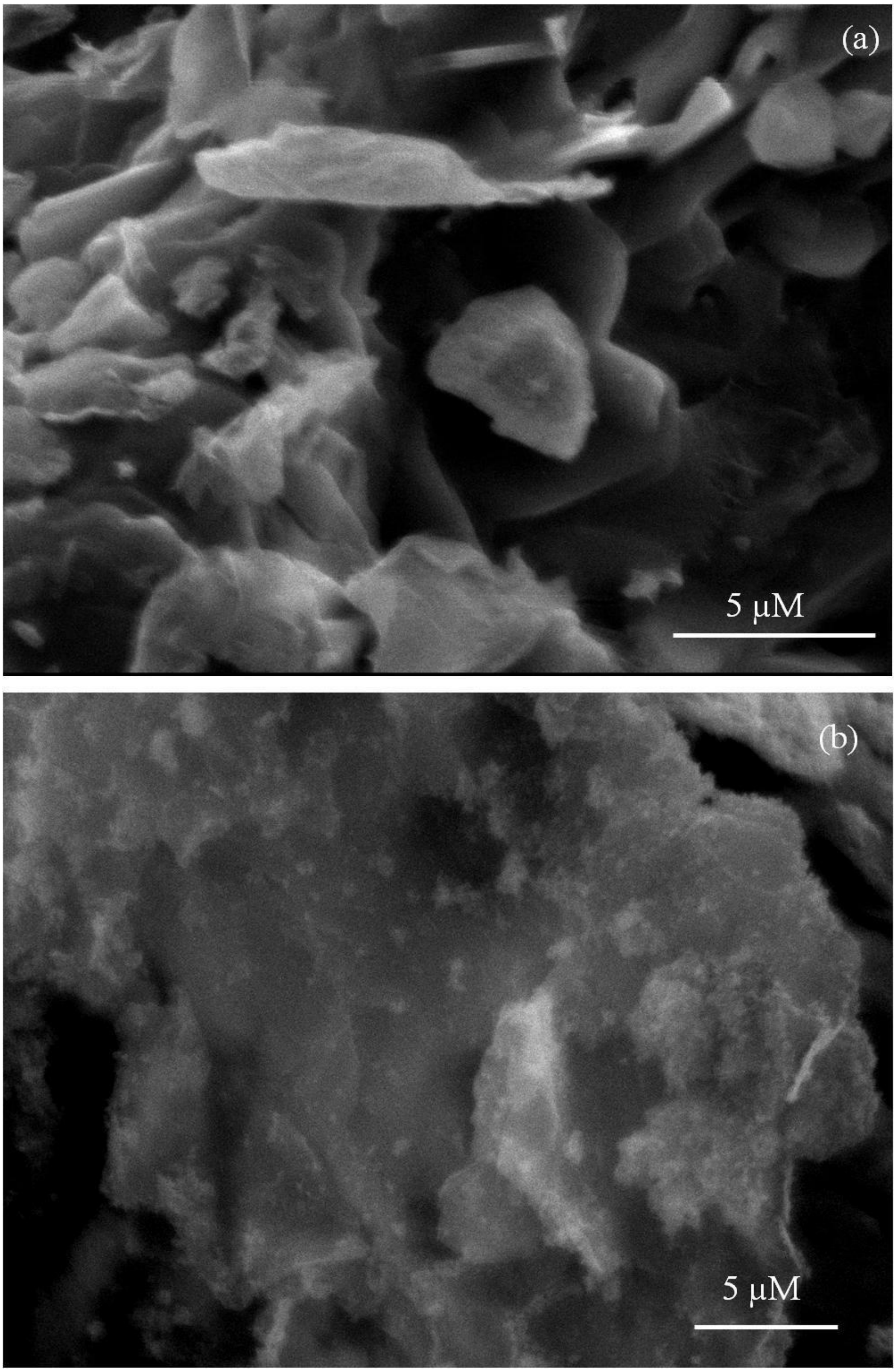


Fig.4: SEM studies of (a) GO and (b) GO-TiO$_2$.

4.2. Photocatalytic activity of GO-TiO_2

Section A: Photo degradation of Paraquat

i) Calibration graph of Paraquat

To study the dark adsorption and photocatalytic degradation of paraquat firstly a calibration graph is plotted. Different concentration of paraquat like 2, 4, 6, 8 and, 10 ppm was prepared. Absorbance of each solution was measured with double beam UV visible spectrophotometer and calibration graph between absorbance vs. concentration was plotted.

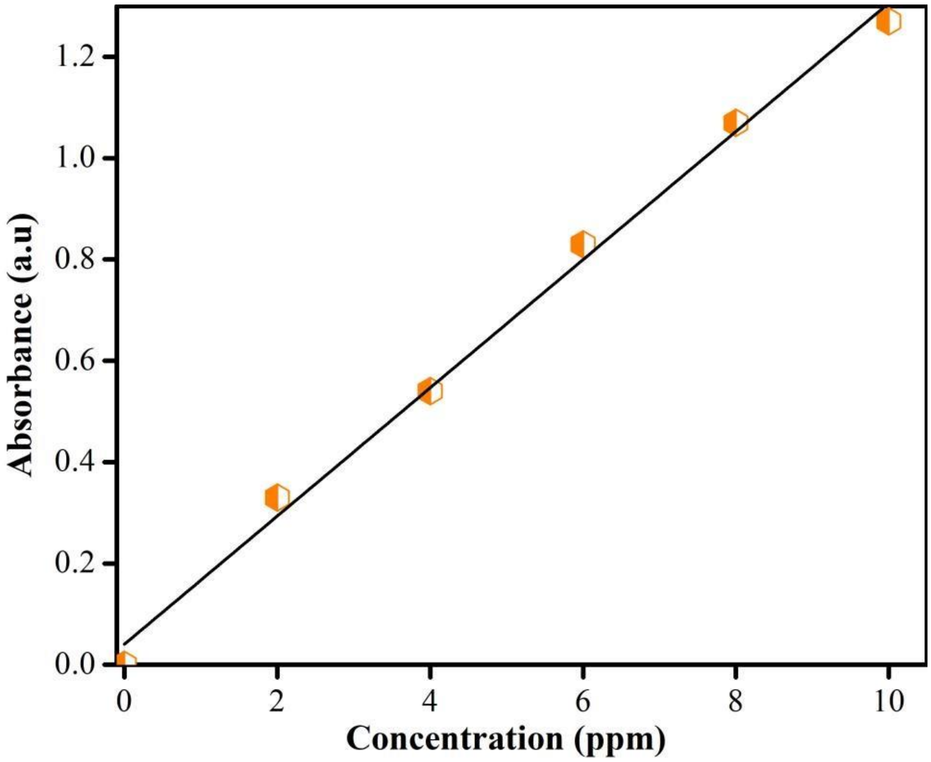


Fig.5: Calibration graph (absorbance vs concentration) of Paraquat herbicide.

ii) Dark Adsorption of Paraquat

Figure 6 shows the dark adsorption of paraquat (8 mg, 10 ppm). It was seen that after 40 minutes almost all of the dye is adsorbed using bare TiO_2 while no considerable changes in the pattern of adsorption with GO-TiO_2 was observed.

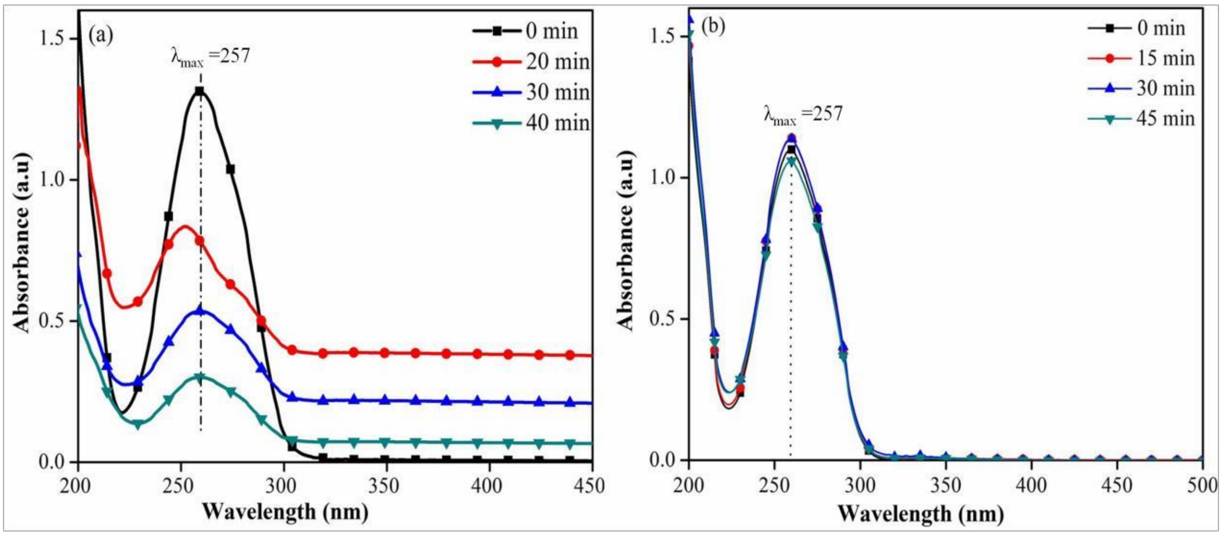


Fig.6: Changes in UV absorption spectra of paraquat herbicide due to dark adsorption over (a) TiO_2 and (b) GO-TiO_2.

iii) Photo degradation of Paraquat herbicide

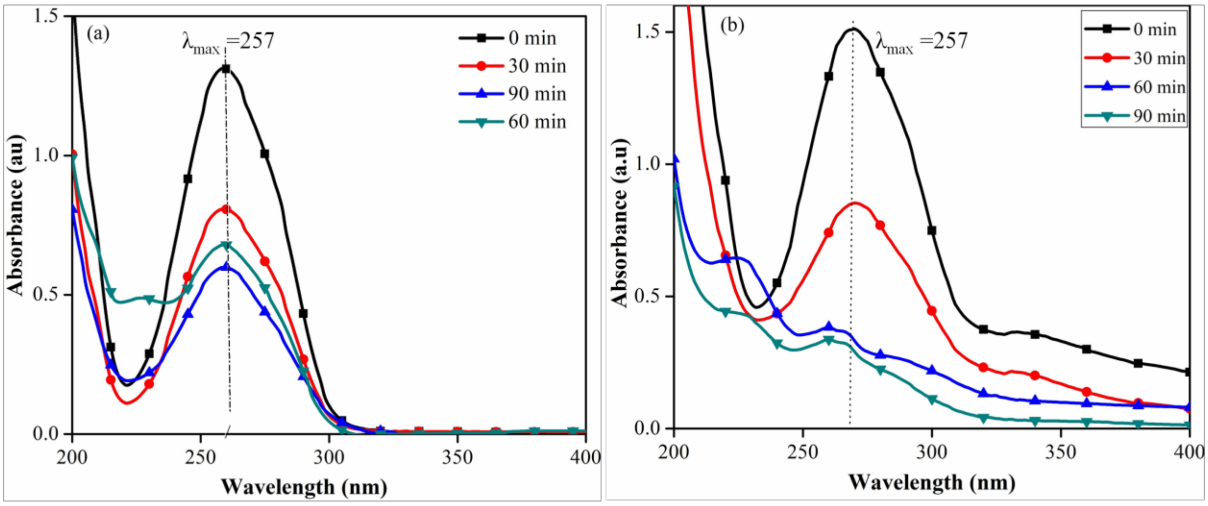


Fig.7: Changes in UV absorption spectra of Paraquat by (a) TiO_2 and (b) GO-TiO_2 due to its photo degradation under UV light irradiation for 90 minutes.

The photocatalytic activity of the prepared TiO_2 and GO-TiO_2 was evaluated under UV and sunlight irradiation for 90 minutes. Figure 7 shows the photo degradation of paraquat under UV light irradiation after 90 minutes with TiO_2 and GO-TiO_2. It was observed that as the time interval is increased decrease in the absorbance from1.303 a.u to 0.595a.u after 90 minutes for GO-TiO_2 NC. Similarly, figure 8 shows the degradation of paraquat under sunlight irradiation for 90 minutes. Compared to degradation under UV light irradiation the absorbance value decreased to 0.314 a.u. after 90 minutes indicating greater photo degradation under sunlight irradiation.

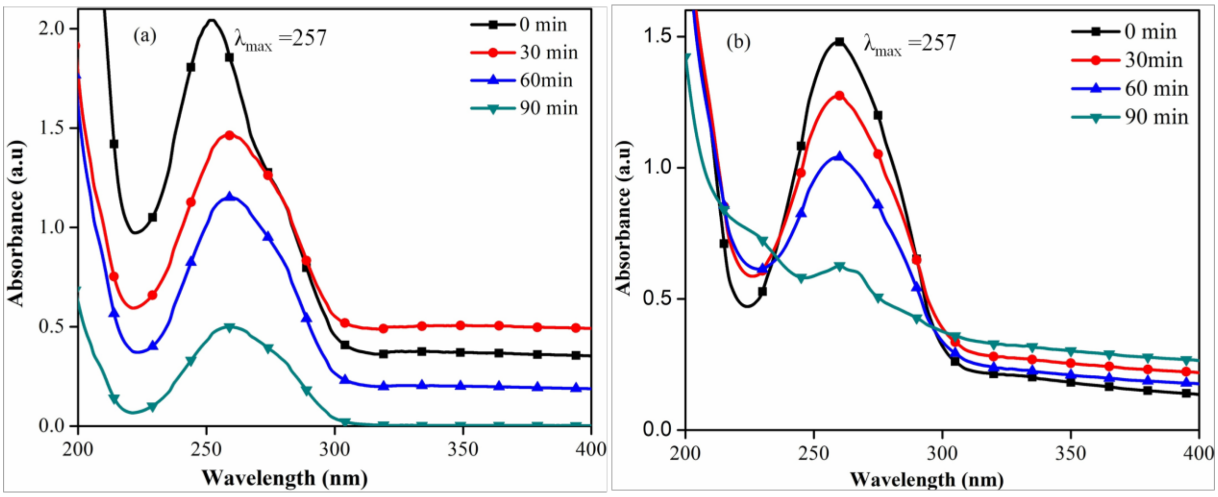


Fig.8: Changes in UV absorption spectra (λ_{max} 257 nm) of Paraquat by (a) bare TiO_2 and (b) GO-TiO_2 due to its photo degradation under sunlight light irradiation for 90 minutes.

Figure 9 and 10 shows the C_0-C_t vs time (min) graph where C_0 is the initial concentration and C_t is the concentration at different time intervals of paraquat photo degraded by bare TiO_2 and GO-TiO_2 under UV and sunlight irradiation after 90 minutes. Zero order kinetics was seen to be followed.

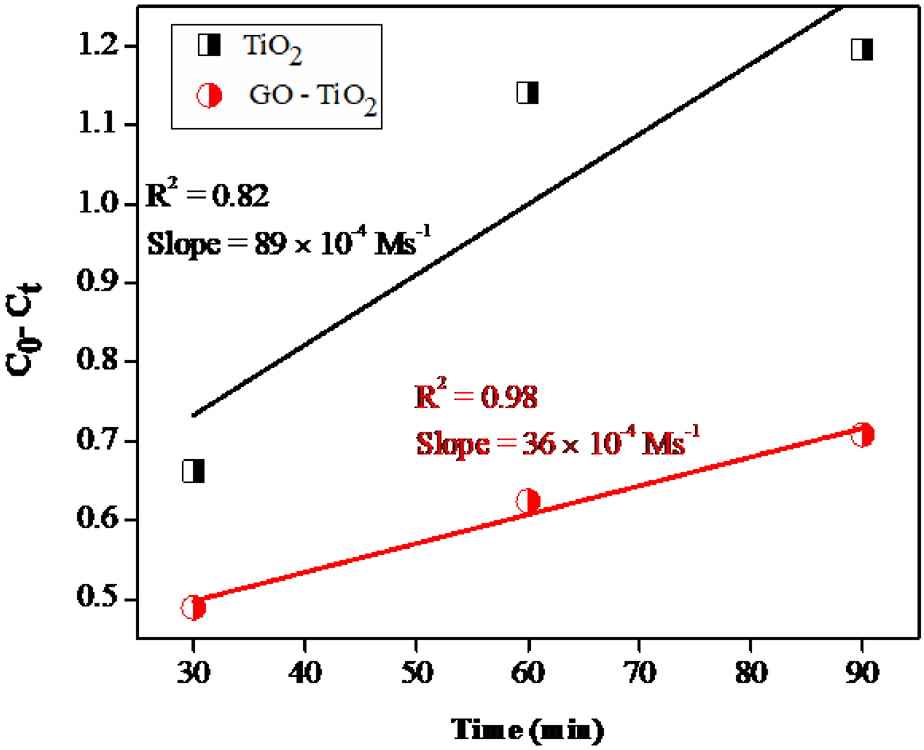


Fig. 9: Time course of paraquat photo degradation by TiO_2 and GO-TiO_2 sample obtained with UV light irradiation for 90 minutes.

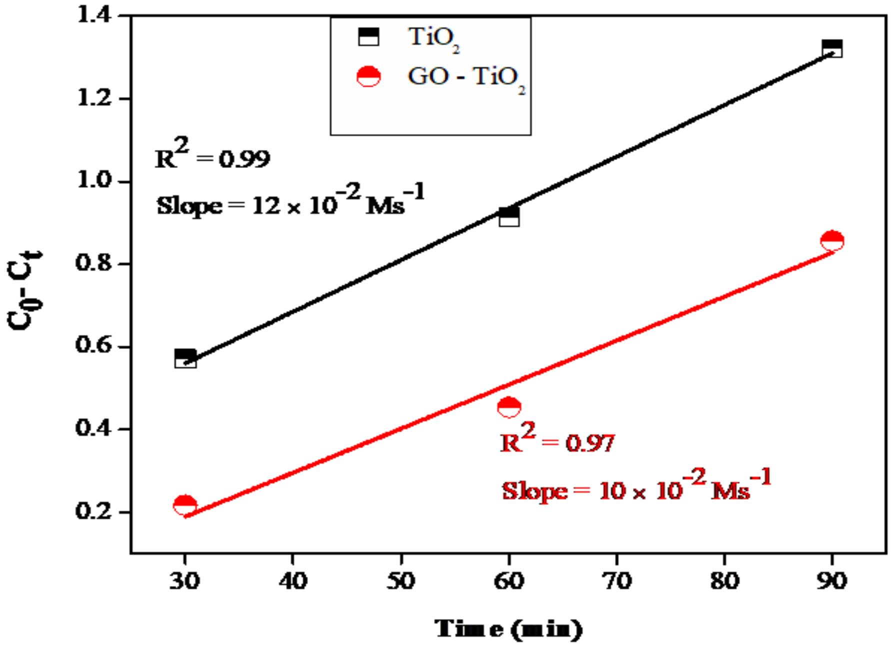


Fig. 10: Time course of paraquat photo degradation by TiO_2 and GO-TiO_2 sample obtained with sunlight irradiation for 90 minutes.

Figure 11 shows the comparative histogram of %age photocatalytic efficiency of paraquat photo degradation by TiO_2 and GO-TiO_2 sample obtained with sunlight irradiation for 90 minutes. 68% and 79% paraquat photo degradation was observed with GO-TiO_2 under sunlight and UV light irradiation. Overall it can be concluded that photo degradation of paraquat under sunlight irradiation showed better results compared to when irradiated under UV light with GO-TiO_2 photocatalyst.

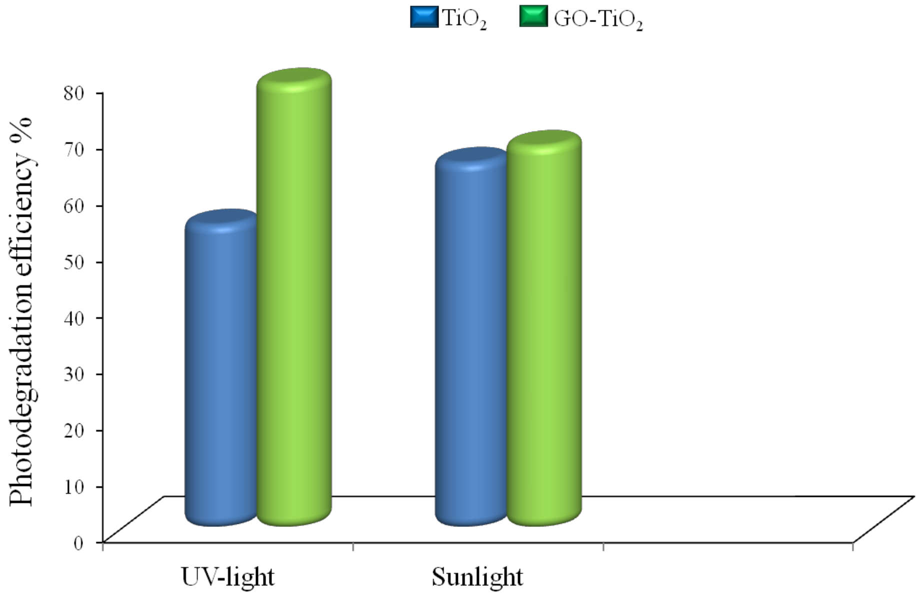


Fig.11: Comparative photodegration efficiency of paraquat herbicide by TiO_2 and GO-TiO_2 under UV and sunlight irradiation.

Section B: Photo degradation of Tie Dye

The photocatalytic activity of the prepared TiO_2 and GO-TiO_2 was evaluated under UV and sunlight irradiation for 3h. Figure12 shows the photo degradation of tie dye under UV light irradiation 3h with TiO_2 and GO-TiO_2.

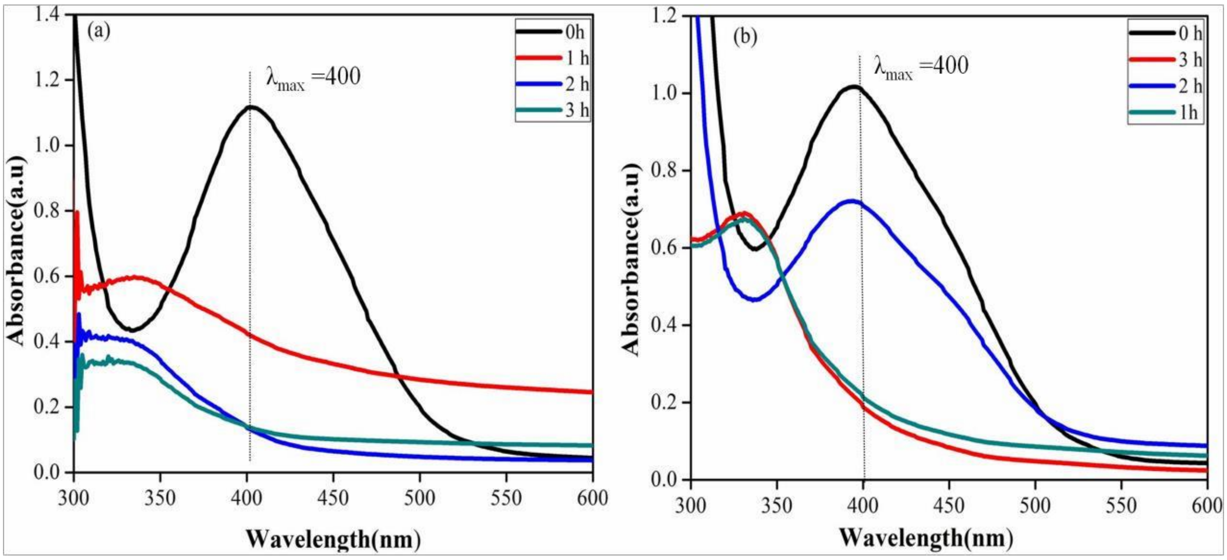


Fig.12: Changes in UV absorption spectra/color of tie dye due to its photo degradation (a) TiO_2 and (b) GO-TiO_2 under UV light irradiation for 120 minutes at λ_{max} 400 nm.

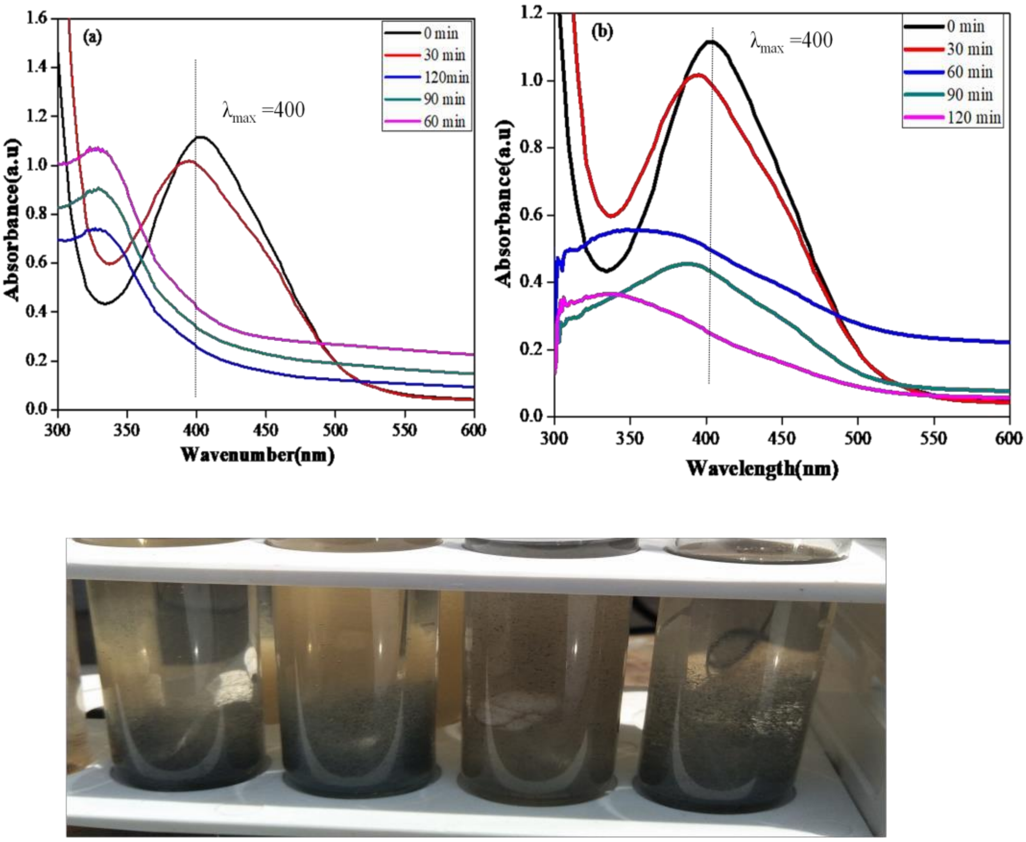


Fig.13: Changes in UV absorption (λ_{max} 400 nm) spectra/color of tie dye due to its photo degradation (a) TiO_2 and (b) GO-TiO_2 under sunlight irradiation for 120 minutes.

Almost complete degradation of the dye was observed with GO-TiO_2 after 3h however, a blue shift in the absorbance spectrum is observed indicating the formation of sum intermediate which further needs to be studied. Similarly figure 13 shows that faster degradation of the dye occurred under sunlight irradiation as almost complete degradation was obtained after 120 minutes with GO-TiO_2 compared to its degradation pattern under UV light irradiation.

Figure 14 shows the C_0-C_t vs time (min) graph where C_0 is the initial concentration and C_t is the concentration at different time intervals of tie dye photo degraded by bare TiO_2 and GO-TiO_2 under UV and sunlight irradiation after different time intervals. Zero order kinetics was seen to be followed.

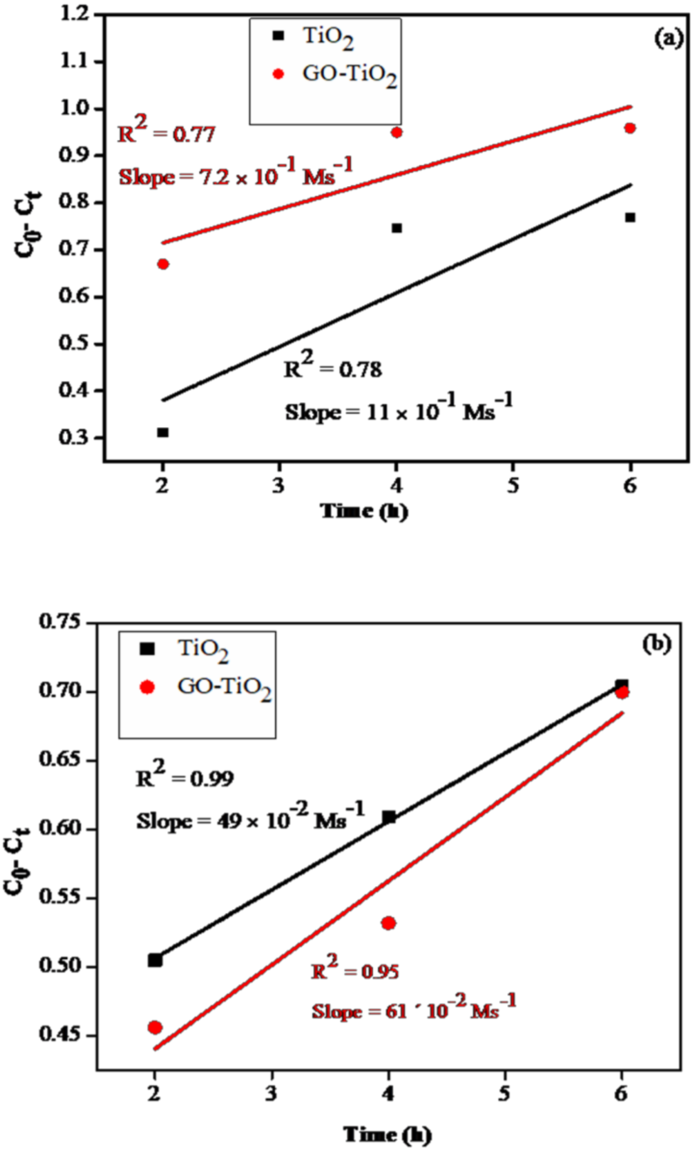


Fig. 14: Time course of tie dye photo degradation by TiO_2 and GO-TiO_2 under (a) UV and (b) sunlight irradiation.

Figure 15 shows the comparative histogram of %age photocatalytic efficiency of tie dye photo degradation by TiO_2 and GO-TiO_2 sample obtained with UV and sunlight irradiation for different time intervals.

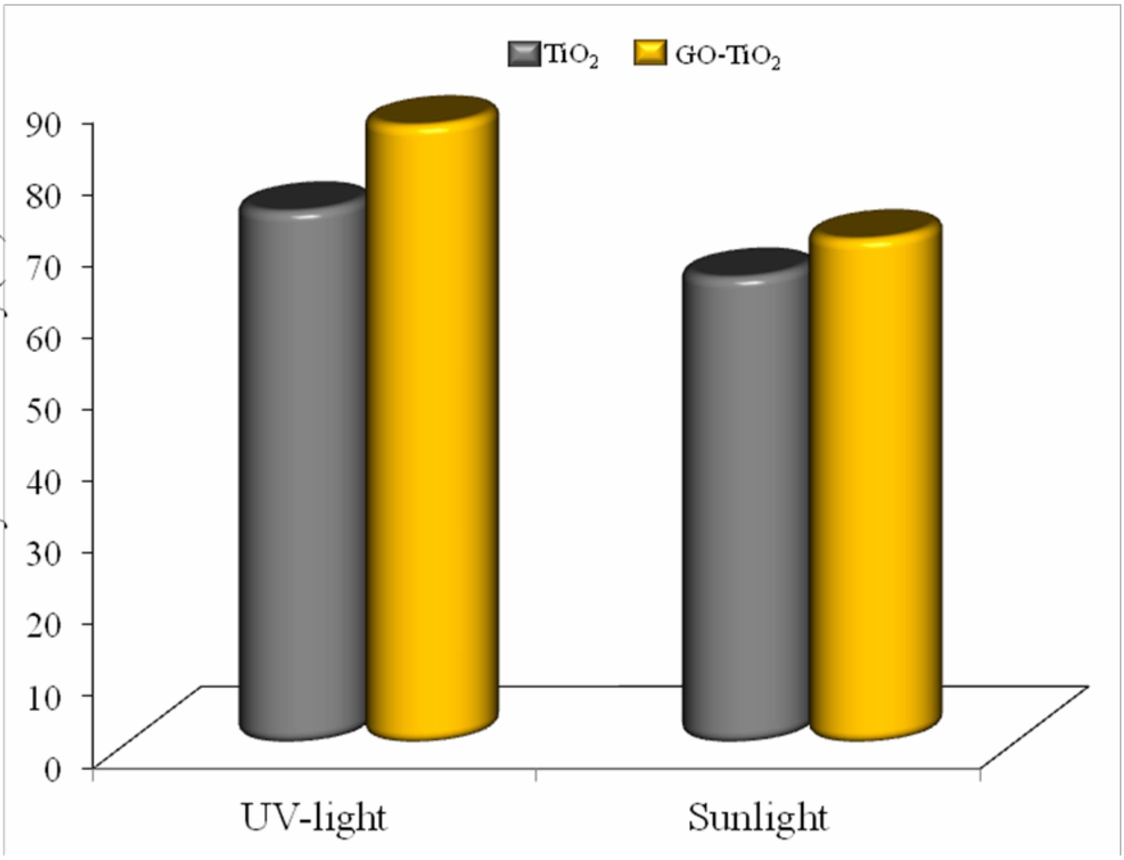


Fig. 15: Comparative photodegration efficiency of tie dye by TiO_2 and GO-TiO_2 under UV and sunlight irradiation.

86% and 70 % degradation was achieved with GO-TiO_2 photocatalyst under UV and sunlight irradiation respectively.

5. Conclusion

In the present study, graphene oxide was used in combination with TiO_2 because of non- toxic, large surface area and excellent conductivity for the preparation of graphene oxide (GO)-TiO_2 nanocomposite. Surface modification with GO enhanced the photocatalytic activity of TiO_2. The prepared nanocomposite was then characterized for its structural properties. Further, GO-TiO_2 was used for the degradation of herbicide paraquat (1, 1`-dimethyl-4, 4`-bipyridinium dichloride) and cotton tie dye under UV and Sunlight irradiation. Degradation at different time intervals was studied by UV absorption at λ_{max} 257 nm for paraquat. While tie dye was studied at λ_{max} 400 nm. Almost complete degradation of paraquat herbicide was achieved as absorbance decreased from 1.509-0.314 a.u after 90 minutes under UV light irradiation. Similarly, very fast degradation of the tie dye was obtained, absorbance decreased from 0.998-0.298 a.u under sunlight irradiation of 120 minutes. The degradation speeded up because graphene prevents the recombination of electron-hole pair. Due to this GO-TiO_2 shows better catalytic activity as compare to TiO_2 both in UV irradiation and Sunlight. It was seen to follows zero order kinetics. k- $36*10^{-4}Ms^{-1}$ for paraquat herbicide and k- $61*10^{-2}Ms^{-2}$ was achieved. High photocatalytic activity for the degradation of paraquat (79 %) and cotton tie dye (86%) was obtained. Hence, it can be concluded that GO-TiO_2 showed better catalytic efficiency compared to TiO_2.

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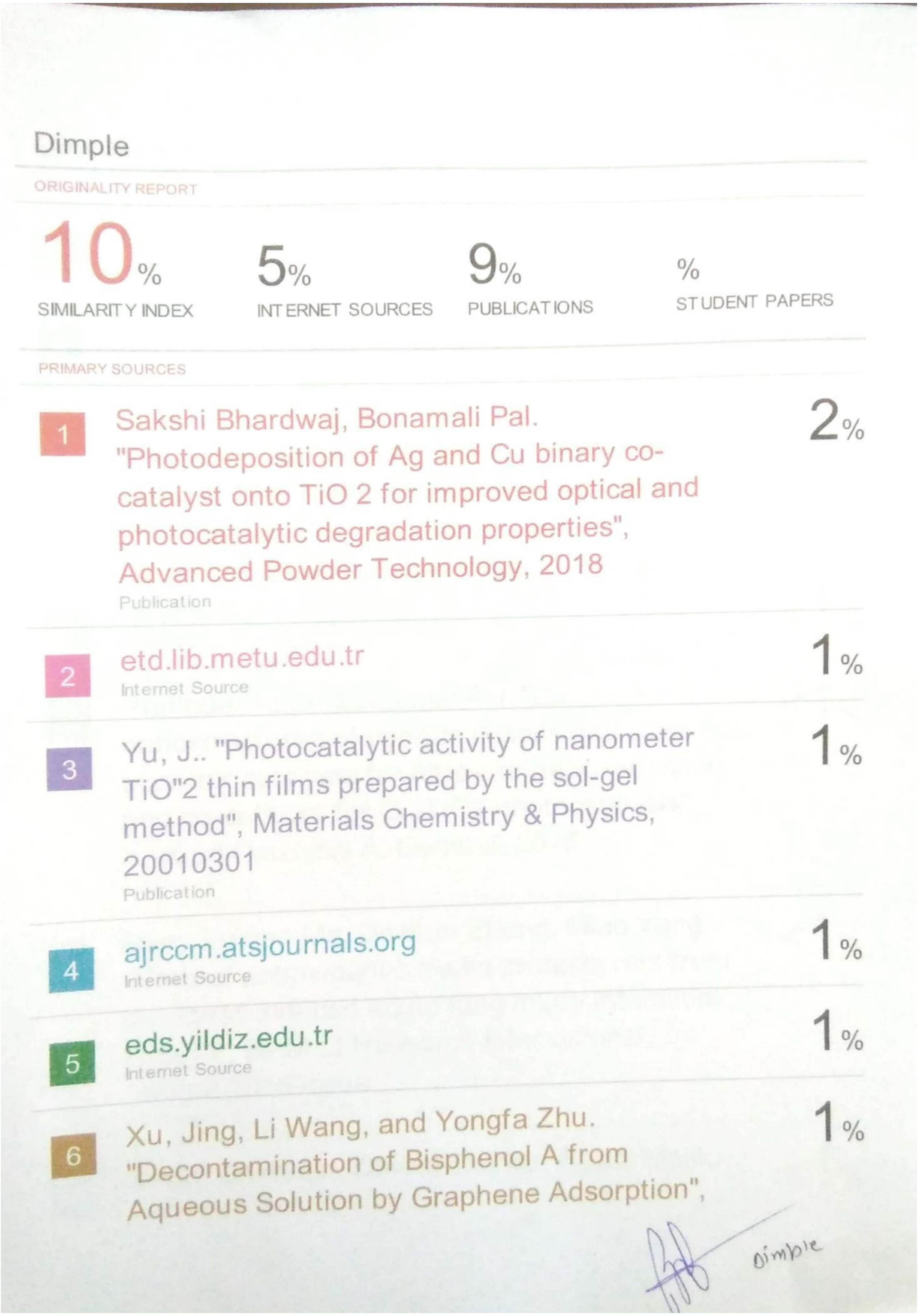

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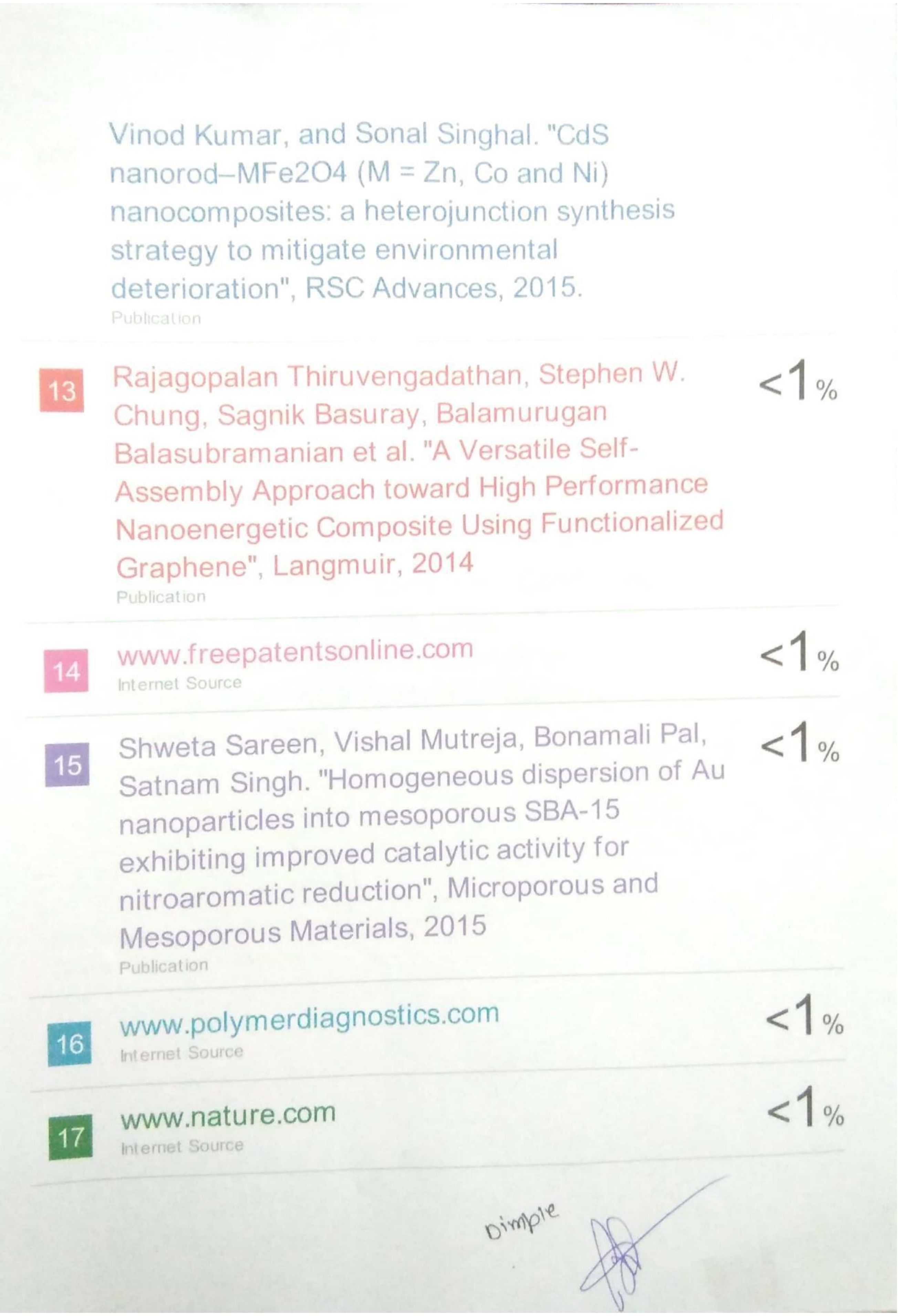

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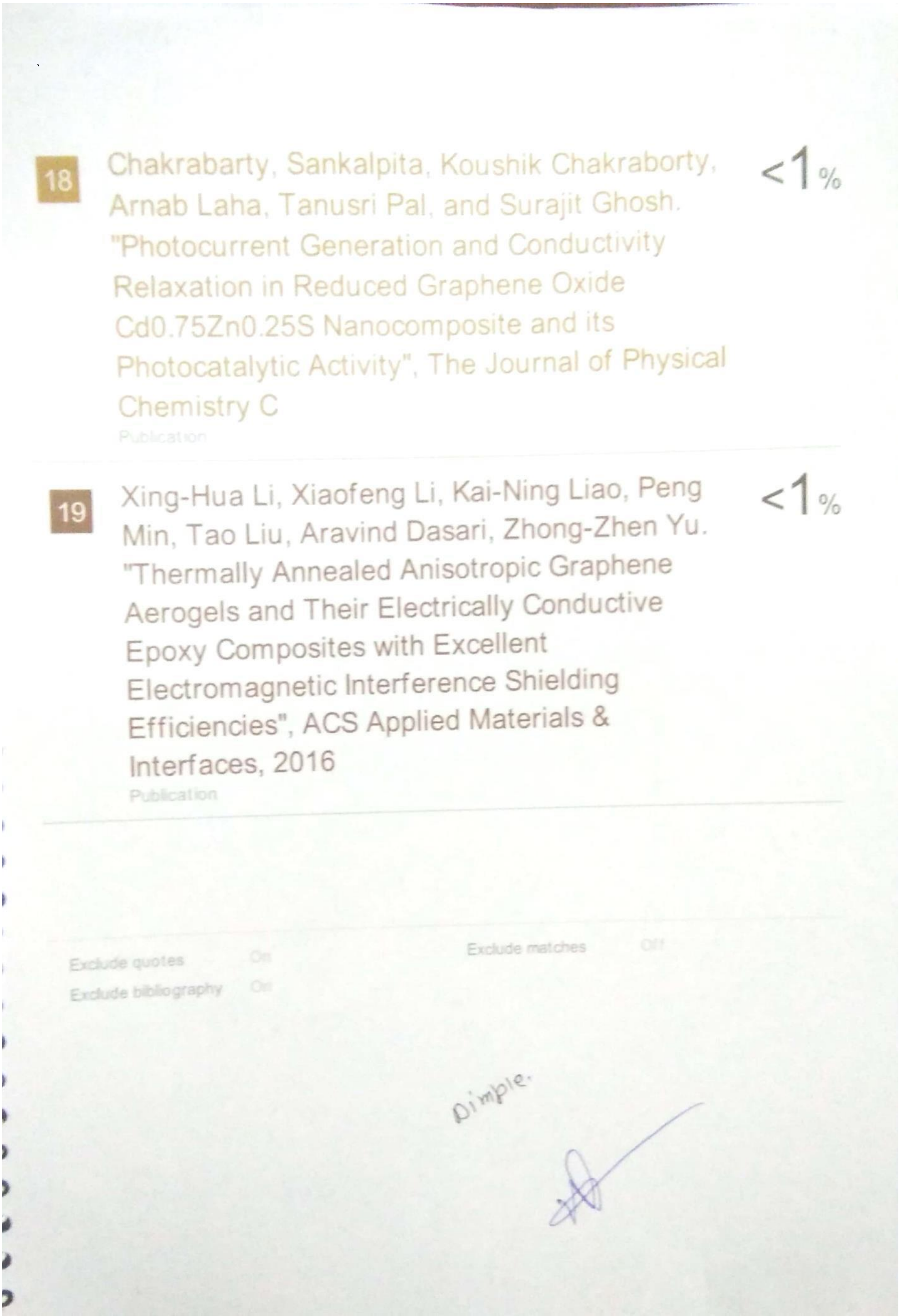

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