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DFT, Experimental and Photocatalytic Efficiency of $CoCl_2$ and $CoCl_2$-Thiourea Codoped TiO_2 Nanoparticles

A. Nixon Thangaraj[1,*], C. Ravi Samuel Raj[2]

[1]*Department of Chemistry, V.V. College of Engineering, Tisayanvilai – 628 656, Tamil Nadu, India.*
[2]*Department of Chemistry, Pope's College, Sawyerpuram – 628 251, Tamil Nadu, India.*

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ABSTRACT

Density Functional Theory (DFT) gives greater idea about the electronic behaviour of molecules. In this work TiO_2 (TTDO) nano particles doped with $CoCl_2$ (CCT) and $CoCl_2$-thiourea codoped (CCTT) were studied by DFT, synthesis, characterisation and photo degrading efficiency for Acid Orange 7 dye. The computations were performed using B3LYP/631G** in gas phase at 25 °C. Important parameters like bond length, bond order, bond angle, dihedral angle, charge density, dipole moment and molecular orbitals were studied using computation. It was found that the photo degrading ability of CCT and CCTT were increased over TTDO due to doping. This may be due to the enhanced electron density on the Ti atom of CCT and CCTT over TTDO. Further the higher dipole moment and narrow band gap of CCT and CCTT were responsible for their higher photo catalytic activity. As a whole the electronic effect governs the higher photocatalytic activity of the CCT and CCTT over TTDO.

1. Introduction

In the past two decades various researches have proved that TiO_2 nano particles (TNP) are considered to be a most suitable photocatalyst for the degradation of organic dyes and pollutants. Along with that doping can enhance the photocatalytic efficiency of TNP [1]. A major aim of doping is to decrease the band gap and their by enhance the photo absorption. The dopants translocate the energy bands of the TiO_2 and act as a trap for electrons and holes to alter the photocatalytic activity of TiO_2 [2].

In recent years density function theory (DFT) has turned out to be a popular method due to its accuracy and computationally less intensive nature. DFT calculates the energy of a molecule from electron density, instead of wave function. It is difficult to compare and draw conclusion for the effect of doping experimentally. So along with experimental, computational approach can also explain the doping effects well [3].

The present work investigates the TiO_2 (TTDO) nano particles doped with $CoCl_2$ (CCT) and $CoCl_2$-thiourea codoped (CCTT) by experimental and DFT using B3LYP/631G**. The catalysts were synthesised and characterised by metal estimation, water of hydration, IR, UV-DRS, XRD and EDX. The photocatalytic effect is tested for the degradation of Acid Orange 7 dye (AO7).

2. Experimental Methods

2.1 Computation

The computations were performed by DFT using B3LYP method and 631G** basis set at 25 °C in gas phase. Softwares DFT, GAMESS, TDDFT, ORCA, Graphics: Gabedit were used.

2.2 Materials

Titanium isopropoxide from Sigma Aldrich, copper chloride dihydrate, thiourea and absolute ethanol from Merck, nitric acid and AO7 dye from Himedia were purchased. UV-DRS spectra were recorded using JASCO V-670 UV-VIS Spectrophotometer. FTIR were recorded in Perkin-Elmer Spectrum-1 using KBr pellets in the range of 4000-400 cm^{-1}. Powder X-ray diffraction (XRD) measurements were recorded with D8 Bruker AXS diffractometer using CuKα radiation (λ=1.5406 Å). Alumina was used as a standard to eliminate instrument peak broadening. EDX were recorded by FE-SEM (JSM-6700F, JEOL, Japan) equipped with an in-situ EDX spectrophotometer. The photocatalytic degradation of AO7 dye was studied in the presence of solar light. 100 mL borosilicate glass beakers were used as reaction vessel.

2.3 Synthesis of Photocatalysts

8.4 mL titanium (IV) isopropoxide was dissolved in 10 mL absolute ethanol (Solution A). Solution B consists of 10 mL absolute ethanol, 1 mL concentrated HNO_3 and 1 mL of distilled water, was slowly added to solution A. The mixture was stirred continuously for 18 hours to yield a wet-gel. The wet-gel was kept aside for 6 hours and dried at 110 °C for 15 hours in a hot air oven. Same procedure was adopted for the synthesis of CCT and CCTT using $CoCl_2.6H_2O$ and thiourea (1 wt %).

2.4 Photocatalytic Degradation

30 mL of 30 mg/L of AO7 solution was taken in a 100 mL beaker. To this 3 mL of 30 mg/L of photocatalyst was added. The solution was stirred continuously during irradiation with solar light for 180 minutes. An aliquot was withdrawn before irradiation and every 30 minute intervals of irradiation. The aliquot was centrifuged immediately and the supernatant solution was evaluated for the residual dye concentration using UV-VIS spectrometer. From the absorbance value the percentage of dye was calculated [4].

3. Results and Discussion

3.1 Stability and Structure

The 2-D, 3-D structures and numbering pattern of $(TiO_2)_3$ (TTDO), $CoCl_2$ doped TTDO (CCT) and $CoCl_2$-thiourea (CCTT) codoped TTDO are given in Fig. 1. Tables 1-3 are showing their geometrical parameters. In order to imitate the experimental studies, (1 0 1) plane of anatase form of TTDO was computed using three molecules of TiO_2. The TTDO is 2490.02 kJ more stable than mono-TiO_2. TTDO exhibits a planar hexagonal geometry with alternate oxygen and titanium atoms. It has bridged and terminal oxygen atoms with single and double bonds with Ti respectively. In the case of CCT the $CoCl_2$ molecule is placed over the TTDO. The chloride atoms of cobalt are also binds with the Ti atoms. Cobalt is attached to the oxygen atom of the TTDO. There is also a metal-metal interaction between Ti and cobalt. The stability of CCT is 350.24 kJ higher than the sum of energies of TTDO and $COCl_2$. CCT is non-planar with rocking chair like structure [5]. In CCTT

*Corresponding Author : nixonthangaraj@gmail.com(A. Nixon Thangaraj)

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the thiourea is attached to the $CoCl_2$ and has non-planar structure. The enhanced stability of CCTT over TTDO, $CoCl_2$ and thiourea is 519.84 kJ.

Table 1 Geometrical parameters and charge density of TTDO

Atom pair	Bond length (Å)	Atom pair	Bond angle (°)	Atom pair	Dihedral angle (°)	Charge Density	
Ti_1-O_2	1.6176	Ti_1-O_2-O_3	123.13	Ti_1-O_2-O_3-O_4	180	Atom	Charge
Ti_1-O_3	1.8525	Ti_1-O_2-O_4	123.07	Ti_1-O_3-O_4-Ti_5	0	Ti_1	1.3399
Ti_1-O_4	1.8523	Ti_1-O_3-Ti_5	126.39	Ti_1-O_2-O_4-Ti_6	180	O_2	-0.5209
O_3-Ti_5	1.8513	Ti_1-O_4-Ti_6	126.45	Ti_1-O_4-Ti_6-O_7	180	O_3	-0.8196
O_4-Ti_6	1.8516	O_4-Ti_6-O_7	123.61	Ti_1-O_3-Ti_5-O_8	180	O_4	-0.8201
Ti_6-O_7	1.6179	O_3-Ti_5-O_8	123.35	Ti_1-O_3-Ti_5-O_9	0	Ti_5	1.3426
Ti_5-O_8	1.6176	O_3-Ti_5-O_9	113.04			Ti_6	1.3429
Ti_5-O_9	1.8512					O_7	-0.5218
						O_8	-0.5218
						O_9	-0.8211

Table 2 Geometrical parameters and charge density of CCT

Atom pair	Bond length (Å)	Atom pair	Bond angle (°)	Atom pair	Dihedral angle (°)	Charge Density	
Ti_1-O_2	1.6109	Ti_1-O_2-O_3	114.46	Ti_1-O_2-O_3-O_4	122.18	Atom	Charge
Ti_1-O_3	1.9464	Ti_1-O_2-O_4	112.79	Ti_1-O_3-O_4-Ti_5	-7.6	Ti_1	1.2201
Ti_1-O_4	1.8259	Ti_1-O_3-Ti_5	131.17	Ti_1-O_2-O_4-Ti_6	-121.47	O_2	-0.4786
O_3-Ti_5	1.9548	Ti_1-O_4-Ti_6	132.13	Ti_1-O_4-Ti_6-O_7	-133.92	O_3	-0.9084
O_4-Ti_6	1.8377	O_4-Ti_6-O_7	114.88	Ti_1-O_3-Ti_5-O_8	-117.69	O_4	-0.7775
Ti_6-O_7	1.6149	O_3-Ti_5-O_8	114.16	Ti_1-O_3-Ti_5-O_9	6.05	Ti_5	1.2262
Ti_5-O_8	1.6105	O_3-Ti_5-O_9	105.14	Ti_1-O_3-Ti_5-Co_{10}	121.02	Ti_6	1.3349
Ti_5-O_9	1.825	Ti_1-O_3-Co_{10}	102.75	Ti_1-O_3-Co_{10}-Cl_{11}	-144.45	O_7	-0.5055
O_3-Co_{10}	1.865	O_3-Co_{10}-Cl_{11}	94.7	Ti_1-O_3-Co_{10}-Cl_{12}	6.02	O_8	-0.4776
Co_{10}-Cl_{11}	2.2647	O_3-Co_{10}-Cl_{12}	95.64			O_9	-0.7798
Co_{10}-Cl_{12}	2.2561					Co_{10}	0.8946
						Cl_{11}	-0.3765
						Cl_{12}	-0.3721

Table 3 Geometrical parameters and charge density of CCTT

Atom pair	Bond length (Å)	Atom pair	Bond angle (°)	Atom pair	Dihedral angle (°)	Charge Density	
Ti_1-O_2	1.646	Ti_1-O_2-O_3	109.33	Ti_1-O_2-O_3-O_4	121.05	Atom	Charge
Ti_1-O_3	1.8958	Ti_1-O_2-O_4	114.81	Ti_1-O_3-O_4-Ti_5	12.9	Ti_1	1.1679
Ti_1-O_4	1.8194	Ti_1-O_3-Ti_5	131.96	Ti_1-O_2-O_4-Ti_6	-131.65	O_2	-0.5926
O_3-Ti_5	1.9333	Ti_1-O_4-Ti_6	130.12	Ti_1-O_4-Ti_6-O_7	-130.19	O_3	-0.9103
O_4-Ti_6	1.8486	O_4-Ti_6-O_7	115.75	Ti_1-O_3-Ti_5-O_8	-131.67	O_4	-0.7767
Ti_6-O_7	1.616	O_3-Ti_5-O_8	110.42	Ti_1-O_4-Ti_6-O_9	4.29	Ti_5	1.1363
Ti_5-O_8	1.6189	O_4-Ti_6-O_9	111.52	Ti_1-O_3-Ti_5-Cl_{10}	112.24	Ti_6	1.3442
Ti_5-O_9	1.8285	O_3-Ti_5-Cl_{10}	89.92	O_2-O_3-Ti_1-Cl_{11}	112.87	O_7	-0.508
Co_{20}-Cl_{10}	2.355	O_3-Ti_1-Cl_{11}	89.05	Ti_1-Cl_{11}-Cl_{10}-S_{12}	47.68	O_8	-0.5088
Co_{20}-Cl_{11}	2.414	Ti_1-O_3-S_{12}	112.74	Ti_1-O_3-S_{12}-C_{13}	62.85	O_9	-0.7785
Co_{30}-S_{12}	2.32	O_3-S_{12}-C_{13}	59.28	O_3-S_{12}-C_{13}-N_{14}	-97.96	Cl_{10}	-0.3867
S_{12}-C_{13}	1.7538	S_{12}-C_{13}-N_{14}	121.08	O_3-S_{12}-C_{13}-N_{15}	81.09	Cl_{11}	-0.3907
C_{13}-N_{14}	1.3342	S_{12}-C_{13}-N_{15}	119.97	S_{12}-C_{13}-N_{15}-H_{16}	-13.24	S_{12}	-0.1787
C_{13}-N_{15}	1.3318	C_{13}-N_{15}-H_{16}	118.78	C_{13}-N_{15}-H_{16}-H_{17}	159.82	C_{13}	0.2713
N_{15}-H_{16}	1.0105	N_{15}-H_{16}-H_{17}	117.5	O2-C_{13}-N_{14}-H_{18}	-118.34	N_{14}	-0.5453
N_{15}-H_{17}	1.0128	O_2-N_{14}-H_{18}	25.29	C_{13}-N_{14}-H_{18}-H_{19}	148.32	N_{15}	-0.5122
N_{14}-H_{18}	1.0298	N_{14}-H_{18}-H_{19}	115.53	Ti_1-O_3-Cl_{10}-Co_{20}	47.62	H_{16}	0.3389
N_{14}-H_{19}	1.0112	Ti_1-O_3-Co_{20}	103.48			H_{17}	0.314
O_3-Co_{20}	1.9542					H_{18}	0.3414
						H_{19}	0.3298
						Co_{20}	0.8447

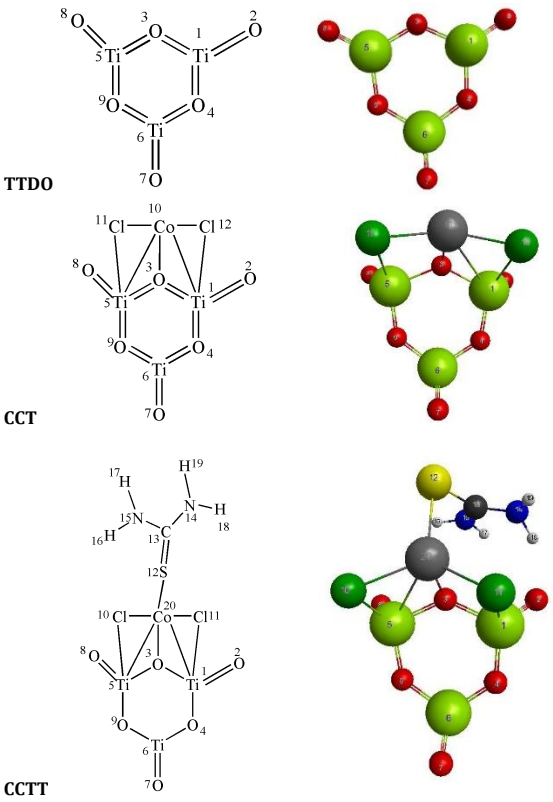

Fig. 1 Optimized structure *(Pale Green - Titanium; Red - Oxygen; Grey - Cobalt; Dark Green - Chloride; Yellow Sulphur; Blue - Nitrogen; White – Hydrogen)*

3.2 Charge Density

Charge density provides the information about the nature of electrostatic interactions. In TTDO, the positive charge on Ti and negative charge on oxygen atoms decreases the cation-cation (Ti-Ti) and anion-anion (O-O) repulsion and increase the cation-anion (Ti-O) attraction. The increased charge on O_3 and metal in CCT may change the density of states of the quantum well between O_3 and metal [6]. In general the increased charge localisation in CCT and CCTT over TTDO may influence the effective mass of holes in the valence band closely to match with the electrons present in the conduction band. The decreased in the charge on sulphur and cobalt in CCTT implies that these two atoms involved in strong bonding [7].

3.3 Dipole Moment

The higher dipole moment of CCT and CCTT than TTDO can influence the dipole-dipole interaction in the formers and may be responsible for their higher photocatalytic activity due to less electron-hole recombination [8]. Further the TTDO doped with 3*d* metal ion creates imbalance in charge distribution along the CCT molecule and their by increase the dipole moment. The increased dipole moment of the CCT and CCTT enhance their solubility in water and also the catalytic activity. The dipole moment values are given in Table 4.

Table 4 Dipole Moment

Molecule	μ_x	μ_y	μ_z	μ_{Total}
TTDO	-0.0101	-0.0153	0	0.0183
CCT	0.1919	2.031	2.4226	3.1672
CCTT	2.2574	5.8272	-0.1259	6.2505

3.4 Frontier Molecular Orbital

The computed band gap of TTDO matches with the theoretical value of anatase (1 0 1 plane) form of TTDO [9]. The computed band gap of TTDO is 28 % higher than that of experimental and this can be accounted for the gas phase study of computation. The reduction in the band gap for CCT and CCTT are due to the interaction of $CoCl_2$ and thiourea with TTDO [10]. CCT and CCTT can effectively degrade the pollutants than TTDO (Table 5). The calculated electronegativities and other electronic parameters also confirm that the CCT and CCTT have greater potential for visible light responsive photocatalytic activity [11].

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Table 5 Frontier Molecular Orbital (Q^{MAX}: TTDO – 3; CCT – 2.8)

Molecule	eV								Q^{Max}
	BG	IP	EA	ECP	CH	GS	EI	EN	
CCTT	3.2	6.1	2.9	-5	1.6	0.6	16	4.5	2.8

BG- Band gap, IP-Ionisation potential, EA-Electron affinity, ECP-Electronic chemical potential, CH-Chemical hardness, GS-Global softness, EI-Electrophilic index, EN-Absolute electro negativity

3.5 Characterisation

UV- DRS Spectra-Band gap for all the three samples were calculated using kubelka-munk formulae [12] and shown in Fig. 2. Doping of cobalt chloride and thiourea has brought little changes in the band gap of TiO_2.

FT-IR Spectra-Band at 478 cm^{-1} for Ti-O bending mode of TiO_2 is shifted to 456 cm^{-1} after doping with $CoCl_2$ due to the formation of Co-O bond. A band at 1620 cm^{-1} is due to the presence of Co-Cl bond. For thiourea doped sample the peaks observed at 1129 cm^{-1}, 1086 cm^{-1} and 1092 cm^{-1} (Fig. 3) are due to thiourea moiety [13, 14]. EDX Analysis- EDAX (Fig. 4) confirms the doping of $CoCl_2$ in to the lattices of TiO_2. The composition of TiO_2 to $CoCl_2$ is 1.03 percentages.

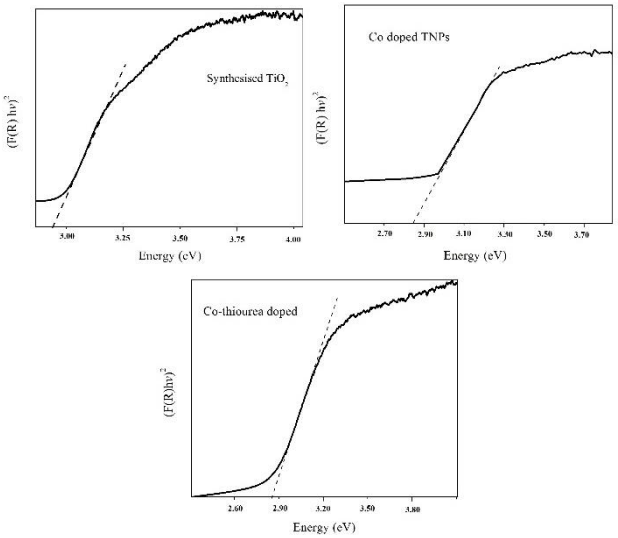

Fig. 2 UV-DRS spectra of a) undoped TiO_2 b) CCT c) CCTT

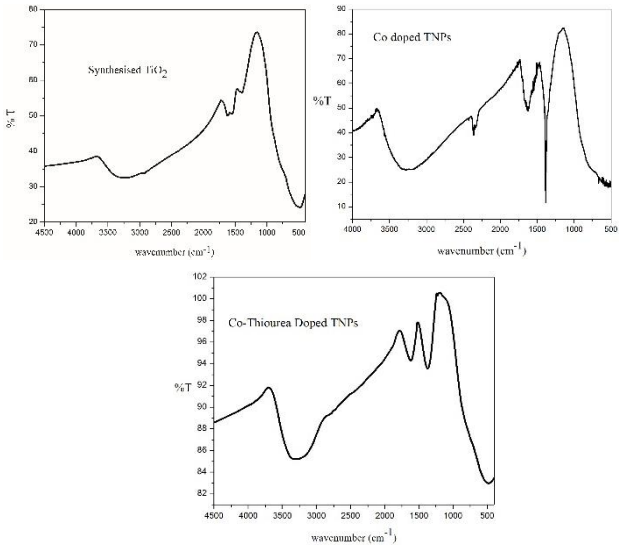

Fig. 3 FT-IR spectra of a) undoped TiO_2 b) CCT c) CCTT

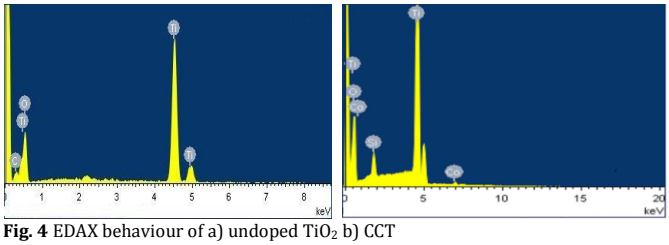

Fig. 4 EDAX behaviour of a) undoped TiO_2 b) CCT

XRD Analysis-The XRD of TiO_2 nanoparticles are agreeable [14]. In the X-ray diffraction pattern of undoped TiO_2, a main peak at 2θ = 25.4° attributed to the 1 0 1 planes (JCPDS 21-1272) of anatase phase (Fig. 5). There is no observation of peak at 2θ near at 27° indicates the absence of any rutile phase in the synthesised undoped TiO_2 [15]. 2θ = 25.6° and 25.4° are the major peaks observed for $CoCl_2$ doped TiO_2 and $CoCl_2$ and thiourea codoped TiO_2 respectively. These values clearly indicate that dopants cobalt chloride and thiourea are not interfering with the major peaks. The reason for this may be due to the occupation of guest metal ions in the sites of titanium ions in the host lattice of TiO_2 [16].

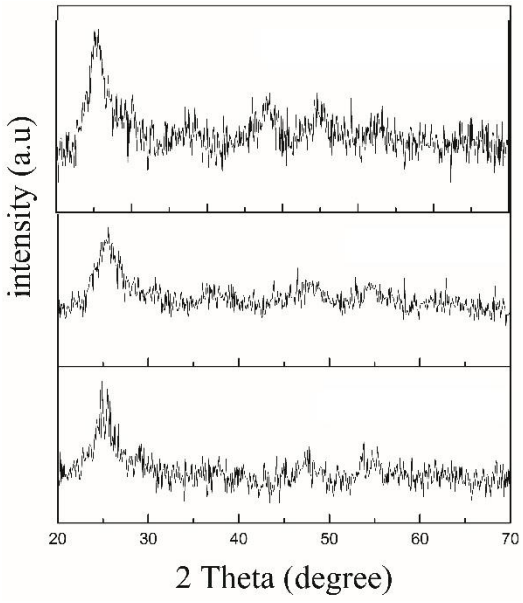

Fig. 5 XRD Pattern of a) undoped TiO_2 b) CCT c) CCTT

3.6 Photocatalytic Degradation Study

The photocatalytic efficiency of the synthesized catalysts was studied through the degradation of AO7 dye in the presence of solar light. The irradiation time is varied from 30 minutes to 180 minutes and the results were given in Table 6 and Fig. 6. Irradiation time is directly related to the amount of degradation of the dye and reaches a saturation level. The higher catalytic activities are due to the pivotal electron-hole formation and insignificant electron-hole recombination [17].

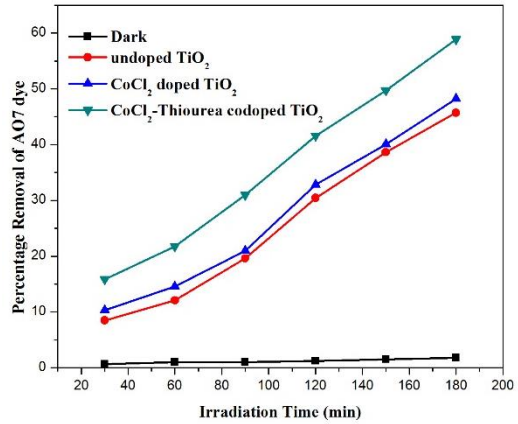

Fig. 6 Effect of contact time of AO7D with photocatalyst under solar light irradiation

Table 6 Photocatalytic degradation of AO7 dye under solar light irradiation (AO7 dye concentration: 30 ppm, Dose of the catalyst: 30 mg)

Irradiation time (min)	Percentage removal of AO7 dye (%)			
	Dark	undoped TiO_2	$CoCl_2$ doped TiO_2	$CoCl_2$-Thiourea codoped TiO_2
30	0.65	8.49	10.33	15.84
60	0.98	12.09	14.57	21.73
90	1.01	19.62	20.97	30.99
120	1.23	30.44	32.82	41.57
150	1.49	38.65	40.05	49.72
180	1.79	45.71	48.26	58.86

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4. Conclusion

$CoCl_2$ and $CoCl_2$-thiourea codoped TiO_2 nanoparticle photocatalysts were synthesised by sol-gel method and optimised using DFT/B3LYP/631G** at 25 °C in gas phase. The catalysts were characterised by UV-DRS, FT-IR, XRD and EDX. The computation and experimental studies showed that the photocatalysts enhanced the degradation of Acid Orange 7 dye than undoped TiO_2 due to electronic effects.

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