X-Ray Photoelectron Spectroscopy Characterization of Fe Doped TiO_2 Photocatalyst

Amir Abidov, Bunyod Allabergenov, Jeonghwan Lee, Heung-Woo Jeon, Soon-Wook Jeong, and Sungjin Kim

***Abstract*—X-ray photoelectron spectroscopy a technique was used in order to characterize, ionic state of Fe and chemical composition of Fe doped TiO_2. XPS detected Iron in form of Fe^{2+} and Fe^{3+}. Surface atomic concentrations were measured. Light exposed and reference samples were compared. Light irradiation affected charge transfer on the surface of Iron doped TiO_2. After light exposing XPS measurements showed that Ti^{4+} peak intensity decreased and shifted positively, O1s spectrum showed presence of increased amount of OH radicals, valence band spectra intensity increased.**

***Index Terms*—XPS, TiO_2, Fe^{3+}, Fe^{2+}, Fe doped TiO_2.**

I. Introduction

TiO_2 is very useful for photocatalysis process. That's why it has attracted much interest recently. However TiO_2 is wide bangap (3.2 eV) semiconductor and can be sensitized by UV light. This makes difficult using it indoor. Many researchers report successful doping Titanium dioxide by metal cations and non metal anions. Fe doped TiO_2 fabricated by mechanochemical milling performed very good photocatalytic properties for photodegradation of Methylene Blue [1]. For better understanding of doping mechanism X-Ray Photoelectron spectroscopy was used. X-ray photoelectron spectroscopy is very powerful technique for analyzing especially photocatalyst materials. Using this equipment we can quickly obtain useful information about chemical composition, chemical state and ionic state of certain elements. This allows researchers to analyze fabricated photocatalyst and improve production process. XPS analysis have been extensively used recently. Mindaugas Andrulevičius et. al. used XPS for analyzing $TiO_2/ZrO_2/SiO_2$ films [2]. Norbert Kruse, Aalbert Zwijnenburg, Kiss J, Lidia Armelao investigated Au/TiO_2 catalysts using XPS [3]-[6].XPS study of Copper doped TiO_2 photocatalyst was reported by Wu Shu-Xin in 2003 [7]. There are only a few studies about Fe doped TiO_2. Most of them were fabricated by CVD, hydrothermal and sol-gel method [8]-[10]. Many studies report about XPS study of doped TiO_2 under normal conditions. The purpose of this work is to investigate Fe doped TiO_2 fabricated by mechanochemical milling.

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II. Experimental

Iron doped TiO_2 photocatalyst prepared by mechanochemical milling was investigated. The average particle size is 25nm. Iron doped samples were two kinds. After fabrication one sample was kept in dark (virgin state), another one was exposed to light (300W Mercury lamp) for 1 hour in order to evaluate charge transfer on the surface of TiO_2 particle. Bare TiO_2 (p25 Degussa) was used ad reference. XPS measurements were performed using Thermo scientific K-Alpha X-Ray spectrophotometer. Peaks were fitted and analyzed using Thermo Avantage software in details using Gaussian mixture. Surface composition and concentrations were calculated from appropriate peak area. Baseline was calculated using Shirley's method. Data was corrected assuming that atmosphere carbon contamination at 284 eV. Wide spectrum was obtained under 1.0 eV resolution. Narrow XPS spectrum was measured under 0.1eV operating mode.

III. Results and Discussion

Appearance of appropriate peaks of main elements can be seen in wide spectra in fig. 1. Fe 2p peak was successfully detected by XPS which is very important since XRD could not detect this element. Calculated surface atomic concentrations are summarized in Table I. Bare TiO_2 Ti/O stoichiometry value is used for comparison. It can be clearly seen that doped titanium dioxide has Ti/O ratio different to pure one [11]. This can be ascribed to presence of Fe on the surface of TiO_2.

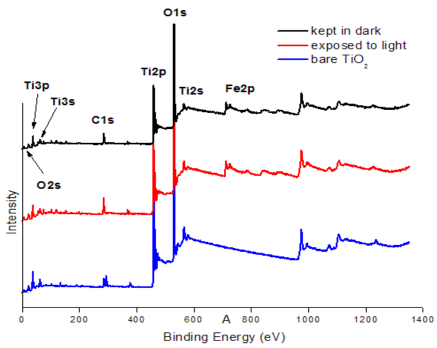

Fig. 1. Wide XPS spectrum of bare TiO_2 (bottom), exposed to light (middle), virgin state (top)

TABLE I: SURFACE ATOMIC CONCENTRATIONS OF SAMPLES MEASURED BY XPS.

Sample number	#1	#2	#3
Elements and molar conc., %	Bare TiO_2 (theoretic)	Exposed to light	Kept in dark
Peak	Surface atomic concentration		
O 1s	66.6%	53.9%	54.3%
Ti 2p	33.3%	12.4%	12.7%
Fe 2p	-	4.4%	4.5%

Fe 2p spectra was measured in order to evaluate the electronic nature of Iron in Fe doped TiO_2. Fe2p core level spectrum is shown in fig 2. From this pattern can be seen that $Fe2p_{3/2}$ and $Fe2p_{1/2}$ peaks binding energies are located at 710.9 eV and 724.6 eV respectively corresponded to Fe^{3+} (oxide). Shake up satellite at 718.9 eV supports that Fe is presented in Fe^{3+} ionic state [12]-[14]. A weak peak at 711.7 eV also presents suggesting presence of minor portion of Fe^{2+} ions [15]. After light exposing Fe 2p $_{3/2}$ peak narrowed and shake up satellite increased which indicates that surface Fe^{2+} species lost their electron changing ionic state to Fe^{3+}.

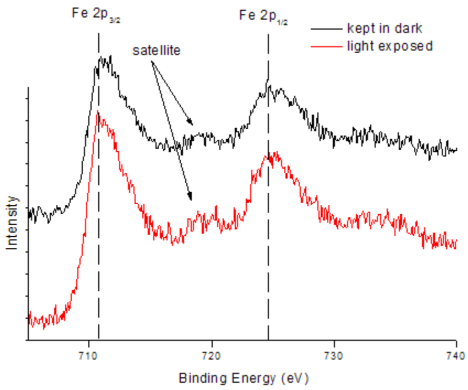

Fig. 2. Fe2p core level spectra. Kept in dark (top), exposed (bottom)

High resolution O1s spectra for bare, virgin state and exposed to light TIO_2 samples are compared in fig 3. O1s peak appears at 531 eV which is attributed to signal of Oxygen in TiO_2 lattice. It can be seen that O1s- peak decreased due to formation of Fe-O bonds on the surface of TiO_2. Another shoulder occurs at 531.5 eV which corresponds to adsorption of OH^- .

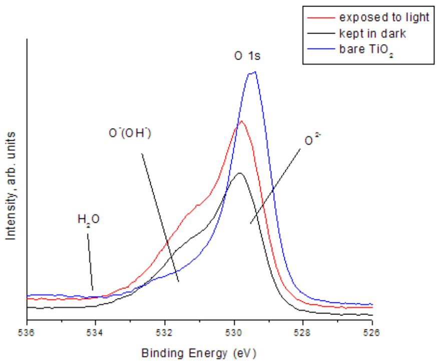

Fig. 3. O1s curves. Bare TiO_2 (top), Exposed to light (middle), Virgin state (bottom) respectively

According to results from fig 4., Ti2p core level spectrum contains two main peaks $Ti2p_{3/2}$ and $Ti2p_{1/2}$. Ti2p spectrum moslty appears in Ti^{4+} oxidation state with the small contribution of Ti^{3+}. Ti^{3+} occurs due to oxygen deficiency in TiO_2 lattice [16]. Peak shift is detected which indicates decrease of the coordination number of Ti and the shortening of the Ti-O bond. This result supports that the presence of Ti^{4+} is decreased.

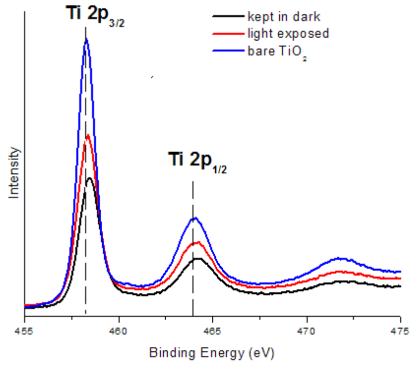

Fig. 4. Ti2p curves. From up to down: Bare TiO_2, Light exposed, Kept in dark respectively.

From Table II can be seen that Ti2p peaks are shifted positive 0.45 eV for virgin state sample indicating formation of Fe-O-Ti bonds. This can be attributed to the formation of binary TiO_2/Fe_2O_3 oxides [17]. After exposing to light positive shift increased to 0.63 eV.

TABLE II: XPS PEAKS SHIFTS

Num.	Sample name	Peak shift, eV	
	Bare TiO_2	O 1s 531.0 eV	Ti 2p 458.8 eV
1	light exposed	0.85	0.63
2	Kept in dark	0.68	0.45

Valence band spectra was measured in order to investigate modification of electronic structure of Fe doped TiO_2. Bare photocatalyst showed three major features at binding energies 7.2 eV, 4.8 eV, and 0.9 eV which well corresponds to those reported in other papers [16-18]. Doped TiO_2 performed another feature at 11 eV. After exposing to light new feature at 2.3 eV occurred. This corresponds to appearance of Ti^{3+} 3d defect state very close to Fermi level [16].

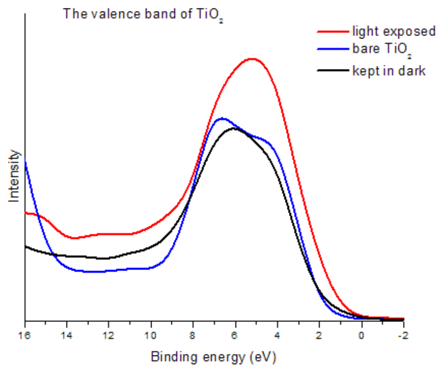

Fig. 5. Valence band spectra form up to down of light exposed, bare TiO_2, kept in dark respectively.

IV. CONCLUSION

Fe doped TiO_2 was investigated by XPS method. In wide spectra main peaks of appropriate elements were detected. Fe2p spectra showed presence of Fe^{2+} and Fe^{3+} species. Changing of Iron's Ionic state and formation of Ti^{3+} defect states formation after exposing to light was observed. Valence band spectra showed formation of defect Ti^{3+} defect states. Ti2p positive shift corresponding to formation of TiO_2/Fe_2O_3 binary oxide was detected. All obtained data is very useful for future process of TiO_2 doping using transition metals.

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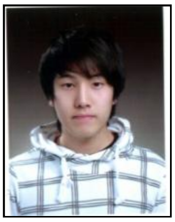

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