



## Photoelectrocatalytic Properties of Mo-CNT/TiO<sub>2</sub> Composite Electrodes under Visible Light

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Molybdenum-carbon nanotube (Mo-CNT) and Mo-CNT/titania (TiO<sub>2</sub>) composite electrodes were prepared *via* a sol-gel method and calcination. The composites were comprehensively characterized by Brauer-Emett-Teller surface area, scanning electron microscopy, energy dispersive X-ray analysis, X-ray diffraction, transmission electron microscopy and UV-vis absorption spectroscopy. The photoelectroactivity of the prepared materials under visible light irradiation was tested using methylene blue in aqueous solution. The result showed that the introduction of molybdenum enhanced the photoelectrocatalytic degradation of methylene blue solution.

**Key Words:** Mo-CNT/TiO<sub>2</sub>, Electrode, Photoelectrocatalytic, Visible light.

### INTRODUCTION

Titanium dioxide (TiO<sub>2</sub>) is a very active photo catalyst, due to its stability, inexpensive and low biological toxicity<sup>1-3</sup>. However, poor adsorption capacity, formation of rapid aggregates in a suspension, excitation only under UV light illumination at wavelengths below 400 nm and also recycling difficulties restricted the utilization of TiO<sub>2</sub>. Therefore, in practical applications, attempts have been made to support TiO<sub>2</sub> nanoparticles on porous adsorbent materials and to extend the light absorption of the photocatalysts to the visible region<sup>4-6</sup>. Moreover, several researchers have already attempted to lower the band gap energy of TiO<sub>2</sub>, which mainly includes doping with transition metal ions<sup>7,8</sup>.

Among these materials, carbon supported TiO<sub>2</sub> catalysts have attracted more and more attentions<sup>9-14</sup>. Carbon nanotubes (CNTs) is a kind of novel carbon material with unique mechanical and electronic properties<sup>15,16</sup>, which can be regarded as hollow graphite fibers with a perfect structure, such as seamless tube-like graphitic walls consisting of *sp*<sup>2</sup> carbon-carbon atoms, nano-sized hollow channels, excellent electron-transporting capability as well as convertible surface properties that can be easily modified. Carbon nanotubes have a large electron-storage capacity (one electron for every 32 carbon atoms)<sup>17</sup>, the ability of CNT can promote the electron-transfer reactions at carbon nanotubes modified electrodes.

Doping is also a promising approach to reduce the absorption threshold of TiO<sub>2</sub> and extends its optical absorption

range from ultraviolet to visible region<sup>18</sup>. Previous works have also emphasized that photocatalytic activity of TiO<sub>2</sub> can be improved by doping of TiO<sub>2</sub> with transition metals<sup>19-24</sup>. Choi *et al.*<sup>19</sup> studied 21 transition metal ions doped TiO<sub>2</sub> and found that when Fe<sup>3+</sup>, Mo<sup>5+</sup>, Ru<sup>3+</sup>, Os<sup>3+</sup>, Re<sup>5+</sup>, V<sup>4+</sup> and Rh<sup>3+</sup> were used at 0.1-0.5 %, a significant increase in the photo-reactivity of TiO<sub>2</sub> samples was achieved for both chloroform oxidation and reduction. Among different transition metals, molybdenum seems to be one of these potentially interesting additives, since it is inexpensive and largely available. However, the partially occupied impurity bands can act as recombination centers where photoinduced charge carriers recombine, resulting in the reduction of charge carrier quantity and photocatalytic activity in some single doped TiO<sub>2</sub>.

Though Mo-doped TiO<sub>2</sub> and CNT-supported TiO<sub>2</sub> have already been, respectively, synthesized and exhibited enhanced vis-photocatalytic activities as compared to the pure TiO<sub>2</sub><sup>8,10,11</sup>. To the best of our knowledge, few research studies have been reported about a binary system of Mo-doped TiO<sub>2</sub> and CNT-supported TiO<sub>2</sub> photocatalyst up to now. Hence it is worthy that Mo deposit on CNT/TiO<sub>2</sub> particles as a photocatalyst. In this study, we focused on the fabrication and characterization of the Mo-CNT/TiO<sub>2</sub> composite electrodes in a preparation procedure. Structural variations, surface state and elemental compositions were investigated for preparation of Mo-CNT/TiO<sub>2</sub> composite. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and transmission electron microscopy (TEM) were employed for

characterization of these new photocatalysts. The catalytic efficiency of the Mo-CNT/TiO<sub>2</sub> electrode was evaluated by the photoelectrocatalytic (PEC) degradation of methylene blue (MB, C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>SCl·3H<sub>2</sub>O).

## EXPERIMENTAL

Carbon nanotubes (CNTs) were selected as the support material. The CNTs (Multiwall nanotubes, diameter: *ca.* 20 nm, length: *ca.* 5 μm) were supplied from Carbon Nano-Material Technology Co., Ltd, Korea and used without further purification. Titanium tetra(*n*-butoxide) [Ti(OC<sub>4</sub>H<sub>7</sub>)<sub>4</sub>] (TNB) as a titanium source for the preparation of composites was purchased from Acros Organics, New Jersey, USA. For the oxidization of the surface of the CNT, *m*-chloroperbenzoic acid (MCPBA) was used as an oxidizing reagent also purchased from Acros Organics, New Jersey, USA. Methylene blue was the analytical grade chemical and purchased from Duksan Pure Chemical Co., Ltd., Korea. Ammonium molybdate was obtained from Samchun Pure Chemical Co., Ltd., Korea. Reagent-grade solvents, benzene and ethyl alcohol, were purchased from Duksan Pure Chemical Co. and Daejung Chemical Co., Korea and used without further purification.

**Preparation of Mo-CNT composites:** 2 g *m*-Chloroperbenzoic acid as oxidizing agent was dissolved in 60 mL benzene. Then 0.6 g CNTs was put into the oxidizing agent, refluxed for 6 h, filtered and dried. The oxidized CNTs were added to solution containing ammonium molybdate and then the solutions were homogenized under reflux at 343 K for 5 h using a magnetic stirrer in a vial. After being heat treated at 773 K for 1 h with a heating rate of 279 K/min, the Mo treated CNT composites were obtained.

**Preparation of Mo-CNT/TiO<sub>2</sub> composite electrodes:** The Mo treated CNT composites were put into the mixing solution of TNB and benzene with a volume ratio of 4:16. Then the solutions were homogenized under reflux at 343 K for 5 h, while being stirred in a vial again. After stirred, the solutions transformed into Mo-CNT/TiO<sub>2</sub> gels and these gels were heat treated at 973 K for 1 h with a heating rate of 279 K/min. After cooling, the Mo-CNT/TiO<sub>2</sub> composites were obtained. Then 0.4 g PR powder was added to the Mo-CNT/TiO<sub>2</sub> composites and the composites were pressed at a pressure of 250 kg/cm<sup>2</sup> in a mould with dimensions of 9.95 mm × 39.5 mm × 5.95 mm. The mixture was then heat treated at 673 K for 1 h. After cooling, the Mo-CNT/TiO<sub>2</sub> composite electrodes were obtained. The preparation conditions and the nomenclatures of the samples are shown in Fig. 1 and Table-1.

**Characterization of the Mo-CNT/TiO<sub>2</sub> composites:** XRD technique was used for crystal phase identification and estimation of the anatase-to-rutile ratio. XRD patterns were

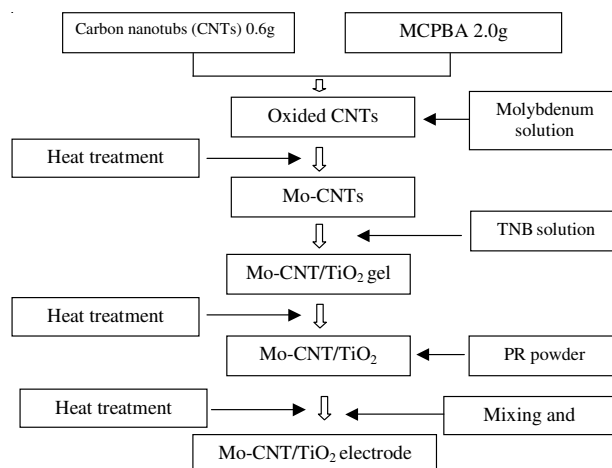


Fig. 1. Flow chart of fabrication of Mo-CNT/TiO<sub>2</sub> composite electrode

obtained at room temperature with a diffractometer (Shimata XD-D1, Japan) using Cu K<sub>α</sub> radiation. SEM was used to observe the surface state and porous structure of the Mo-CNT/TiO<sub>2</sub> composites using a scanning electron microscope (JOEL, JSM-5200, Japan). EDX spectroscopy was used to measure the elemental analysis of the Mo-CNT/TiO<sub>2</sub> composites. TEM (JEOL, JEM-2010, Japan) at an acceleration voltage of 200 kV was used to investigate the size and distribution of the molybdenum and titanium deposits on the CNT surface of various samples. TEM specimens were prepared by placing a few drops of the sample solution on a carbon grid.

**Photoelectrocatalytic (PEC) decolourization of methylene blue:** The PEC decolourization was performed using Mo-CNT/TiO<sub>2</sub> composite electrodes in a 100 mL glass container and then irradiating the system with visible light (8W, KLD-08L/P/N, Fawoo Technology), which was used at the distance of 100 mm from the solution in darkness box. Prior to illumination, the composites were impregnated in the pristine methylene blue solution in the dark for 2 h needed to achieve adsorption/desorption equilibrium. The counter electrode was artificial graphite (TCK, Korea), which dimension was 9.95 mm × 39.50 mm × 5.95 mm. The Mo-CNT/TiO<sub>2</sub> composite electrodes were placed in 50 mL of 1 × 10<sup>-5</sup> mol/L methylene blue solution. The PEC degradation of methylene blue was performed with visible light. The PEC activities of Mo-CNT/TiO<sub>2</sub> composites were investigated using the PEC degradation rate of methylene blue solution, which was measured as function of time. The blue colour of the solution faded gradually with time due to the adsorption and degradation of methylene blue solution. And then the concentration of methylene blue in the solution was determined as a function of irradiation time from the absorbance change at a wavelength of 660 nm. The decolourization rate of methylene blue was calculated by the following equation:

$$\text{Decolourization (\%)} = (C_0 - C)/C_0 \times 100 \%$$

where C<sub>0</sub> = initial concentration of methylene blue and C = concentration of methylene blue after "t" minutes visible light irradiation.

## RESULTS AND DISCUSSION

### Structure and morphology of Mo-CNT/TiO<sub>2</sub> composites:

The values of BET surface areas of CNT/TiO<sub>2</sub>, Mo-CNT and Mo-CNT/TiO<sub>2</sub> composites are shown in Table-1. As shown in

TABLE-1  
NOMENCLATURES AND SURFACE AREAS OF CNT/TiO<sub>2</sub>,  
Mo-CNT AND Mo-CNT/TiO<sub>2</sub> COMPOSITES

Preparation method	Nomenclatures	S <sub>BET</sub> (m <sup>2</sup> /g)
0.6 g CNT + TNB 4 mL	CNT/TiO <sub>2</sub>	198
Ammonium molybdate (0.02 M) + 0.6 g CNT	Mo-CNT	172
Ammonium molybdate (0.02 M) + 0.6 g CNT + TNB 4 mL	Mo-CNT/TiO <sub>2</sub>	101

Table-1, the BET surface areas of molybdenum treated CNT/TiO<sub>2</sub> composites decreased from 198-101 m<sup>2</sup>/g. At the same addition of TNB, it was thought that the Mo and Ti oxide particles were heavily agglomerated to gather into a blocky-shaped particle. These results can be seen clearly from SEM and TEM images (Figs. 3 and 4) obtained from powdered CNT/TiO<sub>2</sub>, Mo-CNT and Mo-CNT/TiO<sub>2</sub> composites. The results showed that there is a decrease in the BET surface area of the Mo-CNT/TiO<sub>2</sub> composites after formation of Mo particles by molybdenum treatment. This was suggested that some porosity was developed during the heat treatment. It was thought that the composites are nano materials that including a lot of micropores. It could be attributed to the micropores being partially blocked by the formation of Mo particles on the CNT/TiO<sub>2</sub> surface during heat treatment. As expected, it is considered that the BET surface area decreases due to the blocking of the micropores by surface complexes introduced through the formation of Mo-CNT/TiO<sub>2</sub> composites.

The results of the EDX elemental microanalysis of the Mo-CNT/TiO<sub>2</sub> composites are listed in Table-2. The contents of the molybdenum component for Mo-CNT and Mo-CNT/TiO<sub>2</sub> are 47.5 and 23.5 %, respectively and the contents were higher. It was thought that the increase of contents of the molybdenum component in the composites will decrease the BET surface areas, which reduce the adsorption of the catalyst.

TABLE-2  
EDX ELEMENTAL MICROANALYSIS OF CNT/TiO<sub>2</sub>,  
Mo-CNT AND Mo-CNT/TiO<sub>2</sub> COMPOSITES

Samples	Element (wt %)			
	C	O	Ti	Mo
CNT/TiO <sub>2</sub>	53.3	23.0	21.7	–
Mo-CNT	31.9	20.6	–	47.5
Mo-CNT/TiO <sub>2</sub>	23.2	38.8	14.5	23.5

The XRD results for the catalyst samples are shown in Fig. 2. The structure of the CNT/TiO<sub>2</sub> and molybdenum treated CNT/TiO<sub>2</sub> composites all showed an anatase crystal. It is well known that the crystal structure of the titanium dioxide is mainly determined by the heat treated temperature. The peaks at 25.3, 37.8, 48.0 and 62.5° (2θ) are the diffractions of (101), (004), (200) and (204) planes of anatase, indicating the developed CNT/TiO<sub>2</sub> composites existed in an anatase state. Therefore, it can be concluded that the developed CNT/TiO<sub>2</sub> composites have an anatase crystal when annealed at 973 K. In the XRD patterns of Mo-CNT and Mo-CNT/TiO<sub>2</sub> samples, the XRD pattern shows clearly diffraction peaks of (111), (211), (312), (210), (310) and (031) of the monoclinic MoO<sub>2</sub> phase, the formation of MoO<sub>2</sub> is searched owing to the variation of transition metal salt into metal oxides during the calcinations process. Intense peaks from anatase still appeared in the Mo-CNT/TiO<sub>2</sub> samples.

The micro-surface structures and morphology of the CNT/TiO<sub>2</sub>, Mo-CNT and Mo-CNT/TiO<sub>2</sub> composites were characterized by SEM (Fig. 3). Fig. 3 shows the macroscopical changes in the morphology of the CNT/TiO<sub>2</sub>, Mo-CNT and Mo-CNT/TiO<sub>2</sub> composites. For CNT/TiO<sub>2</sub> sample [Fig. 3(a)], the TiO<sub>2</sub> particles were well attached to the surface of the CNT network and the distribution was uniform. In the report of

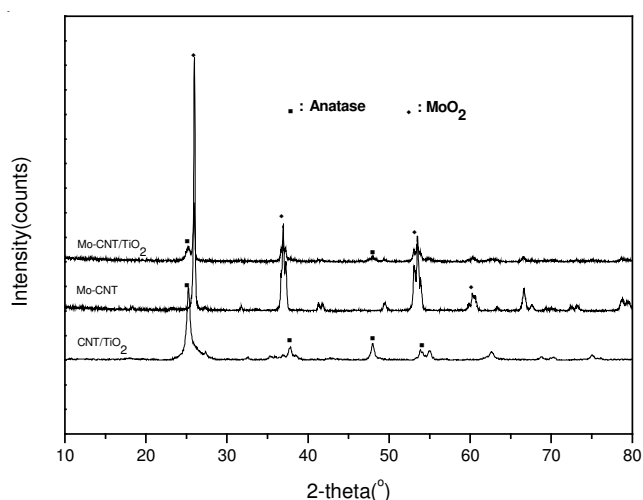
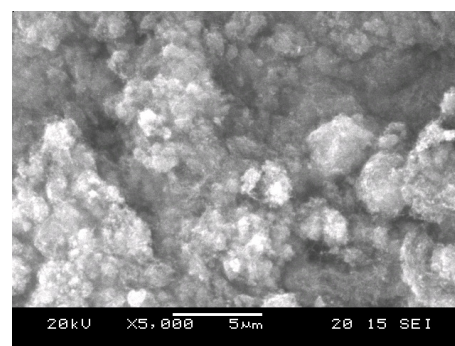
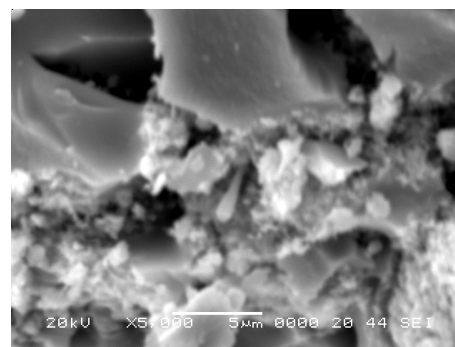


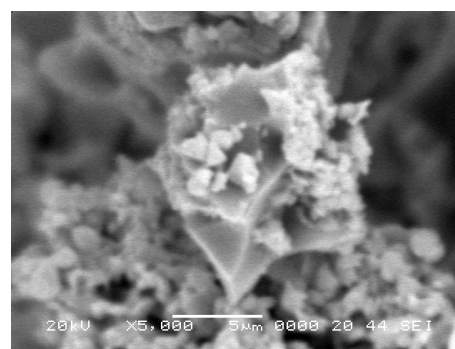
Fig. 2. XRD patterns of powdered CNT/TiO<sub>2</sub>, Mo-CNT and Mo-CNT/TiO<sub>2</sub> composites



(a)



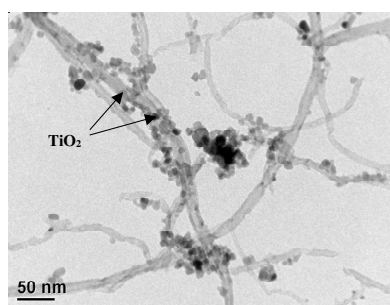
(b)



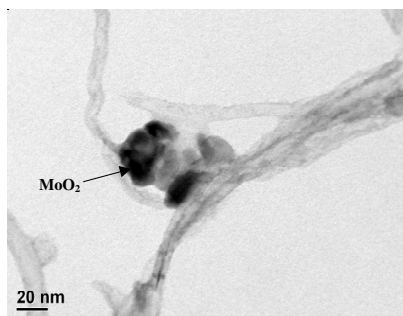
(c)

Fig. 3. SEM images obtained from powdered CNT/TiO<sub>2</sub>, Mo-CNT and Mo-CNT/TiO<sub>2</sub> composites: (a) CNT/TiO<sub>2</sub>, (b) Mo-CNT, (c) Mo-CNT/TiO<sub>2</sub>

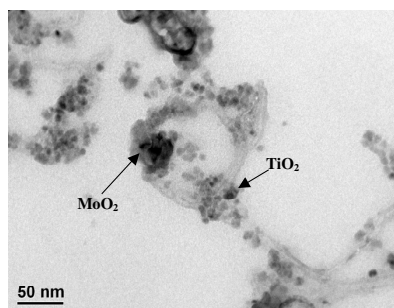
Zhang *et al.*<sup>25</sup>, a good dispersion of small particles could provide more reactive sites for the reactants than aggregated particles. At the same time, the conductivity of the CNT network can facilitate the electron transfer between the adsorbed dye molecules and the catalyst substrate<sup>26</sup>. It was beneficial one for the enhancement of the PEC activity of these composites. Moreover, for the Mo-CNT and Mo-CNT/TiO<sub>2</sub> samples [Fig. 3(b), (c)], molybdenum oxide particles were fixed on the surface of the CNT network in some blocky-shaped particles and the distribution was not uniform. There is no clear difference of the intensity of aggregation molybdenum oxide particles. These results are also confirmed by TEM inspection of the CNT/TiO<sub>2</sub>, Mo-CNT and Mo-CNT/TiO<sub>2</sub> composites. As shown in Fig. 4, for the CNT/TiO<sub>2</sub> composites, the TiO<sub>2</sub> particles were distributed uniformly outside surface of CNT tubes [Fig. 4(a)]. However, for the Mo-CNT composites, the Mo oxide particles were aggregated outside surface of CNT tubes [Fig. 4(b)] and for Mo-CNT/TiO<sub>2</sub> composites as the addition of Mo, the particles attached on the surface of the tubes also caused partial agglomeration to form blocky-shaped particle [Fig. 4(c)].



(a)



(b)



(c)

Fig. 4. TEM micrographs obtained from powdered CNT/TiO<sub>2</sub>, Mo-CNT and Mo-CNT/TiO<sub>2</sub> composites: (a) CNT/TiO<sub>2</sub>, (b) Mo-CNT, (c) Mo-CNT/TiO<sub>2</sub>

**Photoelectrocatalytic decolourization of methylene blue:** Fig. 5 shows the PEC decolourization rate of methylene blue for CNT/TiO<sub>2</sub>, Mo-CNT and Mo-CNT/TiO<sub>2</sub> composite electrodes under visible light irradiation. Prior to illumination, the composites were impregnated in the pristine methylene blue solution in the dark for 2 h. Fig. 5 shows the dark adsorption efficiency of CNT/TiO<sub>2</sub>, Mo-CNT and Mo-CNT/TiO<sub>2</sub> composites for methylene blue degradation. After adsorption in the dark for 2 h, all of samples were reached adsorption-desorption equilibrium. And the decolourization efficiencies of CNT/TiO<sub>2</sub>, Mo-CNT and Mo-CNT/TiO<sub>2</sub> composite electrodes were 50, 45 and 37 %, respectively. The results of adsorption are consistent with the BET surface areas.

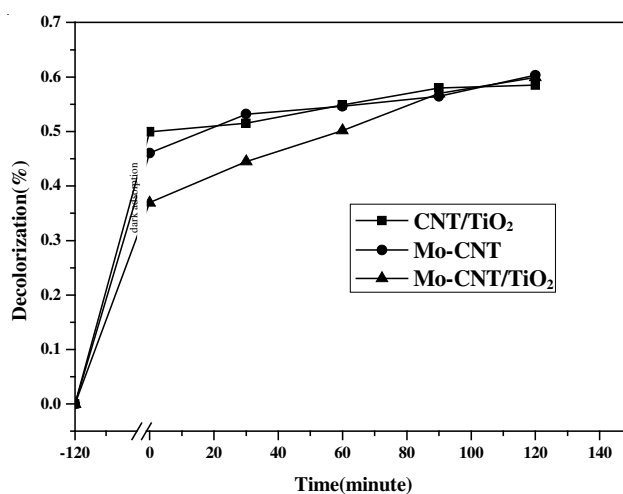


Fig. 5. Effect of the photoelectrocatalytic decolourization rate of methylene blue for CNT/TiO<sub>2</sub>, Mo-CNT and Mo-CNT/TiO<sub>2</sub> composite electrodes: the applied potential of 6.0 V under visible light irradiation

After illumination of 2 h under visible light and the applied potential of 6.0 V, the decolourization efficiencies of CNT/TiO<sub>2</sub>, Mo-CNT and Mo-CNT/TiO<sub>2</sub> composite electrodes were 58, 60 and 60 %, respectively. At the same conditions, the PEC decomposition efficiencies of CNT/TiO<sub>2</sub>, Mo-CNT and Mo-CNT/TiO<sub>2</sub> composite electrodes were 8, 14 and 23 %, respectively. It was indicated that the PEC effects of the Mo treated CNT/TiO<sub>2</sub> composite electrodes were 3 times than that of non-Mo treated CNT/TiO<sub>2</sub> in the irradiation time of 2 h. The PEC activity of metal particles for this reaction is dependent on various factors, which involves the size and dispersion of the particles, supporting materials and their surface conditions. Although the introduction of Mo component increased the aggregation of particles, the decolourization efficiencies of Mo-CNT/TiO<sub>2</sub> composite electrode also arrived at 60 % in this study. It was implied that the introduction of Mo enhanced the PEC degradation of methylene blue solution. The optimization of PEC decolourization of methylene blue using Mo-CNT/TiO<sub>2</sub> composite electrodes will be studied in detail in another paper.

## Conclusion

In this study, we present the synthesis and characterization of CNT/TiO<sub>2</sub>, Mo-CNT and Mo-CNT/TiO<sub>2</sub> composite electrodes. The surface area of the Mo-CNT/TiO<sub>2</sub> composites decreased

due to molybdenum oxide and titania particles coated on the surface of CNTs. XRD results showed that CNT/TiO<sub>2</sub> and Mo-CNT/TiO<sub>2</sub> composite only existed in an anatase state; moreover the crystal structure of MoO<sub>3</sub> was also confirmed in samples of Mo-CNT and Mo-CNT/TiO<sub>2</sub> composite. The result of degradation of methylene blue was indicated that the adding of molybdenum oxide enhanced the photocatalytic activity of the Mo-CNT/TiO<sub>2</sub> composite. And the PEC effects of the Mo treated CNT/TiO<sub>2</sub> composite electrodes were 3 times than that of non-Mo treated CNT/TiO<sub>2</sub> in the irradiation time of 2 h.

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