

THE INFLUENCE OF PLATINUM ON THE STRUCTURE AND PHOTOCATALYTIC PERFORMANCE OF HYDROGEN TITANATE NANOTUBES

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ABSTRACT

Via photoreductive deposition process, platinum-modified TiO₂ photocatalysts (Pt/TiO₂) with various Pt contents are prepared by using H₂PtCl₆ and hydrogen titanate nanotubes as precursors. The structures and photocatalytic performances of Pt/TiO₂ obtained are characterized. The experimental results indicate that platinum has obvious influence on the structure and photocatalytic performances of the hydrogen titanate nanotubes. The tubular structures of some nanotubes are destroyed during the photoreductive deposition process. It is possible that the hydrogen coming from splitting water over formed Pt/TiO₂ results in the breach of nanotubes. The existence of platinum can enhance the photocatalytic performance of titanate nanotubes, and the photocatalytic activity arrives at the highest when the Pt content is 1.5 wt.%.

Keywords: hydrogen titanate nanotubes; platinum; photoreductive deposition; tubular structure; photocatalytic performance

As a common semiconductor and photocatalyst, TiO₂ has been intensively investigated because of its good catalytic activity, non-toxicity, stability and low cost [1-3]. Due to quick recombination of photo-generated charges, the photocatalytic efficiency of pure TiO₂ is not high enough [4,5], which limits its practical application greatly. In the field of improving photocatalytic performance and efficiency of TiO₂, many works on TiO₂ modified with noble metal, metal sulfide, various dopants, etc have been reported [5-12]. It has been proved that photocatalytic performance of TiO₂ modified with noble metals is better than that of primary TiO₂. Many references related to the modification of TiO₂ with platinum have been reported. Shi has reported Pt-doped TiO₂ fiber catalyst with different Pt contents by photoreductive deposition method [13]. Kim has reported titania hollow spheres coated with platinum [14]. Siemon and Bahnemann have reported heterogeneous photocatalytic reaction comparing TiO₂ and Pt/TiO₂ [15]. In most of the reported cases, more active photocatalysts can be prepared via the photoreductive deposition or photodeposition [16]. Compared with photocatalysts with common forms, nanotubes that have larger specific surface area can contact effectively with substrates in the gas or liquid phase, and show better performance. TiO₂ nanotubes have not only high specific surface area, but also high sedimentation rate, which makes TiO₂ nanotubes more suitable to be utilized as catalyst for the heterogeneous photocatalytic reactions [8,17]. To obtain tubular TiO₂, a number of synthetic methods, such as electrochemical anodic oxidation of metal titanium foil [18,19], template-assisted synthesis [20], and sol-gel method [21], have been developed, and TiO₂ nanotubes with different diameters were fabricated. In 1998, Kasuga et al. developed a hydrothermal method to turn TiO₂ powders into tubular structure [22]. The obtained nanotubes have uniform diameter of around 10 nm and high surface area. Compared with other fabrication process, this synthesis process is a cheap one-step reaction, and requires neither expensive apparatus nor special chemicals, which facilitate the scale-up production in low-cost and high-reduplicative. Since then, the characterization and modification of such kind of nanotubes are expansively reported [9,23,24]. However, this kind of hydrogen titanate nanotubes are brittle and can be destroyed easily [25]. In our previous investigation, we observed that the hydrogen titanate nanotubes can be destroyed after calcinations process at 150 °C in H₂ or during the fabrication process under UV irradiation [6,26], and sol treatment have been used to improve the stability of this kind of titanate nanotubes [9,27]. However, the structure transformation of this kind of nanotubes under UV irradiation has not been further investigated. In this paper, platinum-modified TiO₂ catalysts with various platinum contents are prepared via photoreductive deposition process. The influence of Pt content on the structure and photocatalytic activity of the nanotube support is also investigated.

EXPERIMENTAL

Preparation of samples

All of the chemicals are analytical grade and used without further purification. TiO₂ powder is pure anatase crystal. Its specific surface area and

particle size are 10 m²/g and 100 nm, respectively. Water is of ~18 MΩ·cm resistivity.

Titanate nanotubes are synthesized according to the reported procedure [22,26]. In a typical synthesis, 1.5 g raw TiO₂ powder is dispersed in 80 mL NaOH aqueous solution (10 M) and charged into a 100 mL Teflon-lined autoclave. The autoclave is heated in an oil bath at 150 °C for 12 h. Prepared sample is washed with 0.1 M HCl solution and water, respectively. White powder is obtained after they are dried at 80 °C in air. Multilayer nanotubes of high quality can be observed with TEM. The preparation process of Pt-modified TiO₂ catalyst (marked as Pt/TiO₂) is described as follows. The obtained nanotubes are first dispersed in an ethanol solution (1g titanate nanotubes/50 mL H₂O + 50 mL ethanol), and then appropriate H₂PtCl₆ solution (0.9326 mg/mL) is added. After stirring for 0.5 h, the suspension is irradiated for 3 h with a 300 W High-Pressure Mercury Lamp at a distance of 10 cm under stirring at room temperature. The obtained Pt/TiO₂ are washed with water to remove Cl⁻ ions and dried at 80 °C in air. The contents of platinum, which are calculated by the amount of H₂PtCl₆ added, are 0.5 wt.%, 1.0 wt.%, 1.5 wt.%, 2.0 wt.% and 2.5 wt.%, respectively. The color of samples changes from weak yellow to grey with the increase of platinum contents.

Characterization of samples

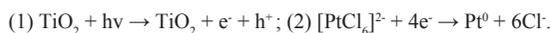
The powder X-ray diffraction (XRD) experiments are carried out at room temperature using a Rigaku D/Max-2500 X-ray diffractometer (CuKα λ = 0.154 nm) to identify crystal phase of the products. The diffraction peaks of samples are compared with those reported in the JCPDS Data File. TEM images are obtained with a Philips T20ST transmission electron microscopy working at 200 kV. UV-visible absorption spectra of the samples are obtained with a JASO V-570 spectrometer. The chemical states of Pt, Ti and O are investigated by X-ray photoelectron spectroscopy (XPS) using an Al Kα X-ray source (Al Kα-150W, Kratos Axis Ultra DLD).

Test of photocatalytic performance

The photocatalytic performances of the samples prepared are evaluated by the degradation rates of methyl orange in water under UV-vis light irradiation. The photocatalyst (50 mg) is dispersed in 100 mL of methyl orange solution (13 mg/L). Then the system is irradiated with a 300W high-pressure mercury lamp at a distance of 10 cm and ambient temperature. The concentration of methyl orange solution is monitored by measuring the absorbency of solution at 463.5 nm using a TU-1901 spectrometer. The results are corrected for the decomposition of the methyl orange in the absence of catalysts and its adhering to the catalyst.

RESULTS AND DISCUSSION

It is well known that when TiO₂ are photoexcited by UV light of High-Pressure Mercury Lamp, photogenerated holes (h⁺) and electrons (e⁻) come into being. The electrons in valence bands can be captured by [PtCl₆]²⁻ ions that adhere to the nanotubes, and the [PtCl₆]²⁻ ions are reduced into metal Pt, forming Pt/TiO₂ as a result. The processes can be described as follows:



In order to get detail microstructures of samples, TEM observations are carried out and obvious difference can be seen between the pure titanate nanotubes and Pt/TiO₂. Fig. 1 shows the TEM and HR-TEM images of the sample with 1 wt.% platinum. It can be seen clearly that the tubular structure of some nanotubes has changed greatly after the irradiation process. Though some nanotubes still keep their tubular structure (Fig. 1A) the length of the most of nanotubes becomes relatively shorter, and some particles appear, which adhere to linear bundles of nanotubes. At high magnification (Fig. 1B), fringes periodicity of the sample is measured as 0.35 nm, which is consistent well with the lattice spacing between {101} planes of anatase TiO₂. It can be concluded that the tubular structure of most nanotubes is broken during the irradiation process.

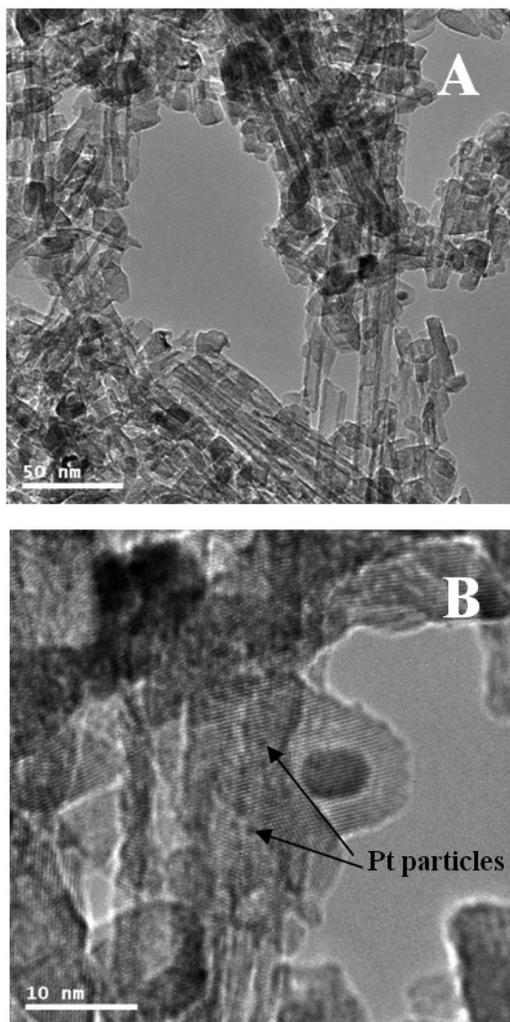


Fig. 1: TEM (A) and HR-TEM (B) images of Pt/TiO₂ with 1wt.% platinum.

From Fig. 1B, black particles with size less than 1 nm (marked with arrow) can be observed, which should be platinum particles come from [PtCl₆]²⁻ ions. As soon as the Pt/TiO₂ forms, the photoelectrochemical cell consisting of Pt and TiO₂ emerges. Reference has reported that Pt/TiO₂ could photocatalyzes water splitting [28]. Under the excitation of UV irradiation, the active intermediate H[•] coming from water splitting on the Pt/TiO₂ can react with some of O atoms on the surface of nanotubes, which may weaken or break Ti-O bonds and mangle the tubular structure of titanate nanotubes. In other words, the formation of platinum particles and the damage of titanate nanotubes may take place at the same time. The similar results appear as the titanate nanotubes

supported [PtCl₆]²⁻ ions are reduced with hydrogen gas at 200 °C. Although photoreductive deposition process can result in formation of very small metal particles and prevent the formed platinum particles from agglomeration, the tubular structure of some nanotubes is destroyed badly. In order to validate the conclusions above, pure titanate nanotubes are dispersed in pure water and treated under UV light for 3 h. Fig. 2 shows TEM images of Pt-free TiO₂ titanate nanotubes treated by UV irradiation. It can be seen that the length of the treated nanotubes is more than hundreds of nanometer. Their tubular structure remains, and no obvious damage is observed. It can be concluded that the platinum particles formed in photoreductive deposition process take a part of an important action for the collapse of the titanate nanotubes. XRD analyses are carried out to further identify crystal phases of the samples.

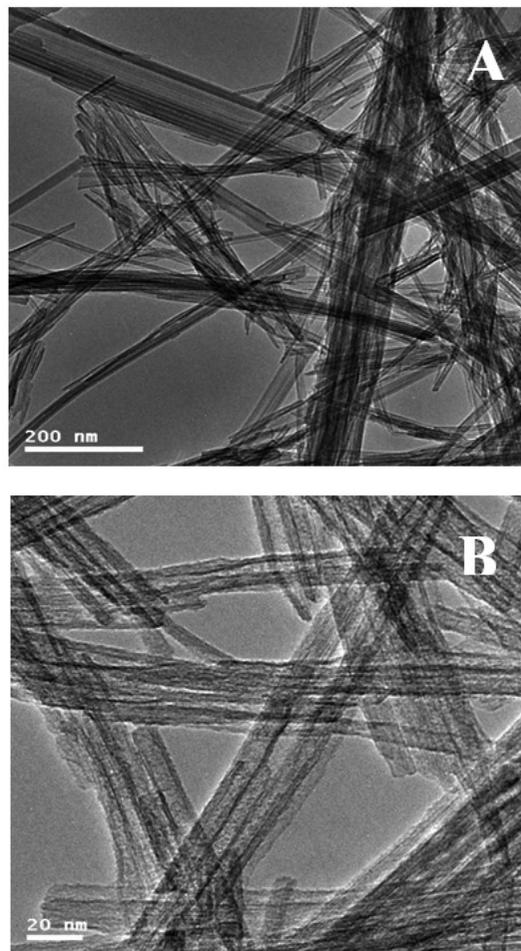


Fig. 2: TEM images of Pt-free titanate nanotubes treated using UV irradiation.

Fig. 3 depicts the XRD patterns of titanate nanotubes and Pt/TiO₂ with different Pt contents. It can be seen that the crystal phase of the nanotubes changes after the photoreduction process. The as-prepared nanotubes, whose diffraction peaks are relatively weak, are composed of titanate H₂Ti₂O₅·H₂O (JCPDS 47-0124) instead of anatase TiO₂ (Fig. 3a), which is confirmed by the peaks at 2θ = 9.2° and 24°. The two peaks correspond well to (2 0 0) and (1 1 0) reflections of H₂Ti₂O₅·H₂O, respectively. After platinum is loaded, the intensity of diffraction peaks at 2θ = 9.2° and 24° decreases obviously, while that of the other diffraction peaks increases. When the content of platinum reaches at 1 wt.%, the reflections of H₂Ti₂O₅·H₂O are hardly detectable, and all peaks of anatase TiO₂ (JCPDS 21-1272) appear, which means the titanate has been converted into anatase completely. It has been reported that the crystal phase influences the structure of nanotubes [25]. So the structure of nanotubes in Pt/TiO₂ may be partly damaged in the process of phase transformation. Furthermore, it can be observed that the peak intensity of anatase TiO₂ increases with the increase of amount of platinum, which indicates that the

titanate turns into anatase TiO₂ in the irradiation process and platinum plays a key role in this transformation. It is also in accord with the results of TEM images. Surface area is an evident parameter for the tubular catalysts. The specific surface areas of hydrogen titanate nanotubes and 2 wt.% Pt/TiO₂ are measured to be 428 and 175 m²/g, respectively. It can be seen that the structure of 2 wt.% Pt/TiO₂ should have been damaged obviously. Although the crystal phase and structure of nanotubes changes after the irradiation process, the diffraction peak of platinum is not found in the Pt/TiO₂ with various platinum contents. The reasonable interpretation should be that the platinum particles in them are too small to be detected by XRD.

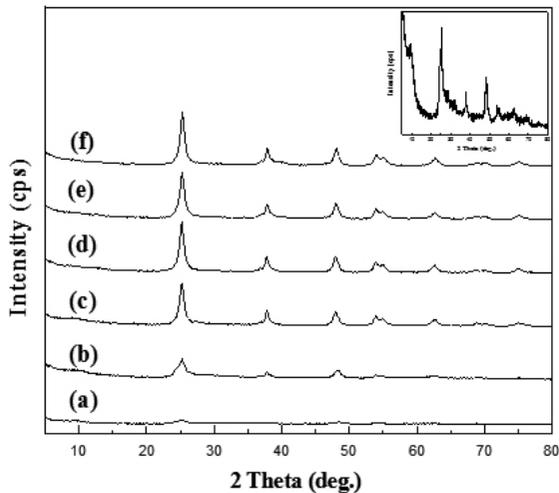


Fig. 3: XRD patterns of as-prepared titanate nanotubes (a), 0.5 wt.% (b), 1 wt.% (c), 1.5 wt.% (d), 2 wt.% (e) and 2.5 wt.% (f) Pt/TiO₂ (inset curve is the enlarged XRD pattern of sample a).

In order to validate the existence of platinum in the samples, XPS spectra are used to analyze the samples. The Pt/Ti atomic ratio of Pt/TiO₂ with 1 wt.% platinum is examined to be 0.03, and is higher than the calculated one. It indicates a certain surface platinum enrichment. The deposition process should be the reason for the above result. In this process, most of the platinum nanoparticles deposited on the surface of nanotubes and relatively high platinum content can be detected by XPS. Fig. 4 shows the high resolution XPS spectra of Ti 2p. The Ti 2p_{1/2} and Ti 2p_{3/2} spin-orbital splitting photoelectrons for the sample are located at binding energies of 464.2 and 458.4 eV, respectively, which is in agreement with the reported literature values^[29,30], showing the presence of Ti⁴⁺.

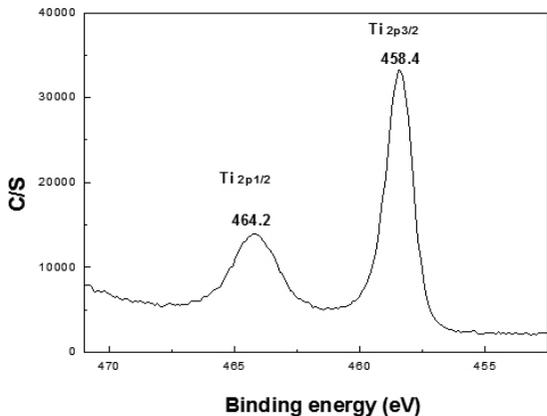


Fig.4: High resolution XPS spectra of the Ti 2p region for 1 wt.% Pt/TiO₂.

Fig. 5 shows the O 1s XPS spectra of Pt/TiO₂. The main peak of O 1s located at about 529.8 eV, which has a similar energy to the O 1s electron binding energy of TiO₂, can be assigned to the peak of lattice oxygen in TiO₂

nanotubes. The O 1s signal shows a “shoulder” located at the side of higher binding energies, indicating a great amount of surface hydroxyl groups or chemisorbed water molecules^[29,30]. As indicated in the XRD patterns, there are still titanate remains in the 1 wt.% Pt/TiO₂ catalyst after 3h irradiation under UV light. As a result, large amounts of hydroxyl exist in the tubular catalyst, and “shoulder” at higher binding energies for O 1s XPS exhibits. Fig. 6 shows the high resolution XPS spectra of the Pt 4f region of Pt/TiO₂. It can be seen that the binding energies of Pt 4f_{5/2} and Pt 4f_{7/2} are 76.6 and 72.6eV, respectively. It has been reported that the binding energies of Pt 4f_{5/2} and Pt 4f_{7/2} are 74.8 and 71.5 eV for Pt⁰, while are 77.7 and 74.4 eV for PtO. It seems that except platinum exists in the Pt/TiO₂, platinum oxide also exists in the samples^[31,32].

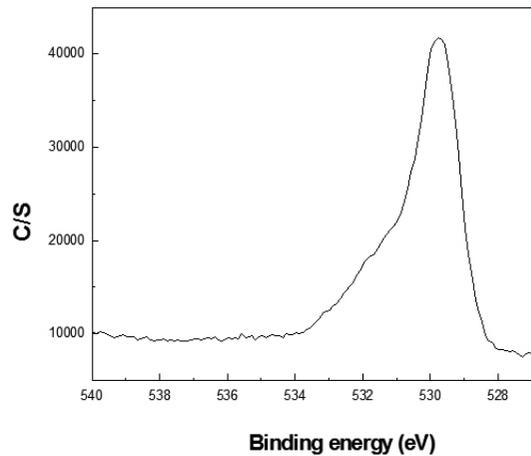


Fig.5: High resolution XPS spectra of the O 1s region for 1 wt.% Pt/TiO₂.

After platinum is loaded, the color of samples shows distinct difference, and the color varies with the contents of platinum. To explore the optical absorption properties of the samples, UV-Vis diffuse reflectance spectra of the samples are measured. Fig. 7 shows the diffuse reflectance spectra of pure nanotubes and Pt/TiO₂ with different platinum concentrations. It can be seen that the optical absorption enhances significantly in the visible region of 400-800 nm after platinum is loaded, and the optical absorption increases with the contents of platinum, corresponding to the buff and grey color of the powder. The increase in absorbance should come from scattering effects from the platinum particles^[33] or from surface resonance^[34].

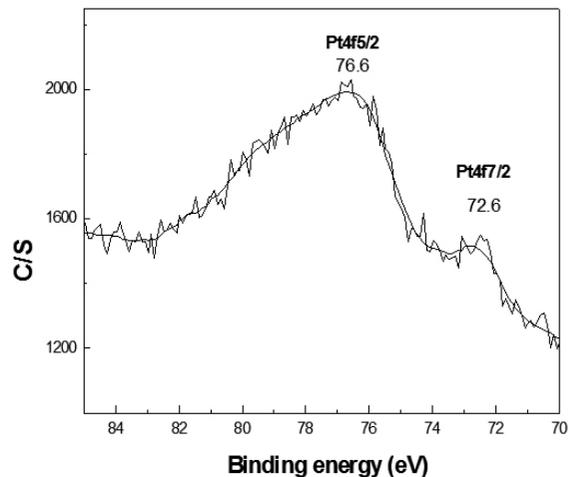


Fig.6: Higher resolution XPS spectra of the Pt 4f region for 1 wt.% Pt/TiO₂.

In order to investigate the photocatalytic performance of the prepared samples, their photocatalytic performances are evaluated by the degradation rates of methyl orange. Fig.8 shows the photocatalytic activity of Pt/TiO₂ as a function of Pt contents, and catalytic performances of the samples are revealed

by the percent of residual methyl orange after different irradiation times. It is obvious that the contents of platinum in samples have great influence on the photocatalytic activity of Pt/TiO₂. A small amount of platinum loading (0.5 wt.%) results in the increase of the photocatalytic activity of TiO₂ greatly. As the contents of platinum are in the range of 0.5 wt.% and 1.5 wt.%, the photocatalytic activity of sample increases with the increase of platinum content. When amount of platinum is 1.5 wt.%, the activity of sample arrives at the highest. 91% of the methyl orange is degraded after 30 min irradiation. However, a further increasing amount of platinum reduces the photocatalytic activity. When the content of platinum reaches at 2.5 wt.%, the activity of Pt/TiO₂ even becomes lower than that of pure titanate nanotubes. In this photocatalytic system, TiO₂ are active centers, and platinum particles act as electron acceptor, which promotes interfacial charge-transfer processes [2,35]. The photocatalytic activities of samples with various platinum contents display that the optimum content of platinum in sample is 1.5 wt.%. As the content of platinum is 0.5 wt.%, more electron acceptor sites (platinum particles) form and the photogenerated hole/electron pairs can be separated before recombination. The 1.5 wt.% loading content could be the most efficient separation of photo-induced hole/electron pairs. When the content of platinum is higher (2 wt.% and 2.5 wt.%), space between the platinum particles becomes narrow; the light can be shielded by the supported platinum particles, and the efficient surface of catalyst decreases. In this case, the platinum particles perhaps turn into new hole/electron recombination sites. As a result, excess platinum loading decrease the photocatalytic active centers on TiO₂. The photocatalytic activity of P25 is also included in this figure for comparison. It can be observed that our Pt/TiO₂ catalysts with 1 wt.% and 1.5 wt.% platinum have higher activity under the same reaction condition. The recycle utilize of Pt/TiO₂ also shows good results. Due to the high sedimentation rate of the one-dimensional catalyst, Pt/TiO₂ can be recycled and expected to be useful in practical application.

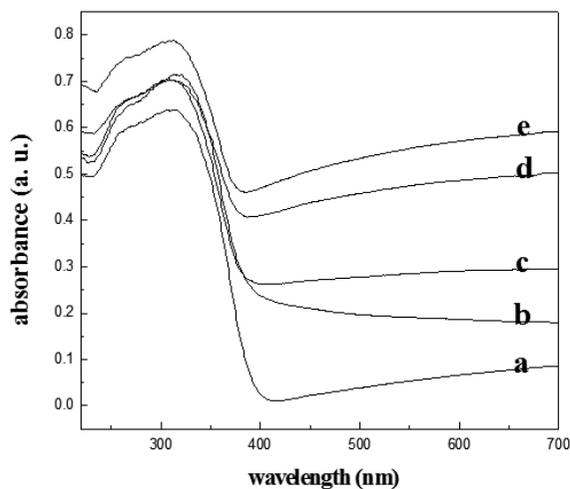


Fig.7: UV-Vis diffuse reflectance spectra of titanate nanotubes (a) and Pt/TiO₂ with 1 wt.% (b), 1.5 wt.% (c), 2 wt.% (d) and 2.5 wt.% (e) platinum.

CONCLUSIONS

Pt-modified TiO₂ with one-dimensional structure can be prepared by using hydrogen titanate nanotubes as support after a photoreductive deposition process. The existence of platinum has obvious influence on the structure and catalytic performance of the hydrogen titanate nanotubes. During the fabrication process of Pt/TiO₂, platinum can induce the transformation of titanate to TiO₂, which results in damage of the tubular structure. The photocatalytic activity of Pt/TiO₂ for degradation of methyl orange is also depended on the content of platinum. When the content of platinum is 1.5 wt.%, the Pt/TiO₂ shows the highest photocatalytic activity.

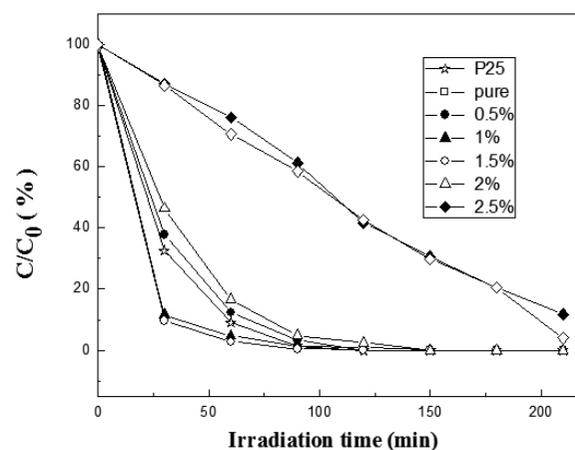


Fig.8: The photocatalytic activity of P25 and Pt/TiO₂ with various contents of platinum.

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