

EXPLORING THE DIVERSE APPLICATIONS OF TiO₂+PT CATALYSTS

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ABSTRACT

Plasmonic solids comprising TiO₂+Pt with 1 wt.% Pt and diverse TiO₂ supports (namely anatase nanoparticles (TNP), polycrystalline nanorods (a-TNR), and single-crystal anatase nanorods (TNR)) were synthesized via the wet impregnation method. These solids were evaluated as catalysts in gas-solid and gas-liquid-solid reactions, serving as photo, thermal, and photothermal catalysts. The distinctive charges on the surfaces of the TiO₂ supports led to the formation of Pt particles with varying sizes, crystallinities, and levels of interaction with the TiO₂ supports during synthesis. Schottky barrier heights (SBH) were determined to be 0.38 eV for a-TNR+Pt, 0.41 eV for TNP+Pt, and 0.50 eV for TNR+Pt samples, respectively. The reduced photocatalytic activity of the TNR+Pt catalyst under visible light for the oxidation of water-dissolved bisphenol A (BPA) is attributed to its high SBH and deactivation of active sites due to BPA adsorption or its oxidation products. Conversely, the TNR+Pt catalyst exhibited the highest photothermal catalytic H₂-assisted NO₂ reduction rate. This superiority can be attributed to several factors, including a narrow particle size distribution of small Pt particles, the absence of Pt-catalyzed reduction of the TNR support at higher temperatures, and a slower re-injection rate of "hot electrons" from the TNR support to the Pt particles.

Keywords: plasmonic noble metal, visible-light illumination, Schottky barrier height, photothermal catalysis.

INTRODUCTION

The plasmonic characteristics of noble metals such as Au, Ag, and Pt can activate the photocatalytic capabilities of the wide band-gap semiconductor TiO₂ under visible-light exposure [1-3]. When illuminated with light of a wavelength equal to or greater than their surface plasmon resonance, noble metals generate "hot electrons". These "hot electrons" are subsequently injected into the conduction band of TiO₂. The effectiveness of this plasmon-induced injection of "hot electrons" is influenced by the height of the Schottky barrier (SB) at the interface between the noble metal and the TiO₂ support [1-3]. The objectives of this study were threefold: i) to comprehensively explore how the optical, electronic, and catalytic properties of TiO₂+Pt catalysts with 1 wt.% Pt loading correlate with the textural and morphological attributes of the TiO₂ support; ii) to employ X-ray photoelectron spectroscopy (XPS) to ascertain the height of the Schottky barrier (SBH); and iii) to examine the versatile application of the prepared catalysts by utilizing the same material as a photocatalyst, thermal catalyst, and photothermal catalyst in various environmental remediation applications.

EXPERIMENTAL

TiO₂+Pt plasmonic composites containing 1 wt.% Pt and employing various TiO₂ supports - namely anatase nanoparticles (TNP, with a specific surface area of 86 m²/g), polycrystalline nanorods (a-TNR, with a specific surface area of 352 m²/g), and single-crystal anatase nanorods (TNR, with a specific surface area of 105 m²/g) - were synthesized using the wet impregnation technique. These synthesized TiO₂+Pt materials were assessed for their potential as photocatalysts in the treatment of wastewater in a batch slurry reactor under visible-light illumination, with bisphenol A (BPA) serving as the model organic pollutant. Furthermore, the prepared composites were subjected to examination in a catalytic model reaction to gauge their activity in the reduction of NO_x in the presence of H₂ as a reducing agent. This served to conceptually illustrate an alternative approach for low-temperature NO_x abatement, which was

further enhanced by employing photocatalysis with visible-light illumination. More information about the experimental data (such as light intensity and wavelength range,..) can be obtained in [3].

RESULTS AND DISCUSSION

The results from TEM and H₂-TPR analyses (Table 1) of the investigated solids reveal the critical influence of the TiO₂ support's nature during the wet impregnation process. This influence extends to the formation of Pt with varying average particle sizes and distributions, as well as the creation of Pt oxides with differing sizes, crystallinity, and levels of interaction with the TiO₂ support. Specifically, the negatively charged surfaces of TNP and a-TNR demonstrate a strong attraction to the positively charged Pt(NH₃)₂²⁺ complex, resulting in the formation of larger Pt particles, typically ranging from 5-7 nm. Conversely, the positively charged surface of TNR promotes the formation of smaller Pt particles, typically around 2-3 nm. The UV-Vis DR spectra of the TiO₂+Pt catalysts under study illustrate their ability to generate charge carriers when exposed to visible light. This phenomenon is ascribed to the formation of a Schottky barrier (SB), which facilitates the separation and prolonged "lifetime" of charge carriers by transferring the "hot electrons" generated by Pt to the TiO₂ support. The SB heights were determined to be 0.38 eV for a-TNR+Pt, 0.41 eV for TNP+Pt, and 0.50 eV for TNR+Pt samples. In the context of thermal catalytic H₂-assisted NO₂ degradation across the temperature range of 30-400 °C (refer to Figure 1), distinct temperature profiles were observed due to the varied reduction properties of the catalysts. The TNP+Pt catalyst displayed the lowest ignition temperature for NO₂ reduction, mainly attributed to the presence of easily reducible Pt oxides (H₂-TPR profiles of the investigated TiO₂+Pt catalysts can be found in [3]). Conversely, the a-TNR+Pt and TNP+Pt catalysts exhibited a decline in NO₂ reduction rate within the temperature range of 120-250°C, attributable to the Pt-catalyzed reduction of TiO₂ supports. Importantly, the TiO₂+Pt catalysts demonstrated enhanced NO₂ conversion and lower ignition temperatures in the deNO_x process when exposed to visible light at temperatures below 200 °C (refer to Figure 1), attributable to the Pt-LSPR effect. The highest catalytic activity observed for the TNR+Pt catalyst can be attributed to several factors, including a narrow particle size distribution of small Pt particles, the absence of Pt-catalyzed reduction of the TNR support at higher temperatures, and the positive impact of a higher SBH value, which prevents the counter flow of "hot electrons" from the conduction band of the TNR into the Pt particles. The limited visible-light-triggered photocatalytic activity of the TNR+Pt catalyst toward the oxidation of water-dissolved BPA is attributed to its high SBH and active site degradation due to the adsorption of BPA and/or BPA products (refer to Figures. 2 and 3).

Table 1. Comparison of the specific surface area (S_{BET}), average pore diameter (d_{pore}), total pore volume (V_{pore}), anatase TiO₂ crystallite size at 25°, band gap values of the investigated materials obtained with the Kubelka-Munk function [4], Schottky barrier height (SBH), the average size of Pt particles and the dispersion of Pt particles.

Sample	S_{BET}	V_{pore}	d_{pore}	^a TiO ₂ crystallite size @ 25°	Band gap	SBH	^b d	Pt dispersion
	m ² /g	cm ³ /g	nm	nm	eV		nm	%
TNP	85.8	0.29	13.7	19.0	3.30	/	/	/
TNP+Pt	63.6	0.26	15.7	19.0	3.20	0.41	~5-7	13
a-TNR	352	0.96	8.9	10.4	3.40	/	/	/
a-TNR+Pt	149.1	0.63	16.9	17.4	3.25	0.38	~5-7	25
TNR	105.0	0.57	19.3	19.0	3.30	/	/	/
TNR+Pt	85.1	0.44	20.0	19.0	3.25	0.50	~2-3	26

^aCalculated using the Scherrer formula and assuming that the TiO₂ particles are spherical.

^bPt particle size was calculated by counting particles from the acquired TEM images.

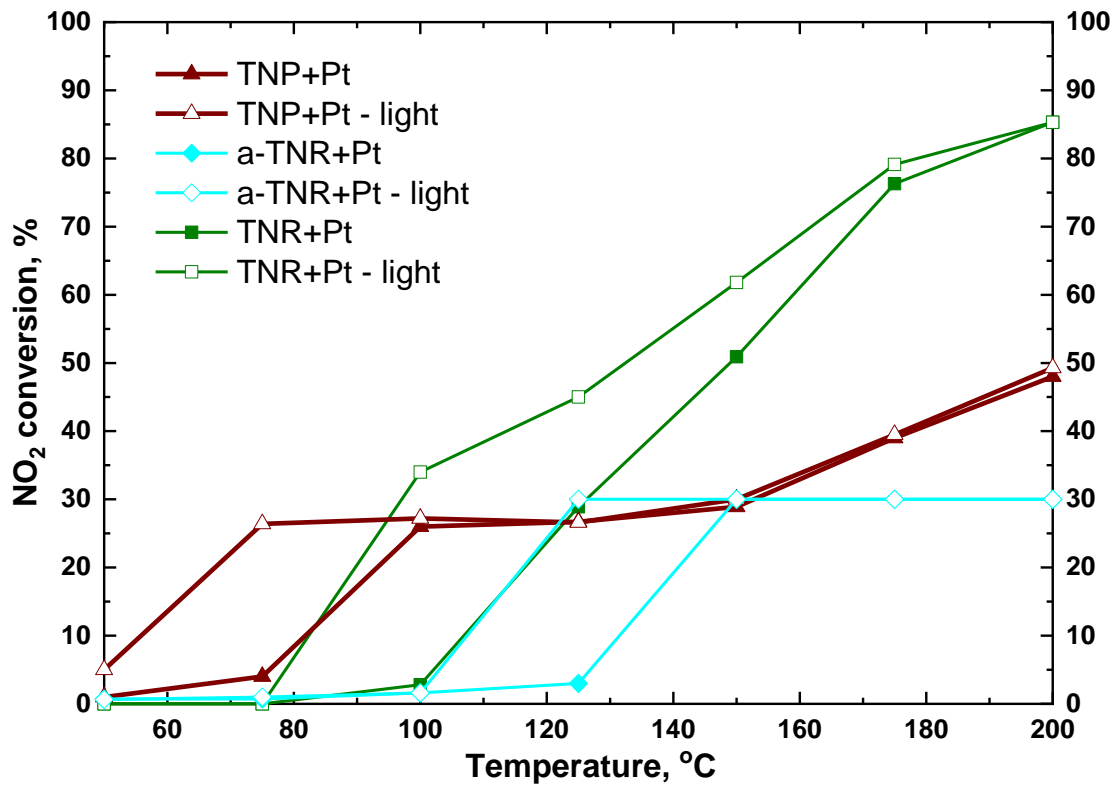


Figure 1. NO₂ conversion versus temperature curves (solid symbols) and visible-light-assisted NO₂ conversion versus temperature curves (open symbols) over bare TiO₂ supports and TiO₂+Pt catalysts.

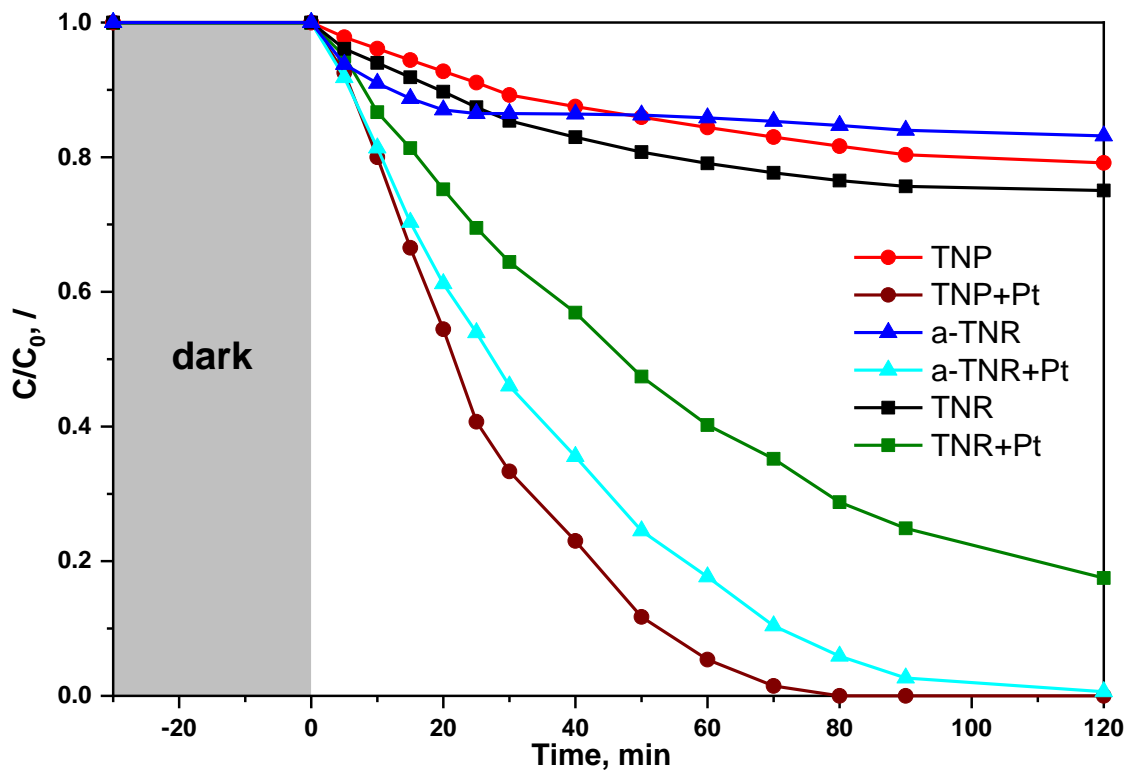


Figure 2. Photocatalytic degradation of an aqueous solution of BPA ($c_0=10.0$ mg/l) conducted at $T=25^\circ\text{C}$ in the presence of bare TiO₂ supports and synthesized TiO₂+Pt catalysts ($c_{\text{cat.}}=125$ mg/l) under visible-light illumination.

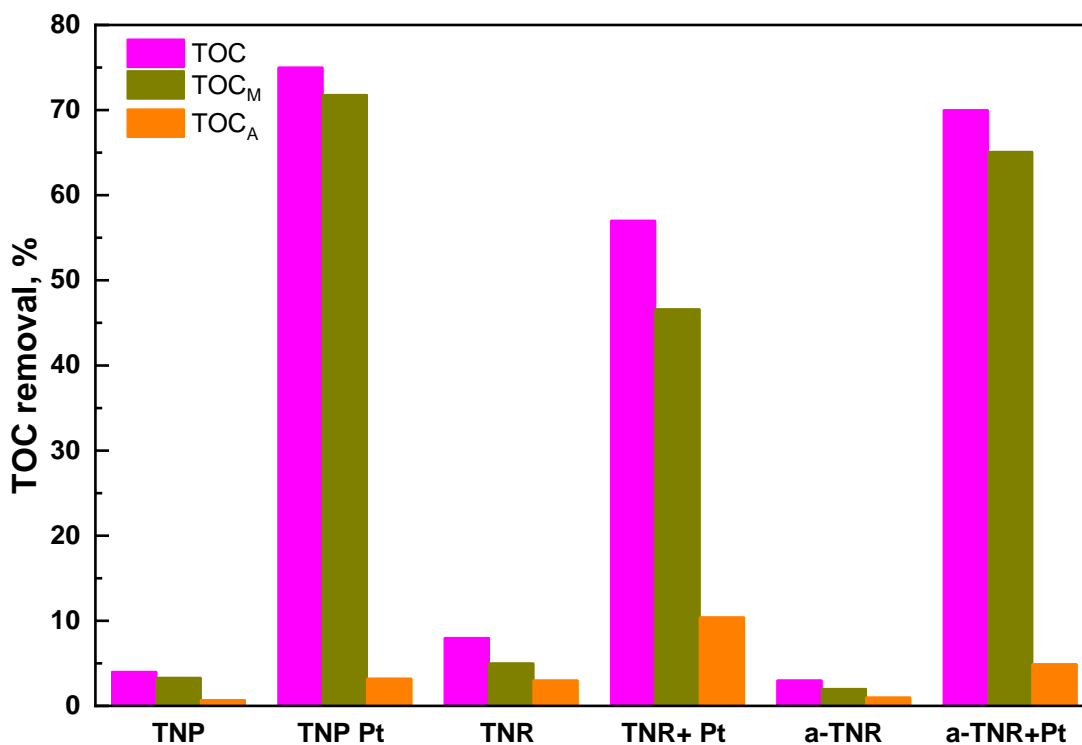


Figure 3. The reported values of total organic carbon (TOC) removal represent a sum of TOC mineralization (TOC_M) and TOC accumulation (TOC_A) measured at the end of the BPA degradation runs.

CONCLUSION

The findings of this study demonstrate that the synthesized TiO₂+Pt plasmonic catalysts exhibit versatility as photocatalysts, thermal catalysts, and photothermal catalysts across various environmental applications involving gas-solid and gas-liquid-solid phases. Furthermore, the catalytic efficacy of the investigated solids is contingent upon their morphological, optical, and electronic attributes, as well as the specific properties and conditions of the application in which they are employed as catalysts.

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