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# Enhancement mechanism of hydroxyapatite for photocatalytic degradation of gaseous formaldehyde over $TiO_2$/hydroxyapatite

Maocong Hu[a,1,*], Zhenhua Yao[a,1], Xuguang Liu[b], Liping Ma[c], Zhong He[d,*], Xianqin Wang[a,*]

[a] Department of Chemical, Biological and Pharmaceutical Engineering, New Jersey Institute of Technology, Newark, NJ 07102, USA
[b] College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China
[c] Oil & Gas Technology Research Institute of Changqing Oilfield Company, Shaanxi Province 710018, China
[d] Primus Green Energy, Hillsborough, NJ 08844, USA

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## ABSTRACT

Hydroxyapatite (HAP) was reported to promote photocatalytic degradation as a support for photocatalysts, but the enhancement mechanism is still unclear. In this study, the promotion role of HAP to $TiO_2$ in photocatalytic degradation is unraveled using experimental observations and kinetic modeling. $TiO_2$/HAP is successfully synthesized by a facile hydrothermal method, which is confirmed by SEM-EDS, TEM, ICP, XRD, and Raman. HAP exhibits a negative effect on the photo absorption ability of $TiO_2$/HAP, which is characterized by UV–vis reflectance spectra (Tauc plot). The formaldehyde-temperature programmed desorption results reveal an affinity between HAP and formaldehyde via a weak chemisorption, which is validated by the estimated adsorption enthalpy/entropy from Van't Hoff plot based on Langmuir–Hinshelwood model. The derived kinetic parameters, including reaction rate constant, Langmuir adsorption constant, apparent activation energy, and adsorption enthalpy and entropy, confirm the experimental results that $TiO_2$/HAP is more active than $TiO_2$. This work verifies the existence of superior chemisorption between HAP and VOCs leading to a better performance of $TiO_2$/HAP for photocatalytic degradation. It helps to understand the role of HAP as an effective support in designing novel HAP-based catalysts.

## 1. Introduction

Photocatalytic degradation of volatile organic compounds (VOCs) and organic wastewater has attracted much attention because it has been recognized as a promising approach to eliminate various organic pollutants without chemical input or output by utilizing solar energy under mild condition [1–9]. $TiO_2$ is the most commonly used and extensively investigated photocatalyst due to its low cost, non-toxicity, favorable band edge positions, high catalytic efficiency and chemical stability [10]. Despite its promising properties, challenges remain for $TiO_2$ in practical application. One of the drawbacks is its low affinity to organic pollutants, which resulted in low photocatalytic degradation rates [11]. One effective and convenient approach improving the low adsorption ability is to immobilize $TiO_2$ onto an adsorbent support. The support absorbs organic pollutants and a higher concentration environment of organic pollutants is formed around $TiO_2$, resulting in a higher photoreaction rate [12]. A number of adsorbents, such as zeolum, alumina, silica, mordenite, ferrierite, and activated carbon, have already been used as the support for $TiO_2$ [13].

Hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$), a major component of the biological hard tissues, has been intensively investigated as a porous support due to the presence of phosphate groups which stabilize the structure of active sites and allow the tuning of acid-base properties by varying the calcium/phosphorus ratio [14]. In recent years, the use of HAP as a photocatalyst or photocatalyst support for wastewater treatment [15–18], $NO_x$ elimination [19,20], and decomposition of organosulfur compound such as dimethyl sulfide (DMS) [21,22] and methyl mercaptan (MM) [23] has also been widely reported. It was suggested that the photocatalytic activity of HAP was attributed to reaction between liquid/gaseous molecules and $O_2{\cdot}$ species under UV ($\lambda = 254\,\text{nm}$) irradiation [24,25]. Photocatalytic degradation of VOCs including formaldehyde [26,27], acetaldehyde [28–30], 2-propanol (IPA) [31,32] and benzene [33] over HAP-based catalysts has been studied in the past two decades. It can be concluded that biphasic $TiO_2$/HAP or titanium-doped HAP shows a greater photocatalytic activity compared with either HAP or $TiO_2$. However, enhancement mechanism is still unclear, especially given that improvement on photo absorption ability is limited [34,35]. Moreover, chemisorption ability assessment (not physical absorption capacity measurement

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* Corresponding authors.
*E-mail address:* mh325@njit.edu (M. Hu).
[1] Authors contribute equally.

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[36]), which is critical for the performance of catalysts, did not draw enough attention in those literature.

The objective of this study is to elucidate the role of HAP in $TiO_2$/HAP catalyst for photocatalytic degradation of VOCs using formaldehyde as a probe. Formaldehyde is selected as the probe since it is one of the major sources of indoor air pollution as well as an intermediate of other VOCs, contributing to the “sick building syndrome”. The $TiO_2$/HAP photocatalyst synthesized via a hydrothermal method were characterized by SEM-EDS, TEM, ICP, XRD, Raman, and BET. The photo-absorption performance was evaluated by bandgaps estimation with Kubelka–Munk (K–M) function from diffuse reflectance spectroscopy (DRS). Formaldehyde-temperature programmed desorption (HCHO-TPD), combined with kinetic study based on the Langmuir–Hinshelwood (L–H) model, is used to investigate the chemisorption of formaldehyde on each catalyst. This work comprehensively investigates the promotion effect of HAP for photocatalytic degradation over $TiO_2$/HAP. It helps to understand the role of HAP as an effective support in designing novel HAP-based catalysts.

## 2. Experimental

### 2.1. $TiO_2$/HAP preparation and characterization

The samples were prepared by a hydrothermal method. Briefly, HAP was synthesized by adding 0.5 mol $L^{-1}$ $NH_4H_2PO_4$ dropwise into 0.5 mol $L^{-1}$ $Ca(NO_3)_2{\cdot}4H_2O$ with a Ca/P molar ratio of 1.67 under stirring. The pH was adjusted to ~10.5 with concentrated ammonia solution (25–28%). After stirring for 2 h, the mixture was transferred into a Teflon-lined stainless-steel autoclave for a hydrothermal treatment at 433 K for 24 h. The separated precipitate was dried to powder HAP. $TiO_2$/HAP were synthesized using HAP and $Ti(SO_4)_2$ as the precursor with the same procedure mentioned before with a Ti/(Ca + Ti) molar ratio of 0.2. Elemental analysis of the samples was carried out by inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkin-Elmer 2100DV, USA). Raman spectroscopy was performed with a Thermo Scientific DXR Raman microscope. X-ray diffraction (XRD) patterns were collected on an X’ pert Pro rotatory diffractometer (PANAlytical Company) using Co Kα radiation ($\lambda = 0.1790$ nm) at 40 kV and 40 mA. The BET (Brunauer, Emmett and Teller) surface areas of the samples were investigated by using $N_2$ adsorption–desorption apparatus (Micromeritics ASAP 2020 M, USA). Surface elemental composition of samples was analyzed through Energy Dispersive X-ray Spectroscopy (EDS) on an Oxford Instrument. Transmission electron microscopy (TEM) images were taken with a JEM-100CXII microscope at an accelerating voltage of 200 kV. Chemisorption performance was characterized by HCHO-TPD. Samples were pre-treated by heating to 423 K under vacuum ($10^{-4}$ Pa) for 2 h. The adsorption of formaldehyde was performed at 298 K until the sample was saturated under the UV irradiation, and then the system was cleared under vacuum of $10^{-4}$ Pa to remove physically adsorbed formaldehyde before heating to 573 K at a heating rate of 0.1667 K $s^{-1}$ in a helium flow. The desorbed gases were analyzed by a LZL-203 quadruple mass spectrometer (Beijing analytic instrument).

### 2.2. UV spectra measurement and band gap calculation

UV–vis spectra were acquired using a Perkin Elmer, Lambda 35 spectrometer in the range 200–1100 nm. $BaSO_4$ was used as a white reference material. To calculate the optical band gap values, the diffuse reflectance is converted to absorption coefficient equivalent using Kubelka–Munk (K–M) function, $F(R_\infty)$ as given below:

$$F(R_\infty) = (1 - R_\infty)^2/2R_\infty = K/S \tag{1}$$

where $R_\infty$ is the reflectance of infinitely thick sample; ‘*K*’ and ‘*S*’ are absorption and scattering coefficients. For a sample with finite thickness, the reflectance is

$$R_\infty = R_{sample}/R_{standard} \tag{2}$$

Afterwards, the Tauc plot was applied. The energy (*E*) dependence of absorption coefficient (*K*) for semiconductor with band edge absorption energy ($E_g$) is given by

$$(\mathrm{F}(\mathrm{R}_\infty)h\upsilon)^\gamma = A(h\upsilon - \mathrm{E}_g) \tag{3}$$

where *A* is a material constant, *h* is the Planck’s constant, $\nu$ is the frequency of the light, $E_g$ is the (optical) energy band gap of the allowed transitions, and $\gamma$ is the power coefficient, characteristic for the type of transition. The value of $\gamma$ is accepted to be equal to 1/2 for HAP and $TiO_2$ because the transition is assumed to be indirectly allowed for such materials [37]. By plotting $[F(R_\infty)h\nu]^{1/2}$ against h$\nu$, the optical $E_g$ of the material can be estimated from the *x*-axis ($K = 0$) intercept of the line that is tangent to the inflection point of the curve.

### 2.3. Photocatalytic degradation of formaldehyde experiment

The schematic diagram of the photocatalytic degradation of formaldehyde experimental set-up was shown in Fig. 1. A leak test was performed before and after each experiment. All of experiments were carried out in a fixed-bed annular quartz reactor with inner diameter of 20 mm and outer diameter of 24 mm with a heater around and an air cooling system in the bottom. The temperature of the irradiated surface of catalyst was monitored by a thermocouple located in the catalyst bed. The light source used was a mercury lamp (power: 125 W; intensity: 40 mW $cm^{-2}$ with dominant wavelength of 365 nm), which was located in the center of the reactor. The catalyst volume is 4 mL. Simulated air, with 20% $O_2$ and 80% $N_2$ (v/v%), was used to carry gaseous formaldehyde and water vapor into the mixing chamber where relative humidity (RH) was monitored by a hygro-thermometer. The different mixing ratios were controlled to keep a constant RH (set as 50%) for each experiment to eliminate the humidity effect on the photocatalytic degradation. Photocatalytic degradation of formaldehyde experiment was performed at varied temperatures (298, 308, 318, and 328 K) under atmospheric pressure. The total flow rate was increased from 10 to 250 mL $min^{-1}$ (*i.e.*, $1.67–41.7 \times 10^{-7}$ $m^3$ $s^{-1}$) with a constant formaldehyde concentration (38 ppm, *i.e.*, $1.58 \times 10^{-3}$ mol $m^{-3}$) to verify if external mass transfer exists. To eliminate internal mass transfer limitation, catalysts with variable particle sizes (40–170 mesh, *i.e.*, $425–90 \times 10^{-6}$ m) were tested for the reaction. The UV irradiation was maintained throughout the whole experiments. Formaldehyde gas concentrations were measured using Agilent-4890 GC system (Agilent, USA). The average value from three sets of independent experiments was reported using three different batches of samples. The conversion was calculated by Eq. (4), where $C_{in}$ and $C_{out}$ are formaldehyde concentration in feed and outlet respectively. The reaction rate of photo degradation of formaldehyde was determined using Eq. (5), where r, $C_{in}$, F, *X* Eq. (4), and V are the reaction rate, formaldehyde feed concentration, total gas flow rate, formaldehyde conversion, and catalyst volume, respectively [38–40].

$$X = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \tag{4}$$

$$\mathrm{r} = \frac{C_{in}FX}{\mathrm{V}} \tag{5}$$

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