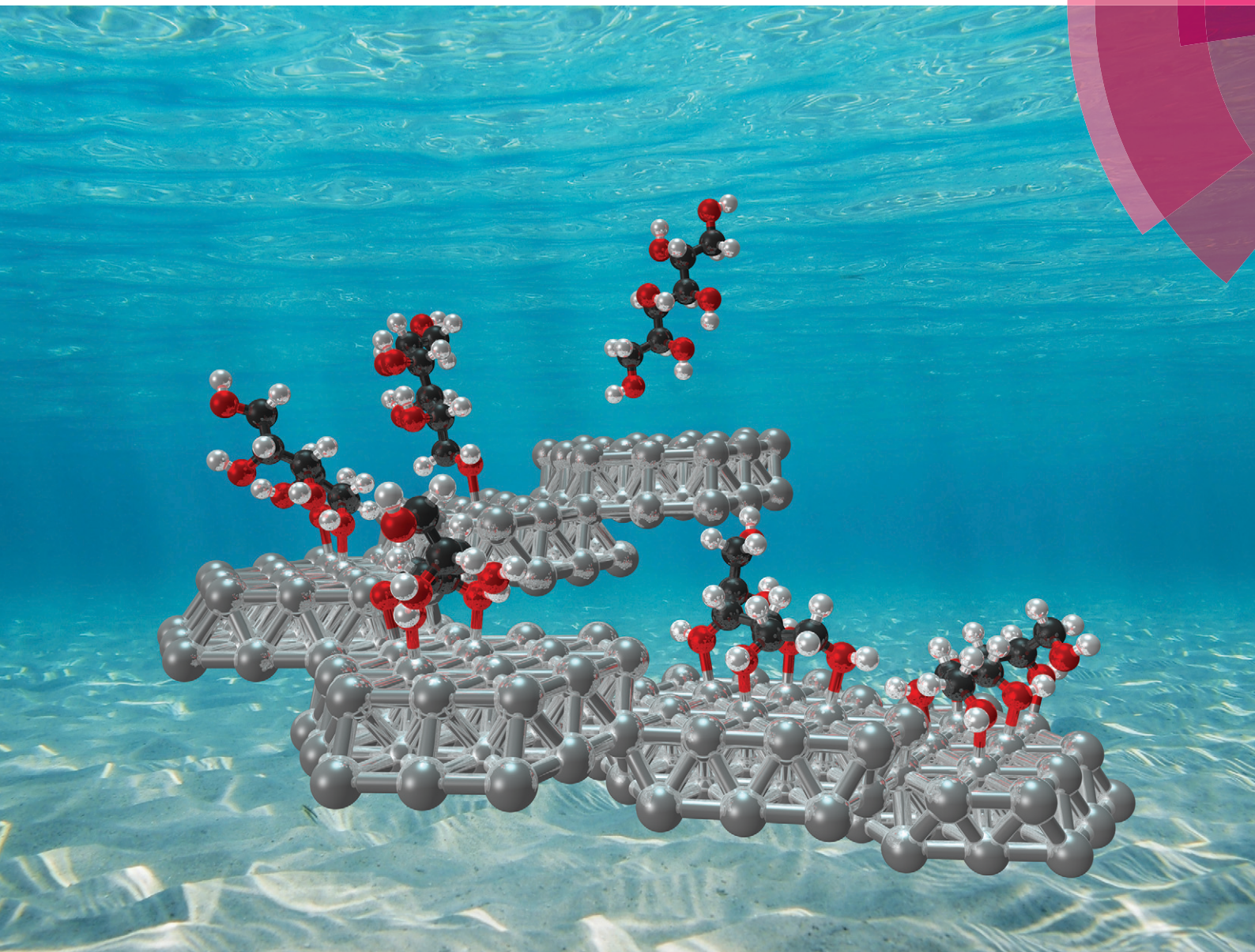


Catalysis Science & Technology

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ISSN 2044-4761



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PAPER

Peter J. C. Hausoul, Regina Palkovits *et al.*
Kinetics study of the Ru/C-catalysed hydrogenolysis of polyols – insight
into the interactions with the metal surface



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Original research articles published in the journal must show new catalytic discoveries that are a significant advance on previously published work, bringing conceptual advances, or molecular insights to catalytic processes, and where appropriate, demonstrate the relationship between synthesis, structure and performance of catalytic systems. Kinetics and mechanisms are a central part of catalysis science and should be included in submitted articles.

Examples of topics within the journal's scope and the expected significance are:

- In-depth mechanistic insights through advanced methods and theoretical methods that are of significant and direct interest and impact in the science and application of catalysts and catalytic processes. Studies using concepts are preferred to trial and error optimisation
- New catalysts and/or processes for conversions of current and future interest within life sciences, pharmaceuticals, polymers, environmental protection, energy and fuels. Studies that report incremental improvement of catalytic performance will not be published in the journal
- New catalytic reactions with significant impact in addressing current challenges and societal demands, for example waste reduction, reduced energy use or efficient use of feedstocks
- Studies that relate chemical reactions at surfaces, reactivity of metal complexes, or macromolecular structure to catalytic function and processes. Studies emphasising sophisticated materials and properties with residual evidence of catalytic function will not be published in the journal
- Theoretical studies of materials and molecules (exhibiting catalytic turnover) that result in significantly greater performance or understanding of existing catalytic reactions
- Studies on multiscale modelling, for example, engineering of catalytic processes from the nano to the macroscale
- Synthesis strategies for inorganic materials, hybrid materials and macromolecules that can be used as catalysts or their supports. Studies that claim catalyst performance must support this with kinetic data and proper mass balances

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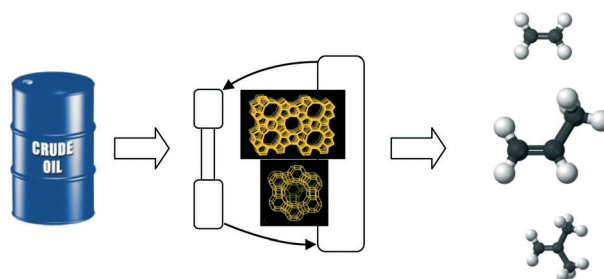
PERSPECTIVE

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Crude oil to chemicals: light olefins from crude oil

A. Corma,* E. Corresa, Y. Mathieu, L. Sauvanaud, S. Al-Bogami, M. S. Al-Ghrami and A. Bourane

The possibility to fulfill the increasing market demand and producers' needs in processing straightforwardly crude oil, a cheap and universally available feedstock, to produce petrochemicals appears to be a very attractive strategy.



COMMUNICATIONS

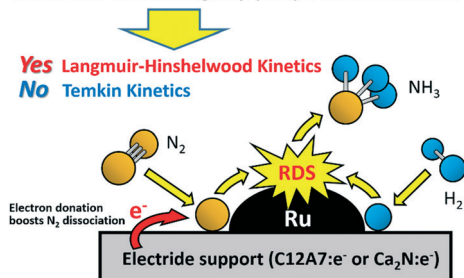
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Kinetic evidence: the rate-determining step for ammonia synthesis over electrone-supported Ru catalysts is no longer the nitrogen dissociation step

Yasukazu Kobayashi, Masaaki Kitano, Shigeki Kawamura, Toshiharu Yokoyama and Hideo Hosono*

The rate-determining step for ammonia synthesis over Ru catalysts supported by electrone, such as $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}(\text{e}^-)_4$ and $\text{Ca}_2\text{N}:\text{e}^-$, is suggested to be the surface reactions of N and H adatoms, in which case the Langmuir–Hinshelwood model should be used to describe the kinetics.

A new rate-determining step (RDS) is surface reactions



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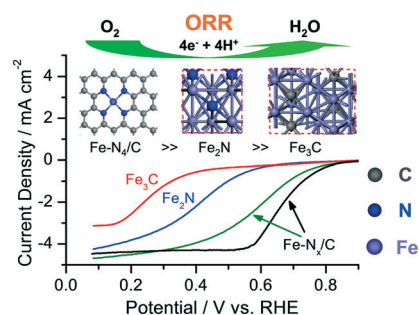


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Is iron nitride or carbide highly active for oxygen reduction reaction in acidic medium?

Tao Sun, Yufei Jiang, Qiang Wu,* Lingyu Du, Zhiqi Zhang, Lijun Yang,* Xizhang Wang and Zheng Hu*

The high ORR activities in acidic medium for the so-called Fe₂N- and Fe₃C-based catalysts actually originate from the trace of Fe–N_x/C moieties (x ≥ 4) rather than the Fe₂N or Fe₃C phases themselves.



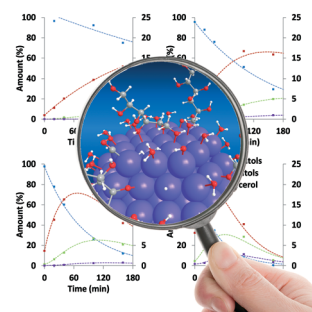
PAPERS

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Kinetics study of the Ru/C-catalysed hydrogenolysis of polyols – insight into the interactions with the metal surface

Peter J. C. Hausoul,* Anna K. Beine, Leila Neghadar and Regina Palkovits*

Kinetic analysis of stereoisomerization, decarbonylation and deoxygenation provides insight into the reactivity and dynamics of polyols on Ru-surfaces.

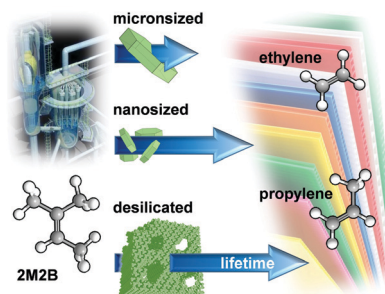


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Engineering of ZSM-5 zeolite crystals for enhanced lifetime in the production of light olefins via 2-methyl-2-butene cracking

Sharon Mitchell, Marilyn Boltz, Jiaxu Liu and Javier Pérez-Ramírez*

ZSM-5 zeolites are tailored for the production of light olefins via 2-methyl-2-butene cracking.

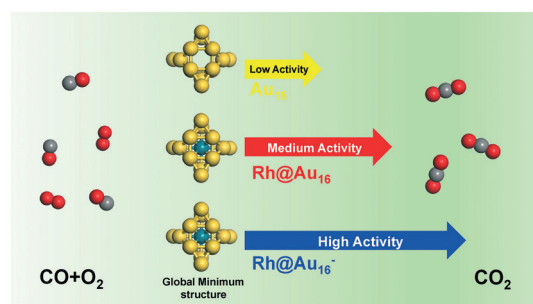


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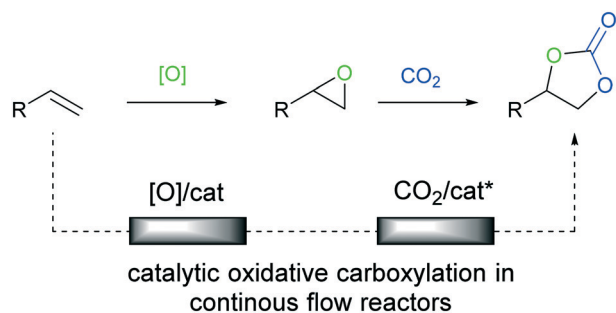
CO oxidation on Rh-doped hexadecagold clusters

Jin-Xun Liu, Zhiling Liu, Ivo A. W. Filot, Yaqiong Su, Ionut Tranca and Emiel J. M. Hensen*

Exploring the unique catalytic properties of gold clusters associated with specific nano-architectures is essential for designing improved catalysts with a high mass-specific activity.



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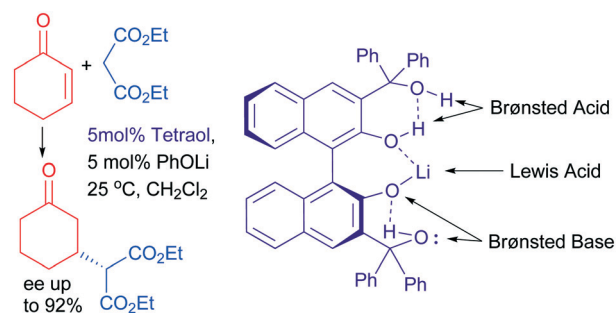


Synthesis of cyclic organic carbonates via catalytic oxidative carboxylation of olefins in flow reactors

Ajay A. Sathe, Anirudh M. K. Nambiar and Robert M. Rioux*

The direct catalytic conversion of olefins into cyclic carbonates using peroxide and carbon dioxide is demonstrated using continuous flow reactors.

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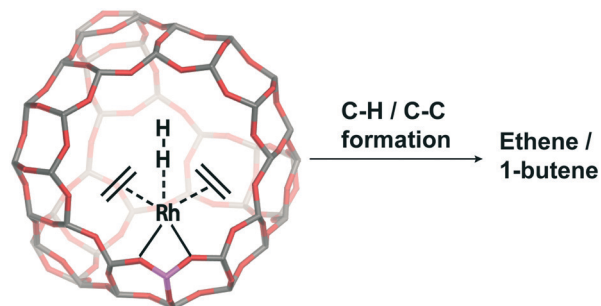


A mechanistic study of the Lewis acid–Brønsted base–Brønsted acid catalysed asymmetric Michael addition of diethyl malonate to cyclohexenone

Yuri Samoilichenko, Veronica Kondratenko, Mariam Ezernitskaya, Konstantin Lyssenko, Alexander Peregudov, Victor Khrustalev, Victor Maleev, Margarita Moskalenko, Michael North, Alan Tsaloev, Zalina T. Gugkaeva and Yuri Belokon*

Reaction shown to exhibit biomimetic behaviour.

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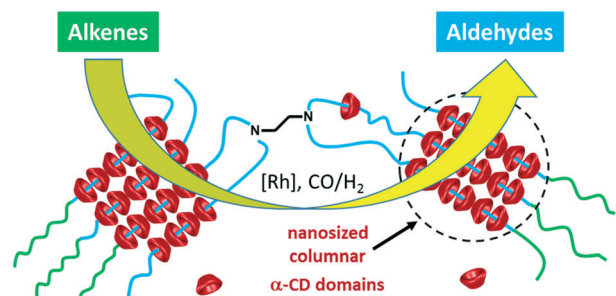


Ethene hydrogenation vs. dimerization over a faujasite-supported $[\text{Rh}(\text{C}_2\text{H}_4)_2]$ complex. A computational study of mechanism

Agalya Govindasamy, Velina K. Markova, Alexander Genest and Notker Rösch*

A DFT study allows one to understand the selectivity for ethene hydrogenation over dimerization by the well-characterized faujasite-supported $[\text{Rh}(\text{C}_2\text{H}_4)_2]^+$ complex.

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Tetronics/cyclodextrin-based hydrogels as catalyst-containing media for the hydroformylation of higher olefins

M. Chevy, T. Vanbésien, S. Manuel, E. Monflier and F. Hapiot*

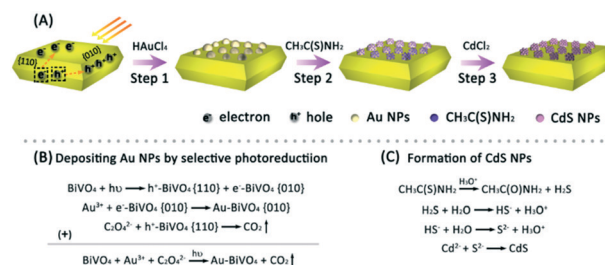
The rhodium-catalyzed hydroformylation of alkenes has been investigated under biphasic conditions using combinations of α -cyclodextrin (α -CD) and poloxamines (Tetronics®).

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Z-scheme CdS–Au–BiVO₄ with enhanced photocatalytic activity for organic contaminant decomposition

Shenyuan Bao, Qiangfang Wu, Shunzhou Chang, Baozhu Tian* and Jinlong Zhang*

A Z-scheme heterogeneous photocatalyst CdS–Au–BiVO₄ was synthesized for the first time by photo-reduction and deposition–precipitation methods.

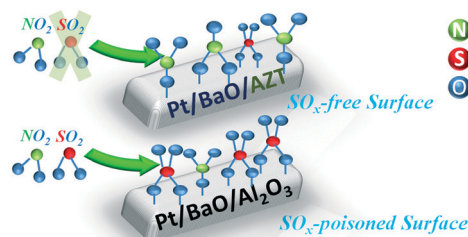


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Sulfur-tolerant BaO/ZrO₂/TiO₂/Al₂O₃ quaternary mixed oxides for deNO_x catalysis

Zafer Say, Oana Mihai, Merve Tohumeken, Kerem Emre Ercan, Louise Olsson and Emrah Ozensoy*

A novel AZT – supported NSR/LNT catalyst with enhanced sulfur regeneration performance.

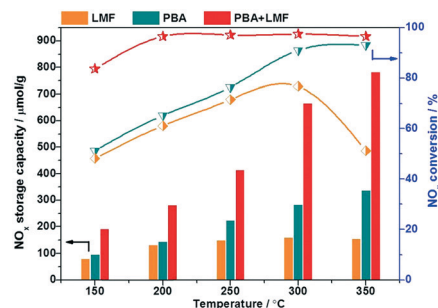


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Low-temperature H₂-plasma-assisted NO_x storage and reduction over a combined Pt/Ba/Al and LaMnFe catalyst

Zhao-shun Zhang, Chuan Shi,* Zhi-feng Bai, Ming-run Li, Bing-bing Chen and Mark Crocker*

With the assistance of H₂ plasma in rich phase, higher NO_x conversions could be obtained over the PBA+LMF sample over a wide temperature range (200–350 °C).

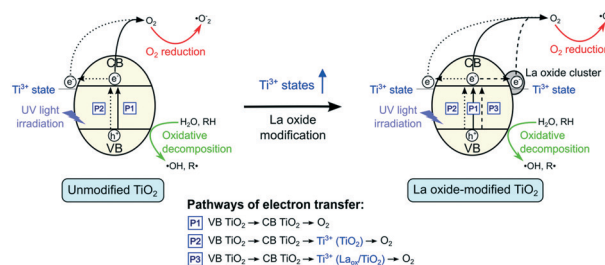


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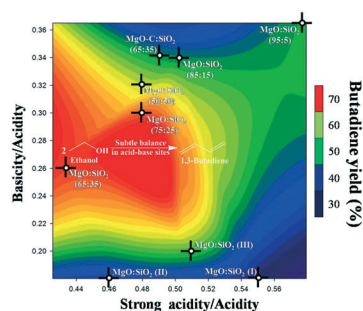
Role of lanthanum species in improving the photocatalytic activity of titanium dioxide

Wai Ruu Siah, Hendrik O. Lintang and Leny Yuliaty*

Lanthanum modification resulted in the additional formation of Ti³⁺ states, which enhanced the charge transfer and separation. Consequently, the photocatalytic activity of TiO₂ under UV light irradiation was significantly improved.



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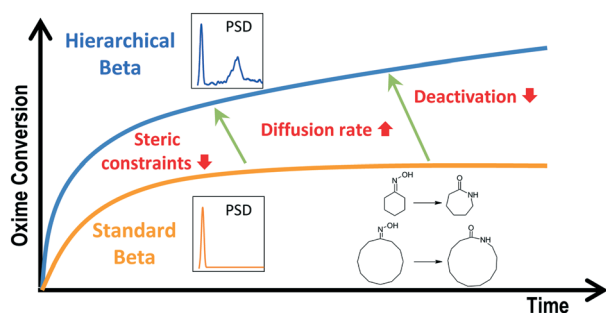


Highly active and selective binary MgO–SiO₂ catalysts for the production of 1,3-butadiene from ethanol

Xiaoxiong Huang, Yong Men,* Jinguo Wang, Wei An and Yuanqiang Wang

Wet-kneaded binary MgO–SiO₂ composite catalysts gave exceptionally high productivity of butadiene governed by a subtle balance of acid–base sites in relation to the formation of an interfacial Si–O–Mg linkage and by varying preparation methods and MgO to SiO₂ ratios.

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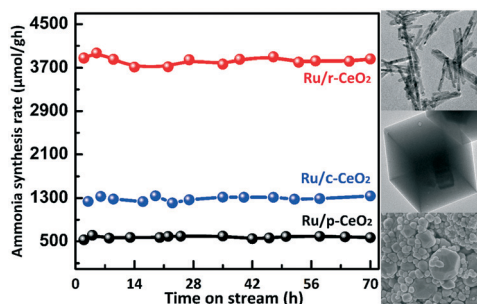


Effect of hierarchical porosity in Beta zeolites on the Beckmann rearrangement of oximes

M. Linares, C. Vargas, A. García, C. Ochoa-Hernández, J. Čejka, R. A. García-Muñoz and D. P. Serrano*

Hierarchical Beta zeolites with different Si/Al molar ratios, synthesized by crystallization of silanized protozeolitic units, were investigated in the liquid-phase Beckmann rearrangement of cyclohexanone and cyclododecanone oximes.

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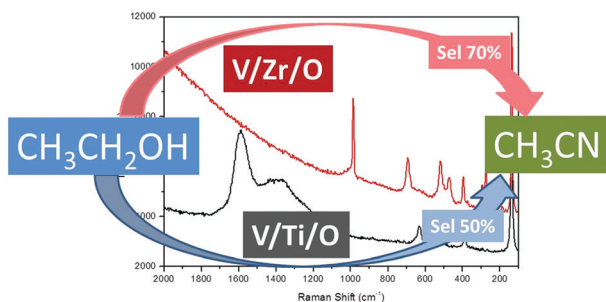


New insights into the support morphology-dependent ammonia synthesis activity of Ru/CeO₂ catalysts

Zhanwei Ma, Shengli Zhao, Xiaoping Pei, Xumao Xiong and Bin Hu*

Different morphologies ceria (nanocubes, nanorods and nanoparticles) were synthesized and exhibited significant support-morphology-dependent catalytic activity towards ammonia synthesis.

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Ethanol gas-phase ammoxidation to acetonitrile: the reactivity of supported vanadium oxide catalysts

F. Folco, J. Velasquez Ochoa, F. Cavani,* L. Ott and M. Janssen

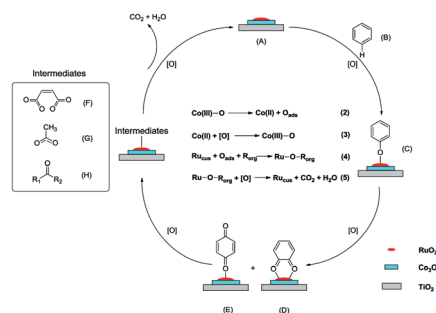
The gas-phase ammoxidation of ethanol, a bio-based platform molecule, has been investigated as a possible more sustainable route for the production of acetonitrile, using supported vanadium oxide catalysts. The nature of the interaction between the support and the active species greatly affected the catalytic performance.

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Catalytic oxidation of benzene over ruthenium–cobalt bimetallic catalysts and study of its mechanism

Xiaolong Liu,* Junlin Zeng, Wenbo Shi, Jian Wang, Tingyu Zhu* and Yunfa Chen

A Ru–Co bimetallic catalyst was well demonstrated in benzene oxidation, and the reaction mechanism was studied.

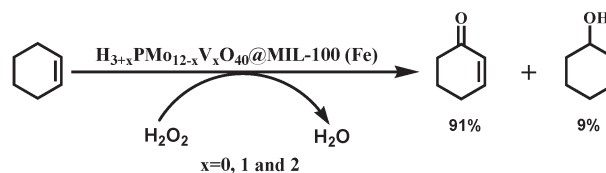


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Highly selective oxidation of cyclohexene to 2-cyclohexene-1-one over polyoxometalate/metal-organic framework hybrids with greatly improved performances

Jinhui Tong,* Wenhui Wang, Lingdi Su, Qing Li, Fangfang Liu, Wenmei Ma, Ziqiang Lei and Lili Bo*

$H_{3+x}PMo_{12-x}V_xO_{40}@MIL-100$ (Fe) ($x = 0, 1, 2$) hybrids were prepared by encapsulation of polyoxometalates (POMs) within the metal-organic framework using a direct hydrothermal method.

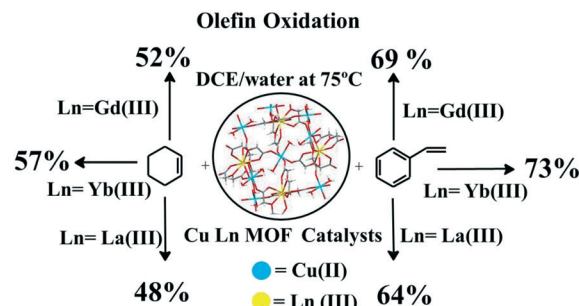


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Influence of the lanthanide(III) ion in $\{[Cu_3Ln_2(oda)_6(H_2O)_6] \cdot nH_2O\}_n$ (Ln^{III} : La, Gd, Yb) catalysts on the heterogeneous oxidation of olefins

P. Cancino, V. Paredes-García, C. Aliaga, P. Aguirre,* D. Aravena and E. Spodine*

$\{[Cu_3Ln_2(oda)_6(H_2O)_6] \cdot nH_2O\}_n$ (Ln^{III} : La, Gd, Yb; $odaH_2$: oxydiacetic acid) are reported as reusable heterogeneous catalysts in the oxidation of olefins.

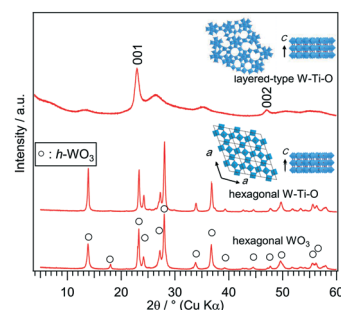


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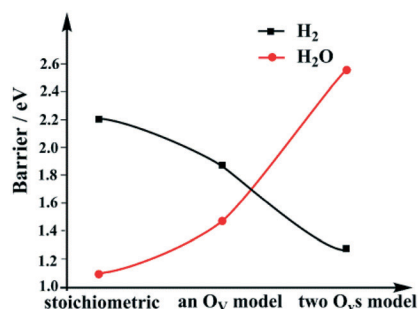
Hydrothermal synthesis of a layered-type W–Ti–O mixed metal oxide and its solid acid activity

Toru Murayama,* Kiyotaka Nakajima, Jun Hirata, Kaori Omata, Emiel J. M. Hensen and Wataru Ueda

A layered-type W–Ti–O mixed oxide was synthesized by hydrothermal synthesis from an aqueous solution of ammonium metatungstate and titanium sulfate.



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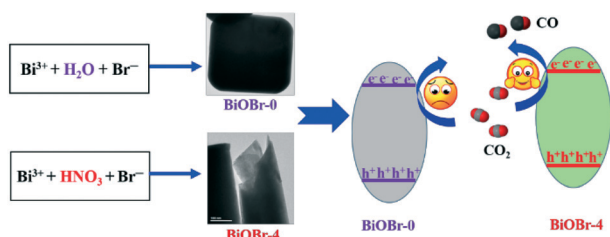


The mechanism of H₂ and H₂O desorption from bridging hydroxyls of a TiO₂(110) surface

Ruimin Wang and Hongjun Fan*

With an increase in BBO vacancies (created by H₂O desorption), the H₂ desorption barrier decreases, while the H₂O desorption barrier increases.

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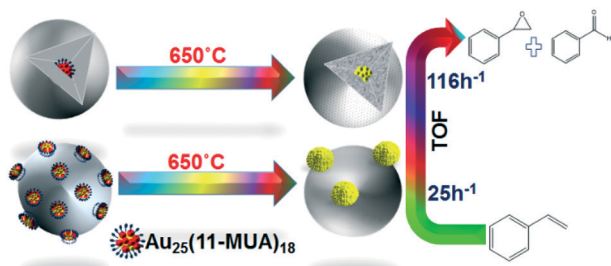


Organic-free synthesis of {001} facet dominated BiOBr nanosheets for selective photoreduction of CO₂ to CO

Dan Wu, Liqun Ye,* Ho Yin Yip and Po Keung Wong*

BiOBr nanosheets synthesized in the presence of nitric acid exhibited high selectivity for photocatalytically converting CO₂ into CO.

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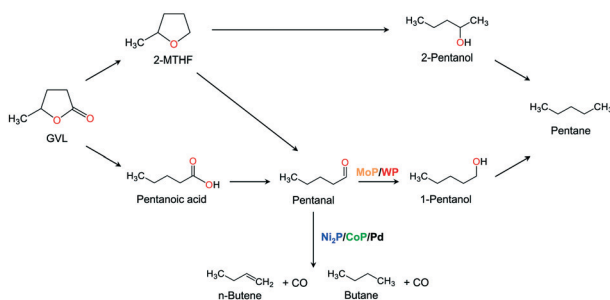


Synthesis of sinter-resistant Au@silica catalysts derived from Au₂₅ clusters

V. Sudheeshkumar, Atal Shivhare and Robert W. J. Scott*

Au₂₅L₁₈ clusters have been encapsulated in silica spheres to create sinter-resistant Au@SiO₂ materials which are active and recyclable epoxidation catalysts.

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Hydrodeoxygenation of gamma-valerolactone on transition metal phosphide catalysts

Gwang-Nam Yun, Atsushi Takagaki, Ryuji Kikuchi and S. Ted Oyama*

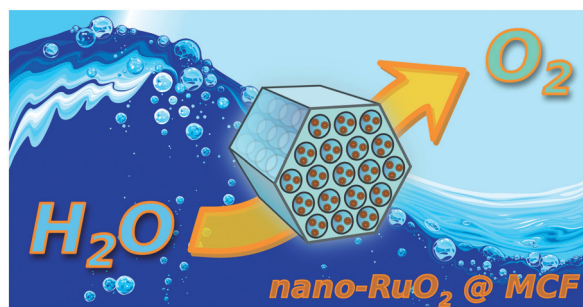
The catalytic hydrodeoxygenation (HDO) of the cyclic five-membered ester gamma-valerolactone (GVL-C₅H₈O₂) on a series of supported metal phosphide catalysts and a commercial Pd/Al₂O₃ catalyst was studied at 0.5 MPa.

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Water oxidation mediated by ruthenium oxide nanoparticles supported on siliceous mesocellular foam

Karl P. J. Gustafson, Andrey Shatskiy, Oscar Verho, Markus D. Kärkäs, Bastian Schlusshass, Cheuk-Wai Tai, Björn Åkermark,* Jan-Erling Bäckvall* and Eric V. Johnston*

An efficient catalyst for chemical and photochemical water oxidation was developed by immobilization of RuO₂ nanoparticles on pyridine-functionalized mesoporous silica.



300

Consequences of secondary zeolite growth on catalytic performance in DMTO studied over DDR and CHA

I. Yarulina, A. Dikhtiarenko, F. Kapteijn and J. Gascon*

Zeolites with DDR (Sigma-1 and ZSM-58) and CHA (SSZ-13) topology were synthesized by seed assisted and direct hydrothermal synthesis in order to investigate the effects of fast crystal growth on catalytic performance.



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Role of lanthanum species in improving the photocatalytic activity of titanium dioxide

Wai Ruu Siah,^a Hendrik O. Lintang^{ab} and Leny Yulianti^{*ab}

Series of lanthanum-modified TiO₂ catalysts were prepared by a UV photodeposition method to exclude any heat treatments that may affect the properties and photocatalytic activity of TiO₂. Results showed that the lanthanum modification did not significantly affect the properties of TiO₂, but increased the formation of Ti³⁺. Under UV light irradiation, the activity for 2,4-D decomposition rose by a maximum factor of 5.5 when TiO₂ was loaded with 5 mol% La; further increase of La deposition led to a decrease in photocatalytic activity. From the electrochemical impedance and photocurrent results, it was shown that the positive influence of La on TiO₂ photocatalytic activity was caused by the increased charge separation in the TiO₂ photocatalysts, owing to the additional formation of Ti³⁺ states. On the other hand, when tested with the colourless 2,4-D model pollutant under visible and solar simulator irradiation, the presence of lanthanum species did not improve the photocatalytic activity of TiO₂ significantly. Hence, it was shown that lanthanum species only improved the UV photocatalytic activity of TiO₂.

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Introduction

In recent years, photocatalytic degradation has attracted considerable attention as this approach could be used to remove organic pollutants, hence providing a promising solution for wastewater treatment and purification of polluted air. Titanium dioxide (TiO₂) is one of the main photocatalysts used for this purpose due to the strong oxidizing power of its photogenerated holes, its chemical stability, non-toxicity and low cost.¹ However, the photocatalytic performance of TiO₂ was limited by the fast recombination of its photogenerated electrons and holes. Transition metal oxide^{2–4} and rare earth metal oxide^{5,6} co-catalysts supported on TiO₂ have been found to enhance the photocatalytic activity of TiO₂. Among the rare earth elements, lanthanum oxide^{7–39} is considered as a suitable co-catalyst due to its ability to suppress electron–hole recombination of TiO₂ and its relative abundance. To date, there are numerous reports on the effects of lanthanum modifications on the photocatalytic activity of TiO₂ either under UV,^{7–13} visible^{14–32} or solar^{33–39} irradiation. While all studies reported the enhanced activity under UV light, there are some contradictions on the effect of lanthanum species on the visible light activity of TiO₂. Some studies showed that lanthanum modification of TiO₂ led to the occurrence of visible light ac-

tivity of TiO₂,^{14–28} while others reported that the added lanthanum did not contribute to the photocatalytic activity of TiO₂ under visible light irradiation.^{29–32} Taking into account that visible light is the main component of solar light, in contrast all papers reported the beneficial effect of lanthanum species in improving the activity of TiO₂ under solar irradiation.^{33–39}

Besides the contradicting activity enhancement between those under visible and solar light, there is also unclear discussion on the role of lanthanum species in improving the activity of TiO₂ photocatalysts. In these reported studies, the La-modified TiO₂ photocatalysts were prepared by sol-gel,^{7–11,14–18,29,30,33–36} co-precipitation,⁷ hydrothermal synthesis,^{19,20} cathodic electrochemical processes,³⁷ and impregnation methods,³⁸ which generally involved calcination of the La–TiO₂ catalysts at high temperatures (200–800 °C). Due to the use of high temperatures, the properties of TiO₂ such as the crystallite size^{7–11,14–20,30,33–38} and anatase–rutile ratio^{7–9,15–18,20,29,33,34,36–38} were affected. Since these properties also contributed to the photocatalytic activity of TiO₂, the role of lanthanum species alone in improving the photocatalytic activity of TiO₂ might not be addressed correctly.

In order to directly investigate the role of the lanthanum species, a synthesis method that does not involve heat treatment shall be employed. One of the promising methods for deposition of lanthanum oxide on the surface of TiO₂ without any heat treatments is UV photodeposition. This method is recognized as an effective and environmentally friendly method as it could be carried out at room temperature under mild experimental conditions. The photodeposition process involves the photodecomposition of metal precursors in the

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presence of TiO₂ and UV irradiation, releasing metal ions that in turn interact with the surface of TiO₂.

In the present study, we deposited the lanthanum oxide on the TiO₂ support *via* a simple UV photodeposition method conducted at room temperature. Such mild synthesis temperature allowed us to investigate the role of lanthanum species while excluding the effects of other factors aforementioned. The photocatalytic activity of the catalysts was evaluated for the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D), which is a colourless pollutant, under UV, visible, and solar simulator irradiation. The colourless 2,4-D was selected to avoid the possibility that the enhancement in the activity was caused by the effect of pollutant sensitization when the reaction was performed under visible or solar light irradiation. This study demonstrated that under UV irradiation, La-modified TiO₂ showed an excellent photocatalytic activity compared to the unmodified TiO₂, while such enhancement was not observed for reactions under visible and solar light irradiation, suggesting that the lanthanum species did not contribute to the visible light activity.

Experimental

Preparation of La_{ox}/TiO₂ photocatalysts

The series of La oxide-modified TiO₂ catalysts were prepared by a UV photodeposition method. Hombikat UV100 TiO₂ (HK UV100) was used as-received from Sachtleben Chemie. In the first step, the required amount of lanthanum(III) acetylacetonate hydrate (TCI, >98.0%) was combined with HK UV100 TiO₂ (1 g) and added to 20 mL of water/ethanol mixture (1 : 1 v/v) in a beaker (100 mL). The mixture was sonicated for 5 min to obtain a homogeneous suspension, followed by exposure to a UV lamp (200 W, $\phi_1 = 8 \text{ mW cm}^{-2}$) from the top for 5 h under ambient conditions. The irradiated mixture was then centrifuged (3500 rpm, 20 min) to collect the solid sample. After rinsing with ethanol and distilled water, the sample was dried in an oven overnight at 80 °C and ground to a fine powder. The samples were denoted as La_{ox}(x)/TiO₂, where x represented the ratio of added La to TiO₂ (0.1–10 mol%).

Characterization of photocatalysts

The diffraction patterns of the samples were recorded by X-ray diffraction (XRD; Bruker D8 Advance diffractometer) at room temperature, using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 40 mA. The data were measured in the 2θ range of 20 to 80°. The crystalline phases were matched with the reference patterns from the International Centre for Diffraction Data (ICDD) database. The mean crystallite sizes of the unmodified TiO₂ and La_{ox}/TiO₂ samples were calculated by using the Scherrer equation.^{14,19–22,34,38} A Shimadzu UV-2600 spectrophotometer equipped with an integrated sphere was used to obtain the diffuse reflectance ultraviolet-visible (DR UV-vis) spectra of the samples. The spectra were collected in the range of 220 to 800 nm under ambient conditions, using BaSO₄ as the reference. The absorption spectra were obtained by transformation of the reflectance data on the Kubelka–

Munk function. All spectra were arbitrarily normalized to the intensity of 1.0 for comparison. The bandgap energies of the samples were determined from the extrapolation of the linear fit for the Tauc plot onto the photon energy axis.^{14,18,39}

The amount of lanthanum present in the La_{ox}/TiO₂ photocatalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using an Agilent Technologies 700 series spectrometer. Transmission electron microscopy (TEM) was used to investigate the morphology of the catalysts. The sample was dispersed in ethanol and a drop of the suspension was deposited on a carbon-coated copper grid and allowed to dry under ambient conditions. The prepared samples were then viewed using a JEOL JEM-2100 TEM at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) spectra were measured using a Kratos Axis Ultra system with monochromatic Al K α X-rays (1486.6 eV) operated at 10 W and 15 kV with a background pressure of approximately 5.0×10^{-9} Torr. Survey spot size and 20 eV pass energy were used for the measurement. Photoelectrons emitted perpendicularly to the sample surface were recorded. A charge neutralizer was used and all the binding energies were calibrated with respect to the adventitious contamination hydrocarbon C_{1s} peak at 284.6 eV.

The photocurrent and the electrochemical impedance (EIS) data were measured with an Interface1000 potentiostat/galvanostat (Gamry Instruments Inc.) on the Gamry Framework software. The catalyst sample (10 mg) was dispersed in 5 mL of deionized water and sonicated for 10 min to form a homogeneous suspension. For the photocurrent measurements, 200 μL of the suspension was pipetted onto an indium tin oxide (ITO) coated glass slide ($1.5 \times 1.5 \text{ cm}$) and allowed to dry under ambient conditions. The photocurrent was recorded by a standard three-electrode configuration *via* the chronoamperometry method, with the as-prepared sample coated ITO as the working electrode, Pt wire as the counter electrode and Ag/AgCl (saturated 3 M NaCl) electrode as the reference electrode. The potential of the working electrode against the Pt counter electrode was fixed at 0 V. A 60 mL volume of 0.1 M Na₂SO₄ solution was used as the electrolyte. The light source used was a 200 W Xe–Hg UV lamp, and the light intensity on the photoanode was fixed at 8 mW cm^{-2} . All photocurrent measurements were carried out under ambient conditions. For the EIS measurements, 20 μL of the catalyst suspension (10 mg catalyst per 5 mL deionized water) was dropped onto a screen-printed electrode (SPE) and allowed to dry in air before measurements. The EIS measurements were performed in 0.1 M Na₂SO₄ electrolyte (6 mL), along with the presence of 2.5 mM K₃[Fe(CN)₆] as the redox probe. The impedance spectra were measured under an AC perturbation signal of 10 mV over the frequency range of 1 MHz to 0.1 Hz.

Photocatalytic activity studies

The photocatalytic activity of the unmodified TiO₂ and La-modified TiO₂ catalysts was evaluated by using photocatalytic

degradation of 2,4-D as a model reaction. The photoreactor used was a top-irradiation reactor. Firstly, the catalyst (50 mg) was dispersed in 50 mL 2,4-D solution (0.5 mM, Sigma, $\geq 98\%$). The suspension was then stirred under dark conditions for 1 h to reach absorption-desorption equilibrium. While under continuous stirring, the mixture was then exposed for 1 h to a 200 W UV lamp (Hamamatsu, Lightningcure™ LC8, L10852) with a cut off filter that removed emission above 400 nm. The light intensity at 365 nm near the surface of the 2,4-D solution was fixed at 8 mW cm^{-2} . In order to provide sufficient oxygen for the oxidative degradation of 2,4-D, all reactions were made open to air. The photocatalytic activity of the catalysts was also investigated under solar simulator (Peccell Technologies) irradiation under the same conditions, whereby a 150 W Xenon short arc lamp with an A.M 1.5 G filter was used and the reaction time was 3 h. Photocatalytic activity testing was also performed under visible light conditions, a filter that cuts off wavelengths < 400 nm was fitted with the solar simulator. All reaction conditions were kept constant, with the exception of the reaction time, which was set to 6 h for the visible light irradiation reactions. When the reaction was completed, about 3 mL of suspension was taken and filtered using a 0.2 μm nylon membrane filter. The amount of 2,4-D degraded after UV lamp irradiation was measured by a high performance liquid chromatograph (HPLC, Shimadzu Prominence LC-20A) equipped with a 150 \times 4.6 mm Hypersil GOLD PFP column and the eluent was a mixture of acetonitrile/ H_2O 60 : 40 (v/v), whereby the concentration of 2,4-D was monitored at 283 nm. In order to investigate the long-term photocatalyst activity, $\text{La}_{0.05}/\text{TiO}_2$ was used to degrade the 2,4-D solution over four cycles. After the first run (UV light irradiation for 6 h) the solution was centrifuged and the photocatalyst was washed with deionised water and dried at 80 $^\circ\text{C}$ overnight. The recovered photocatalyst was subsequently used to degrade a fresh 2,4-D solution under the same reaction conditions for 6 h. The third and fourth cycles were also carried out under the similar process conditions.

Results and discussion

The powder XRD patterns of the unmodified TiO_2 and the $\text{La}_{0x}/\text{TiO}_2$ samples with different amounts of lanthanum loadings are shown in Fig. 1. The HK UV100 TiO_2 showed the typical diffraction pattern of a pure anatase phase (JCPDS file no.: 21-1272). All the $\text{La}_{0x}/\text{TiO}_2$ samples also exhibited the same diffraction pattern of the anatase phase, indicating that the loading of lanthanum oxide has no appreciable effect on the crystal structure of TiO_2 . Characteristic diffraction lines of La_2O_3 were also not detected even in the sample with the highest lanthanum content, further indicating a high degree of dispersion of lanthanum oxide, which might have formed small clusters on the surface of TiO_2 .⁸

The average TiO_2 crystallite size of the samples was estimated based on the Scherrer equation with a line width analysis of the anatase (101) diffraction peak and the values are

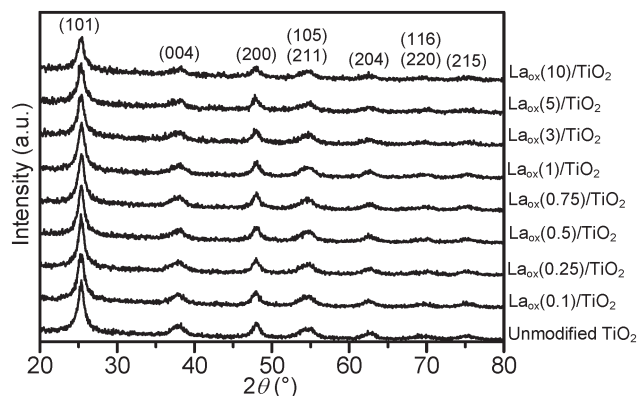


Fig. 1 Powder XRD patterns of the unmodified and La-modified TiO_2 samples.

shown in Table 1. It can be seen from Table 1 that the crystallite size of the unmodified TiO_2 and $\text{La}_{0x}/\text{TiO}_2$ samples was in the range of 8 to 10 nm. The unaffected crystal phase and crystallite size clearly demonstrated that under the current synthesis conditions, La^{3+} did not enter the TiO_2 crystal lattice to substitute for Ti^{4+} . This was reasonable since the radius of La^{3+} (1.15 Å) was much larger than that of Ti^{4+} (0.64 Å).^{8,23}

Table 1 also displays the lanthanum contents of the unmodified TiO_2 and $\text{La}_{0x}/\text{TiO}_2$ samples that were estimated with ICP-OES. For samples with low loadings of La (0.1–5 mol%), the added nominal La loadings were found to be similar to the actual loading measured from ICP-OES. On the other hand, the high loading sample (10 mol%) has a lower measured La content, suggesting that UV lamp exposure might not be sufficiently long to completely deposit all the lanthanum acetylacetonate hydrate precursor.

Shown in Fig. 2(a) are the ultraviolet-visible (UV-vis) absorption spectra of the unmodified TiO_2 and the $\text{La}_{0x}/\text{TiO}_2$ samples. The characteristic band edge for titanium dioxide appeared at about 370 nm, which is associated with the $\text{O}^{2-}(2p) \rightarrow \text{Ti}^{4+}(3d)$ charge transfer process and related to electron excitation from the valence band (VB) to the conduction band (CB) of TiO_2 .^{41,42} It was obvious that after modifications with lanthanum oxide, TiO_2 did not display extended absorption into the visible region in the range of 400 to 800 nm. The bandgap of the samples was estimated by the Tauc plot, $[(\alpha h\nu)^{1/2} \text{ versus } h\nu]$,^{14,18,39} whereby the extrapolation of the linear part of the curve gives direct values of the bandgap. The Tauc Plots are shown in Fig. 2(b) and the estimated bandgap values are listed in Table 1. The unmodified HK UV100 sample has a bandgap of about 3.33 eV. The lanthanum-modified samples showed a similar bandgap value to the unmodified TiO_2 , in the range of 3.28–3.34 eV. Since there is no significant shift in the bandgap and no absorption in the visible range, it can be concluded that La^{3+} ions were not incorporated into the crystal lattice of TiO_2 . As discussed above, the ionic radius of the La^{3+} species is too large to substitute for Ti^{4+} in the lattice of TiO_2 . Thus, they are considered to be dispersed on the surface of the TiO_2 particles.²⁹

Table 1 Crystallite size, lanthanum content and bandgap energy of the unmodified and La-modified TiO₂ samples

Samples	Crystallite size ^a (nm)	Amount of loaded La ^b (mol%)	Bandgap ^c (eV)
Unmodified TiO ₂	9.3	0.00	3.33
La _{ox} (0.1)/TiO ₂	8.3	0.12	3.30
La _{ox} (0.25)/TiO ₂	9.9	0.22	3.28
La _{ox} (0.5)/TiO ₂	8.8	0.46	3.28
La _{ox} (0.75)/TiO ₂	8.3	0.69	3.30
La _{ox} (1)/TiO ₂	8.8	0.91	3.30
La _{ox} (3)/TiO ₂	8.8	2.67	3.32
La _{ox} (5)/TiO ₂	9.9	4.44	3.32
La _{ox} (10)/TiO ₂	9.9	7.82	3.34

^a Estimated from a full width at half maximum (FWHM) of the XRD anatase (101) reflection by the Scherrer equation. ^b Estimated from ICP-OES. ^c Estimated using the Tauc plot of DR UV-vis data.

TEM studies provided some relevant information on the particle size and morphology of the samples. Fig. 3(a) and (b) show representative images obtained from the unmodified TiO₂ and La_{ox}(5)/TiO₂. In both cases, the samples appeared similar in both size and morphology. No distinct lanthanum oxide particles were observed from the TEM analysis. The La₂O₃ particles were likely to be highly dispersed on the surface of the TiO₂ support. As a result, the La₂O₃ clusters were too small to be observed, which supported the XRD results.

More detailed information regarding the elemental and chemical states of the unmodified TiO₂ and La_{ox}(5)/TiO₂ samples was also ascertained by analyzing the X-ray photoelectron spectroscopy (XPS) data. The full scan survey spectra (Fig. 4(a) and (b)) showed that the Ti, O and C elements were present on the surface of the unmodified TiO₂ sample, while Ti, O, C and La were identified on the surface of the La_{ox}(5)/TiO₂ sample. The C element detected could be ascribed to the adventitious carbon-based compounds, mostly coming from the carbon tape. The high resolution XPS spectra of La 3d, Ti 2p and O 1s are displayed in Fig. 4(c)–(e).

Regarding the La 3d core level spectra (Fig. 4(c)), a splitting of the La 3d_{5/2} and La 3d_{3/2} lines was observed around 834.6 and 851.4 eV, respectively. The peaks at 834.6 and 851.4 eV are identified as the main peaks, and the peaks at 838.8 and 855.6 eV are ascribed to the shake-up satellite peaks of La 3d_{5/2} and La 3d_{3/2}. As reported in previous works, this La XPS profile indicates the presence of lanthanum oxide species, such as La₂O₃.^{15,16,23,24,34,42} In addition to the peak

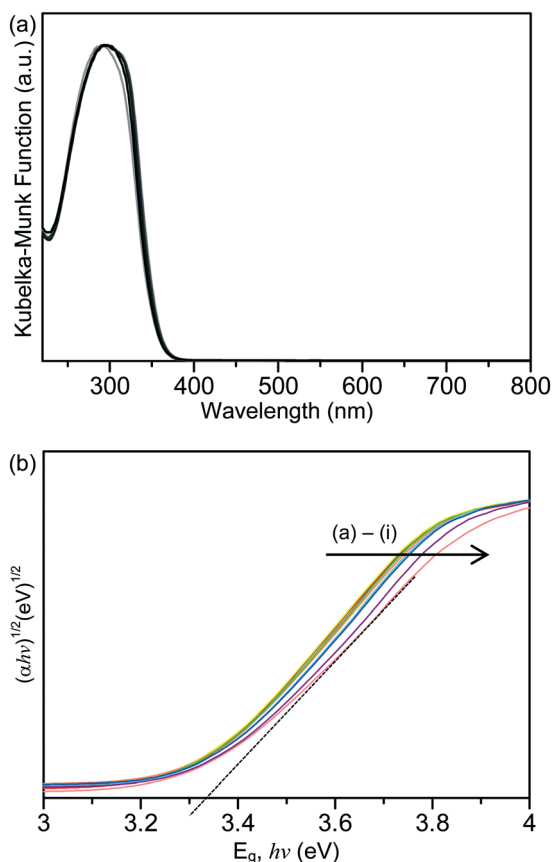


Fig. 2 (a) Absorption spectra and (b) Tauc plot of the unmodified and La-modified TiO₂ samples. Key: (a) La_{ox}(0.5)/TiO₂, (b) La_{ox}(0.25)/TiO₂, (c) La_{ox}(0.1)/TiO₂, (d) La_{ox}(1)/TiO₂, (e) La_{ox}(0.75)/TiO₂, (f) La_{ox}(3)/TiO₂, (g) La_{ox}(5)/TiO₂, (h) La_{ox}(10)/TiO₂ and (i) unmodified TiO₂.

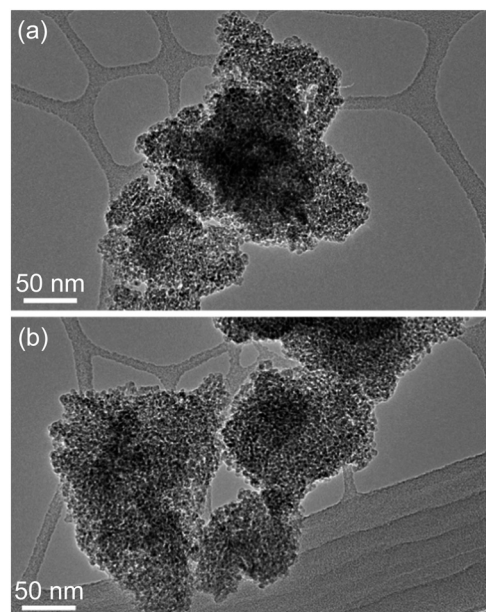


Fig. 3 TEM images of (a) unmodified TiO₂ and (b) La_{ox}(5)/TiO₂ samples.

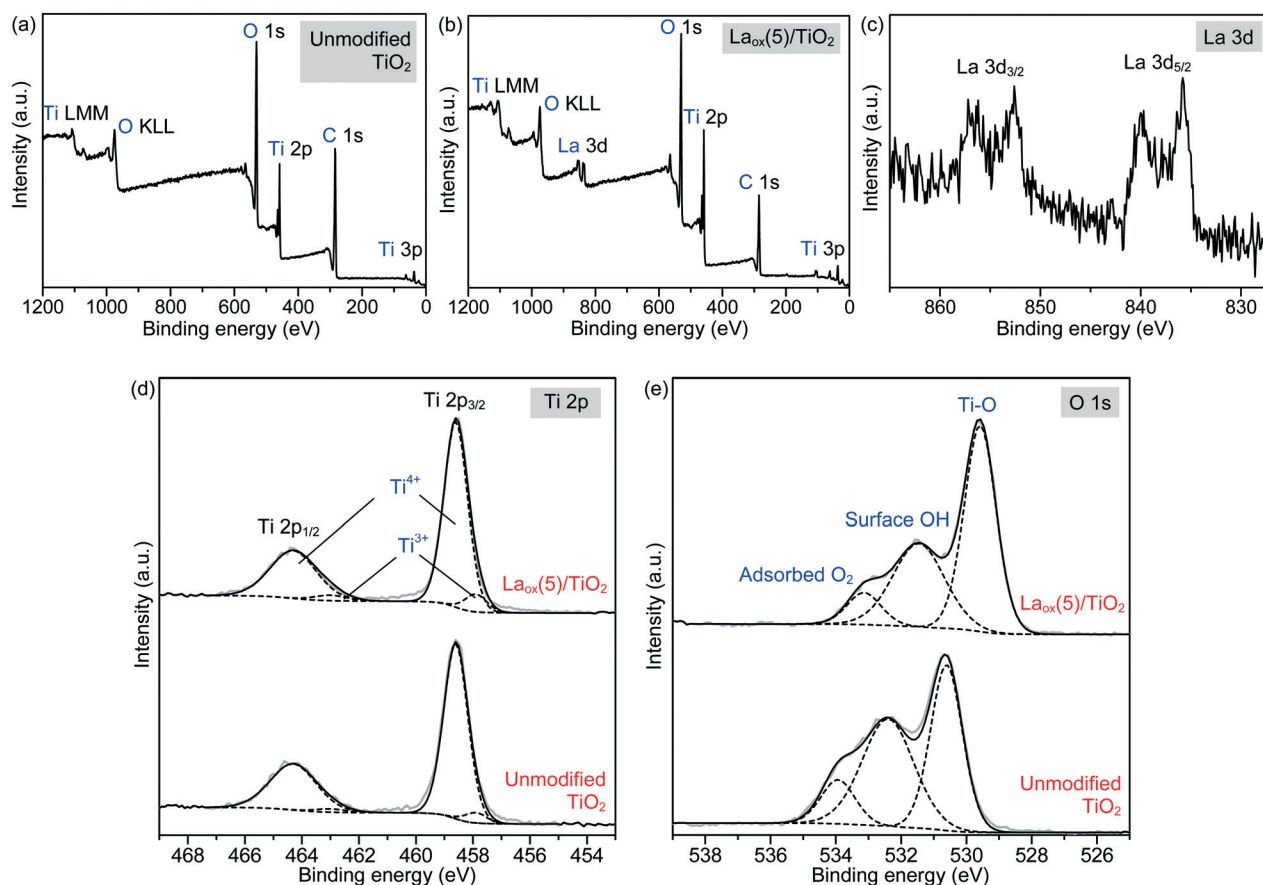


Fig. 4 XPS survey spectra of (a) unmodified and (b) $\text{La}_{\text{ox}}(5)/\text{TiO}_2$ samples. The high resolution XPS spectra of the (c) La 3d region, (d) Ti 2p region and (e) O 1s region of the unmodified and $\text{La}_{\text{ox}}(5)/\text{TiO}_2$ samples. Key for (d) and (e): grey solid line = measured data, black solid line = overall model fit, black dashed line = decomposed components.

position and splitting, the binding energy difference between the main and satellite peaks (ΔE) in the multiplet split can be used to distinguish La_2O_3 from other La^{3+} compounds. It has been reported that the ΔE values for La_2O_3 are in the range of 3.9–4.5 eV for the La $3d_{5/2}$ spectrum.⁴³ The $\text{La}_{\text{ox}}(5)/\text{TiO}_2$ sample gave a ΔE of 4.2 eV, clearly suggesting that the La species in the sample was La_2O_3 . The photodeposition of La_2O_3 is feasible owing to the oxidative conditions used in this study, as has been also reported to occur in the oxidative photodeposition of Rh_2O_3 ⁴⁴ and CuO .⁴⁰ Since the photodeposition of oxide particles would not occur in the absence of UV light irradiation and oxygen,⁴⁴ the main species to oxidize the lanthanum precursor to form La_2O_3 would be the photogenerated oxygen radicals. The proposed reaction is shown in the following equation.

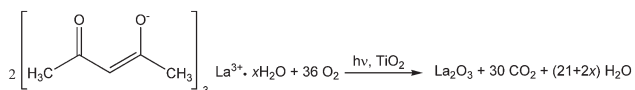


Fig. 4(d) shows the Ti 2p spectrum of the unmodified TiO_2 and $\text{La}_{\text{ox}}(5)/\text{TiO}_2$, each consisting of two obvious peaks at about 458.6 and 464.3 eV, which were assigned to $\text{Ti}_{2p_{3/2}}$ and $\text{Ti}_{2p_{1/2}}$, indicating that titanium predominantly existed in the core level in a Ti^{4+} chemical state. By using the CasaXPS

peak fitting program, the XPS peak for $\text{Ti}_{2p_{3/2}}$ was further resolved into two components at binding energies of 458.6 and 457.6 eV, which were ascribed to Ti^{4+} and Ti^{3+} species, respectively.^{9,46} It was obvious that the Ti^{4+} was the dominant surface state, with a small quantity of Ti^{3+} states.⁴⁷ Upon modification with 5 mol% La, the Ti^{3+} increased by approximately 62% from 4.75 to 7.69%. This result suggests that the presence of La might have led to the additional formation of Ti^{3+} valence states, in good agreement with previously reported studies.^{9,16,42}

The high resolution XPS O 1s spectra of the unmodified TiO_2 and $\text{La}_{\text{ox}}(5)/\text{TiO}_2$ are shown in Fig. 4(e). The wide and asymmetric O 1s spectra indicate that there was more than one component and they could be further decomposed into three peaks, which are the crystal lattice oxygen ($\text{O}_{\text{Ti-O}}$ at 529.6–530.6 eV), surface hydroxyl groups ($\text{O}_{\text{O-H}}$ at 531.5–532.4 eV) and adsorbed O_2 (at 533.2–533.9 eV). The binding energies of these three peaks agree well with reported values in the literatures.^{9,23,24,46} As shown in Table 2, the surface hydroxyl groups accounted for 45.7% of the total oxygen species on the surface of the unmodified TiO_2 . After La modification, the proportion of surface hydroxyl groups decreased to 36.0%, which may be due to La being trapped on the surface of TiO_2 .^{9,16} Additionally, the O 1s core level peak positions of

Table 2 The O 1s XPS fitting data of the unmodified and La_{ox}(5)/TiO₂ samples. Key: BE = binding energy, O_{Ti-O} = lattice oxygen, O_{O-H} = surface OH

Catalysts	O _{Ti-O}		O _{O-H}		Adsorbed O ₂	
	BE (eV)	Area (%)	BE (eV)	Area (%)	BE (eV)	Area (%)
Unmodified TiO ₂	530.6	43.6	532.4	45.7	533.9	10.7
La _{ox} (5)/TiO ₂	529.6	55.0	531.5	36.0	533.2	9.0

the La-modified TiO₂ was slightly shifted to lower binding energy, indicating the presence of interaction between the La species and TiO₂.³⁷

Photocatalytic activity

The photocatalytic activities of the La_{ox}/TiO₂ samples were evaluated for 2,4-D-degradation under UV light irradiation as shown in Fig. 5(a). It was confirmed that under the same conditions 2,4-D could not be degraded under UV irradiation in the absence of TiO₂ photocatalysts. In the presence of the unmodified TiO₂ catalyst, 5.3% of 2,4-D was removed after 1 h UV irradiation. Upon lanthanum modification, all of the TiO₂ samples showed improved activity when compared with the unmodified TiO₂ catalyst. In particular, the La_{ox}(5)/TiO₂ catalyst showed the highest photocatalytic activity, approximately 5.5 times more active than the unmodified TiO₂ catalyst. The results indicated that the photocatalytic performance of TiO₂ could be significantly enhanced by the presence of lanthanum oxide species. With a La loading above 5 mol%, the decrease of photocatalytic activity might be due to excessive La₂O₃ covering the surface, which blocked the TiO₂ active sites from UV irradiation. This result agreed well with previously reported works^{7–10,12,13} and similar to the masking effect reported on copper oxide modified TiO₂.⁴⁰

As shown in Fig. 2, the lack of optical absorption of the La-modified TiO₂ photocatalysts in the visible region suggested that La would not assist in improving the visible light absorption of TiO₂. The activity of the La-modified samples was further evaluated by conducting visible light activity testing. The results are shown in Fig. 5(b). The unmodified TiO₂ led to a 1.2% degradation of 2,4-D after 6 h of irradiation. The low activity observed on the unmodified TiO₂ might be originated from defect states that allow for limited visible light activity.^{40,45} The La-modified samples displayed a very similar activity to the unmodified TiO₂, obviously indicating that lanthanum species did not contribute to the visible light activity of TiO₂.

The photocatalytic activity of the catalysts was also evaluated under solar simulator irradiation and the results are shown in Fig. 5(c). The solar simulator consists of mostly visible light, with the presence of a small fraction of UV irradiation. Therefore, the activity trend between visible and solar activity shall be similar to each other. As expected, upon modification with various loadings of La, the activity of the La_{ox}/TiO₂ remained nearly unchanged as compared with the unmodified TiO₂. Further increase of lanthanum loading beyond 1 mol% led to a decrease in photocatalytic activity.

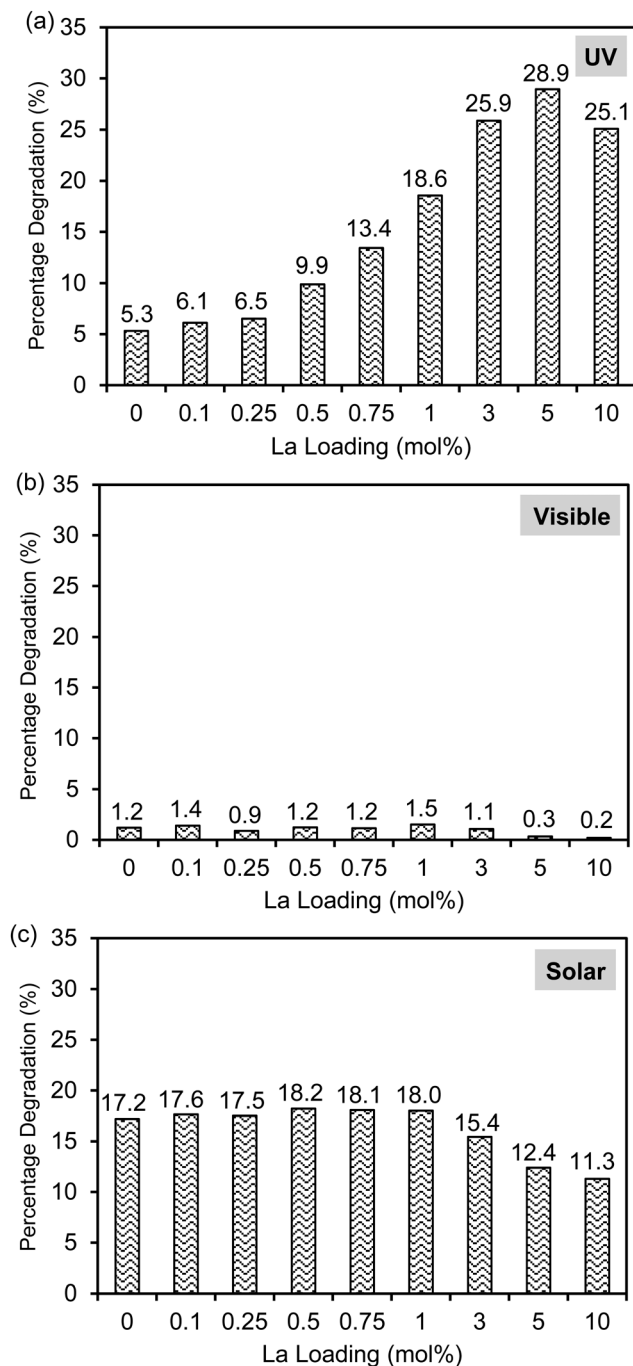


Fig. 5 Photocatalytic activities of unmodified and lanthanum-modified TiO₂ photocatalysts under (a) UV, (b) visible, and (c) solar simulator light irradiation for 1, 6, and 3 h, respectively.

These results supported that La modification did not give rise to the enhancement of TiO₂ visible light activity. In

comparison with previous works that reported the occurrence of visible light activity of La-TiO₂ catalysts, the visible light activity was most likely caused by the photosensitization effect, when organic dyes were used as the model pollutants.^{14,15,19–27}

Four recycling runs of the best photocatalyst, the La_{ox}(5)/TiO₂ sample, were carried out to investigate the stability of the photocatalyst. The reactions were each carried out under UV light for 6 h. As shown in Fig. 6, the regenerated photocatalyst exhibited good performance and stability. Over all four cycles, the degradation rate of 2,4-D remained almost unchanged compared to the fresh photocatalyst. The consistent photocatalytic performance indicated that the photocatalyst has an excellent long-term stability and good potential for wastewater treatment applications.

The charge separation and transportation characteristics of the unmodified TiO₂ and the best photocatalyst were investigated with EIS. The typical EIS spectra of the unmodified TiO₂ and the La_{ox}(5)/TiO₂ were presented as Nyquist plots and simulated with the equivalent circuit. As shown in Fig. 7(a), each sample exhibited a partial semicircle at the high-frequency region of the EIS measurement. Upon the introduction of lanthanum species, the diameter of the semicircle in the plot became smaller, which indicated a decrease in the charge transfer resistance on the TiO₂ surface.²³ Furthermore, model fitting (with the constant phase element (CPE) with a diffusion model) revealed a lower charge transfer resistance value of the La_{ox}(5)/TiO₂ sample (2.65 kΩ) as compared to the unmodified TiO₂ sample (3.66 kΩ). The significant decrease in the electron-transfer resistance in the presence of lanthanum species resulted in an effective charge transfer and separation of TiO₂, leading to an enhanced photocatalytic degradation of the 2,4-D pollutant.

In order to investigate the effect of lanthanum modification on the photo-electrochemical properties of the resulting La-TiO₂ composites, measurements of the time-dependent photocurrent response were performed. As shown in Fig. 7(b), anodic (positive) photocurrent responses indicate that the samples exhibited n-type semiconductor characteristics under UV light illumination. The photocurrent traces of

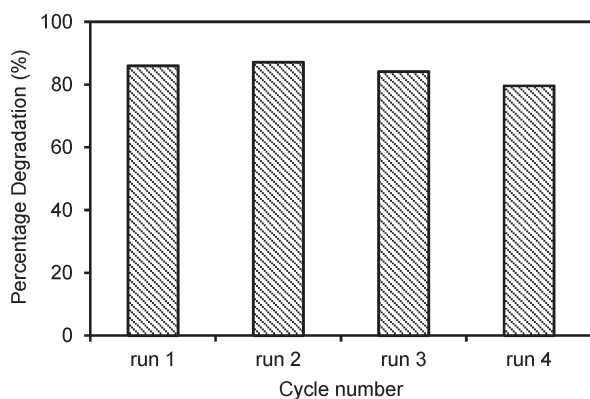


Fig. 6 Recycling tests on the La_{ox}(5)/TiO₂ sample for photocatalytic degradation of 2,4-D under UV light for 6 h.

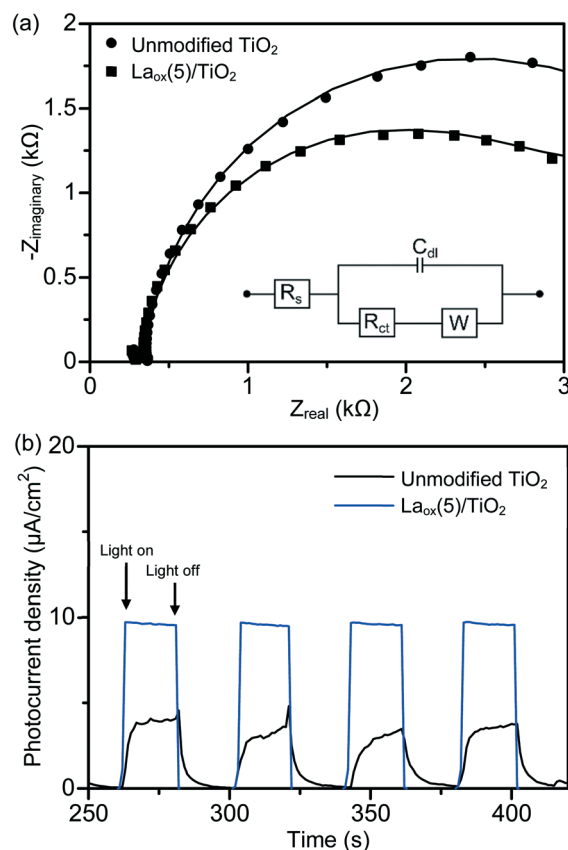


Fig. 7 (a) Nyquist plots (solid circles and squares) of the EIS changes of the unmodified TiO₂ and La_{ox}(5)/TiO₂ samples, with the corresponding circuit model fits (line). The EIS measurements were performed in the presence of 2.5 mM K₃[Fe(CN)₆] in 0.1 M Na₂SO₄ aqueous solution. Inset: Equivalent circuit for fitting the charge transfer impedance of the photocatalysts, where C_{dl} = double layer capacitance, R_s = solution resistance, R_{ct} = charge transfer resistance and W = Warburg impedance. (b) Photocurrent vs. time response of the unmodified TiO₂ and La_{ox}(5)/TiO₂ samples measured under pulsed UV light illumination in Na₂SO₄ (0.1 M) electrolyte vs. Ag/AgCl reference electrode at an applied potential of 0 V.

the unmodified TiO₂ and La_{ox}(5)/TiO₂ showed a rapid response and good reproducibility at each of the turn-on and turn-off instances. In the absence of applied biased potential, the photoelectrodes of the La_{ox}(5)/TiO₂ photocatalyst generated a significantly higher photocurrent density than the photocurrent of the unmodified TiO₂ photoelectrode. These results further confirm the ability of the La species to improve the separation of photogenerated electron-hole pairs.^{37,48}

Proposed mechanism

Based on the results shown above, a mechanism for the role of lanthanum species in enhancing the activity of TiO₂ under UV irradiation is proposed and depicted in Fig. 8. As shown in Fig. 8, there are three possible pathways of electron transfer in the photocatalytic system, denoted as P1, P2 and P3, respectively. The first pathway (P1) involves the conventional

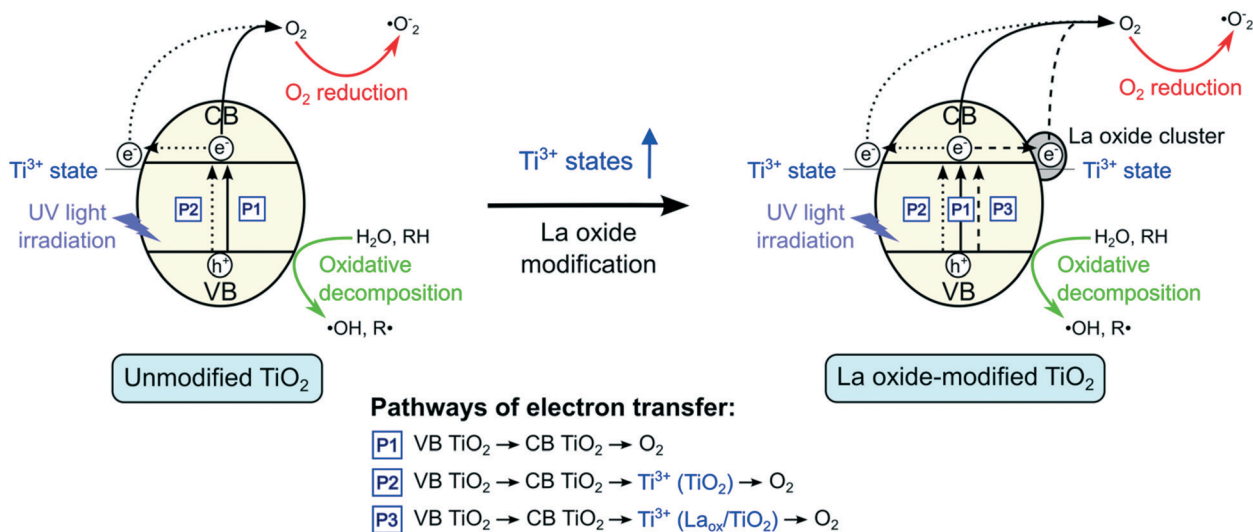


Fig. 8 Proposed mechanisms on the lanthanum-modified TiO₂ under UV light irradiation.

bandgap transition of TiO₂. When illuminated, the electrons in the VB of TiO₂ were excited to the CB, leaving holes in the VB. The excited electrons could then react with adsorbed oxygen to form superoxide radicals. Due to the short lifetime of the photogenerated electron-hole pairs, they normally tend to recombine quickly.

As shown by the XPS results, in addition to the dominant Ti⁴⁺ states, there is also a small proportion of Ti³⁺ species present in the unmodified TiO₂. When the TiO₂ is excited, the electrons in the VB could be transferred to the 3d states of Ti³⁺. The Ti³⁺ species that have accepted the electrons could then transfer the electrons to form other active species, such as superoxide anions (O₂⁻) and hydroxyl radicals (•OH),^{10–12,26,34} which could further degrade the 2,4-D molecules. Hence, in the absence of lanthanum modifications, this pathway (P2) and the conventional excitation of electrons from VB TiO₂ to CB TiO₂ (P1) were expected to contribute to the photocatalytic activity of the unmodified TiO₂.

The EIS and photocurrent results shown above suggested that in the presence of lanthanum species on the surface of TiO₂, the recombination of the electron-hole pairs was reduced, resulting in the improved photocatalytic activity. However, previous reports proposed that the CB edge of La₂O₃ is located at a far more negative position (~-1.8 to -3.5 V vs. standard hydrogen electrode (SHE)) than that of anatase TiO₂ (~-0.3 V vs. SHE). Since La₂O₃ does not possess the suitable potential, electron transfer from the CB edge of TiO₂ to La₂O₃ is not possible.^{7,9,10} Hence, there might be another species that led to the improved charge separation of TiO₂.

From the XRD and DR UV-vis results, it was shown that the crystal structure, crystallite size and bandgap of TiO₂ were not significantly affected by the La modification. These suggested that only surface modification took place. At the La₂O₃ and TiO₂ interface, a charge imbalance of TiO₂ might be created in the presence of La³⁺ species. In order to overcome this charge imbalance, Ti⁴⁺ is thus reduced to

Ti³⁺.^{7,9,10,12,14,16,17,33,34,37} In this study, as indicated by the XPS Ti_{2p} analysis, the increase of Ti³⁺ species on the surface of the TiO₂ photocatalysts was attributed to the lanthanum modification. The incorporation of La³⁺ species led to the formation of additional impurity Ti³⁺ states that resulted in the increased charge transfer and separation. Therefore, upon modification with lanthanum species, there is an additional pathway (P3) where electrons could be captured. As such, lanthanum modified TiO₂ photocatalysts showed decreased charge recombination, leading to the increased photocatalytic activity. However, if the amount of Ti³⁺ was too high, it might act to promote electron-hole recombination.^{7,9,10,12} Therefore, the optimum amount of La₂O₃ that gave the optimum photocatalytic performance under UV light irradiation could be also related to the optimum amount of Ti³⁺.

Conclusions

Lanthanum oxide was successfully loaded onto the surface of HK UV100 TiO₂ by a photodeposition method, which did not require any heat treatment processes. This method resulted in the formation of highly dispersed La(III) oxide species on the TiO₂ surface, and it did not alter the crystallite size and the phase structure of TiO₂. The photocatalytic activity testing under UV irradiation showed a notable improvement of La-modified TiO₂ photocatalytic activity over the unmodified TiO₂ up to 5.5 times at 5 mol% La loading. The added lanthanum species was proposed to create additional Ti³⁺ states that improved the charge separation of TiO₂. Recycling tests confirmed that the La_{ox}(5)/TiO₂ catalyst showed good stability. On the other hand, when under visible or solar simulator irradiation, there was no significant improvement of photocatalytic activity of the La_{ox}/TiO₂ catalysts as compared to the unmodified TiO₂. This observation confirmed that the lanthanum species did not contribute to the visible light activity of TiO₂ under visible or solar irradiation conditions.

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