In This Issue

Cover: Dr. Zhang and Prof. Fan in their article on pages 251–258 reported a facile grinding strategy to successfully produce a series of PdAg alloy nanoparticles with a small size and good distribution on the carbon matrix. Those samples as the electrocatalysts could exhibit excellent activities and stabilities for the alkaline hydrogen oxidation and evolution reactions.

封面: 张云和樊光银等发展了一种可持续化策略，即于室温下在玛瑙研钵中直接研磨合成了一系列高分散在碳载体上的小尺寸 PdAg 合金纳米颗粒。此法无需任何溶剂和有机试剂，整个过程简单便捷，绿色环保，同时确保了 PdAg 合金纳米颗粒表面洁净无污染。将系列样品用于碱性电催化氢氧化和析氢反应时，均展现出高的催化性能。见本期第 251–258 页。

About the Journal

Chinese Journal of Catalysis is an international journal published monthly by Chinese Chemical Society, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, and Elsevier. The journal publishes original, rigorous, and scholarly contributions in the fields of heterogeneous and homogeneous catalysis in English or in both English and Chinese. The scope of the journal includes:

- New trends in catalysis for applications in energy production, environmental protection, and production of new materials, petroleum chemicals, and fine chemicals;
- Scientific foundation for the preparation and activation of catalysts of commercial interest or their representative models;
- Spectroscopic methods for structural characterization, especially methods for in situ characterization;
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- Relationship between homogeneous and heterogeneous catalysis;
- Theoretical studies on the structure and reactivity of catalysts.
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- **Perspectives** are short reviews of recent developments in an established or developing topical field. The authors should offer a critical assessment of the trend of the field, rather than a summary of literatures.

- **Viewpoints** describe the results of original research in general in some area, with a view to highlighting the progress, analyzing the major problems, and commenting the possible research target and direction in the future.

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Evolution of catalytic activity driven by structural fusion of icosahedral gold cluster cores

Dan Yang, Yan Zhu *
Nanjing University

Atomically precise gold cluster catalysts have emerged as a new frontier in catalysis science and exhibited unexpected catalytic properties. Here, we demonstrate that the structural fusion of icosahedral Au_{13} cores to form vertex-fused (vf), face-fused (ff), and body-fused (bf) structures can control the catalytic activity of the clusters.

Sustainable solid-state synthesis of uniformly distributed PdAg alloy nanoparticles for electrocatalytic hydrogen oxidation and evolution

Caili Xu, Qian Chen, Rong Ding, Shengtian Huang, Yun Zhang *, Guangyin Fan *
Sichuan Normal University;
Sichuan University of Science and Engineering

A facile grinding strategy is developed to produce a series of PdAg alloy NPs that are highly dispersed on various carbon supports. The resulting electrocatalysts exhibit excellent activities and stabilities in both the HOR and HER.
**Photocatalytic Cr(VI) elimination over BUC-21/N-K_2Ti_4O_9 composites: Big differences in performance resulting from small differences in composition**

Xun Wang, Yu-Xuan Li, Xiao-Hong Yi, Chen Zhao, Peng Wang, Jiguang Deng*, Chong-Chen Wang*

*Beijing University of Civil Engineering and Architecture;*  
Beijing University of Technology

BUC-21/N-K_2Ti_4O_9 composites show high photocatalytic activity under UV and white light, which can be used to reduce Cr(VI) to Cr(III) effectively.

**Direct growth of holey Fe_3O_4-coupled Ni(OH)_2 sheets on nickel foam for the oxygen evolution reaction**

Yu Ding, Bo-Qiang Miao, Yue Zhao, Fu-Min Li, Yu-Cheng Jiang*, Shu-Ni Li*, Yu Chen

Shaanxi Normal University

Herein, ultrathin holey Fe_3O_4-coupled Ni(OH)_2 sheets (Ni(OH)_2-Fe H-STx) were easily synthesized, which showed outstanding activity for the OER due to special structural features and synergistic effect between the Fe and Ni atom.

**Morphology evolution of acetic acid-modulated MIL-53(Fe) for efficient selective oxidation of H_2S**

Xiaoxiao Zheng, Sihui Qi, Yanning Cao, Lijuan Shen*, Chaktong Au, Lilong Jiang*

Fuzhou University

Using acetic acid coordination modulation, a series of MIL-53(Fe) with morphology evolving from irregular bulky particles to highly uniform short hexagonal prisms were synthesized and applied for H_2S selective oxidation.
Orbital symmetry matching: Achieving superior nitrogen reduction reaction over single-atom catalysts anchored on Mxene substrates
Jiale Qu, Jiewen Xiao, Hetian Chen, Xiaopeng Liu, Tianshuai Wang, Qianfan Zhang *
Beihang University

Single atom doped on MXene, which can synergize with the adjacent titanium atom on the matrix. With this synergy, the nitrogen reduction reaction can be proceeded at a low limiting potential.

Honeycomb-structured solid acid catalysts fabricated via the swelling-induced self-assembly of acidic poly(ionic liquid)s for highly efficient hydrolysis reactions
Bihua Chen, Tong Ding, Xi Dong, Xin Wang, Dawei Zhang, Sanguan Ma, Yongya Zhang, Bing Ni, Guohua Gao *
East China Normal University, China; University of Cambridge, U.K.

The catalytic activity of SAPILs with micron-sized 3D honeycomb structure in water and high enrichment ability for the reactants of hydrolysis and hydration reactions was much higher than that of homogeneous acid catalysts.

Selective photocatalytic reduction of CO$_2$ to CO mediated by a [FeFe]-hydrogenase model with a 1,2-phenylene S-to-S bridge
Minglun Cheng, Xiongfei Zhang, Yong Zhu, Mei Wang *
Dalian University of Technology

An [FeFe]-hydrogenase model was demonstrated to be highly active for the photochemical reduction of CO$_2$ with a TOF of 7.12 min$^{-1}$ and CO selectivity of 97%. The CO/H$_2$ ratio can be adjusted by the addition of TEOA.
Small-sized cuprous oxide species on silica boost acrolein formation via selective oxidation of propylene

Ling-Ling Guo, Jing Yu, Wei-Wei Wang, Jia-Xu Liu *, Hong-Chen Guo, Chao Ma *, Chun-Jiang Jia *, Jun-Xiang Chen, Rui Si *

Shanghai Institute of Applied Physics, Chinese Academy of Sciences; Shanghai Synchrotron Radiation Facility, Zhangjiang Laboratory; Shanghai Institute of Measurement and Testing Technology; Shandong University; Dalian University of Technology; Hunan University; TILON Group Technology Limited; University of Chinese Academy of Science

Small-sized copper oxide clusters have been fabricated on silica for the efficient formation of acrolein via the selective oxidation of propylene. The reaction mechanism was explored using in situ X-ray diffraction and in situ dual beam Fourier transform infrared spectroscopy.

Acrolein formation rate = 111.2 mmol·h⁻¹·gCu⁻¹

Acetylene hydrochlorination over supported ionic liquid phase (SILP) gold-based catalyst: Stabilization of cationic Au species via chemical activation of hydrogen chloride and corresponding mechanisms

Jia Zhao *, Saisai Wang, Bolin Wang, Yuxue Yue, Chunxiao Jin, Jinyue Lu, Zheng Fang, Xiangxue Pang, Feng Feng, Lingling Guo, Zhiyan Pan, Xiaonian Li *

Zhejiang University of Technology

Cationic Au species coordinate with [Bmim][N(CN)_2] to form strong Au-IL complexes, which greatly increase the thermal and reaction stability of Au-based catalysts.

Complete removal of phenolic contaminants from bismuth-modified TiO₂ single-crystal photocatalysts

Wenjie Tang, Juanrong Chen, Zhengliang Yin, Weichen Sheng *, Fenglian Lin, Hui Xu, Shunsheng Cao *

Jiangsu University

The Bi-SCTiO₂ photocatalyst exhibits complete degradation of phenolic contaminants under simulated sunlight due to the synergistic effect of the small band overlap and the low charge carrier density (Bi) as well as high conductivity (single crystal).
Solvothermal synthesis of Co-substituted phosphomolybdate acid encapsulated in the UiO-66 framework for catalytic application in olefin epoxidation

Dianwen Hu, Xiaojing Song, Shujie Wu, Xiaotong Yang, Hao Zhang, Xinyu Chang, Mingjun Jia *
Jilin University

Hybrid composites based on Co-substituted phosphomolybdic acid (PMo11Co) and UiO-66 were synthesized by the direct solvothermal method. PMo11Co@UiO-66 showed high catalytic activity and stability for the epoxidation of a variety of olefins with t-BuOOH as the oxidant.
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Photocatalytic Cr(VI) elimination over BUC-21/N-K₂Ti₄O₉ composites: Big differences in performance resulting from small differences in composition

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ABSTRACT

A series of BUC-21/N-K₂Ti₄O₉ composites (B1NX) were facilely fabricated from BUC-21 and N-K₂Ti₄O₉ via ball-milling, and they were fully characterized using various techniques. The photocatalytic reduction of Cr(VI) over the B1NX composites was investigated systematically under various conditions, including different light sources, pH values, hole scavengers, and inorganic ions, in both real lake water and tap water. The BUC-21/N-K₂Ti₄O₉ composites demonstrated remarkable photocatalytic Cr(VI) reduction performance, good reusability, and stability under both UV and white light irradiation. The introduction of N-K₂Ti₄O₉ into BUC-21 not only broadened its light absorption region to white light, but also strongly inhibited the recombination of the photo-generated electrons and holes. Mechanisms of photocatalytic Cr(VI) reduction under both UV light and white light were proposed and verified by electrochemical measurements, active species capture experiments, and ESR measurements.

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1. Introduction

Due to increasing industrialization, hexavalent chromium (Cr(VI)), which is produced mainly from electroplating, photography, mining, and other processes [1–3], has become an important research topic in wastewater treatment [4–6]. The presence of Cr(VI) in water negatively affects the environment and increases the risk of some cancers [7–9]. Therefore, the removal of Cr(VI) from water is necessary. Among the various treatment methods available, including adsorption, electro-reduction, chemical reduction, and others, photocatalysis is typically used to reduce highly toxic Cr(VI) to low-toxicity Cr(III) because of its simple working conditions and environmental sustainability [10–12].

Metal-organic frameworks (known as MOFs) and coordination polymers (CPs) are periodic porous materials with ultra-high porosity and are constructed from metal ions or clusters and organic linkers through coordinative bonding interac-
tions and self-assembly [13–15]. Due to their advantages of various synthesis methods and adjustable active sites, MOFs and CPs are considered star materials and are widely studied in the field of gas adsorption/separation [16–18], sensing [19–21], catalysis [22–24], and absorptive pollutant removal applications [25]. In recent years, MOFs and CPs have been adopted as efficient photocatalysts to accomplish photocatalytic Cr(VI) reduction [26,27], photocatalytic CO$_2$ reduction [28,29], photocatalytic decomposition of organic pollutants [30,31], and photocatalytic H$_2$ production via water splitting [32,33]. However, disadvantages such as low conductivity, fast recombination of electrons and holes, and limited response under UV light have inhibited their photocatalytic activities. To overcome these problems, several strategies involving the fabrication of composites of MOFs or CPs with semiconductors (such as g-C$_3$N$_4$[34,35], Ag$_2$CO$_3$[36], TiO$_2$[37], and Bi$_2$O$_3$Br$_{10}$[38]), electroactive polymers (such as PANI [39]), conductors (like RGO [40]), and noble metal nanoparticles (such as Ag [41] and Pd [42]) have been introduced. BUC-21 is a stable 2D coordination polymer produced by our research group using cis-1,3-dibenzyl-2-oxo-4,5-imidazolidinedicarboxylic acid (H$_2$L) and 4,4’-bipyridine (bpy) as organic linkers and Zn$^{2+}$ as the metal ion. BUC-21 exhibited superior photocatalytic performance toward Cr(VI) reduction and organic pollutant decomposition under UV light [43]. Furthermore, g-C$_3$N$_4$ [44] and Bi$_2$O$_3$Br$_{10}$ [38] were introduced to broaden the light absorption range of BUC-21 from the UV region to the visible region and enhance its photocatalytic activity. K$_2$Ti$_4$O$_9$ is a two-dimensional layered material composed of octahedral TiO$_2$ units bridged by oxygen atoms [45]. Because of its low cost, non-toxicity, and distinctive photoelectric properties, it has been recognized a potential photocatalyst. However, due to its wide band gap (3.2–3.4 eV), it is only responsive to UV light [46]. Doping nitrogen into K$_2$Ti$_4$O$_9$ is a convenient and effective way to adjust its band gap, as it has been confirmed by previous works [47,48]. In this study, N-K$_2$Ti$_4$O$_9$ was successfully synthesized by a calcination method, and BUC-21/N-K$_2$Ti$_4$O$_9$ composites were prepared by ball milling. The structure, morphology, and photoelectric performance of the BUC-21/N-K$_2$Ti$_4$O$_9$ composites were characterized and measured, and their photocatalytic activities were assessed under ultraviolet (UV) and white light irradiation. The results indicated that the introduction of N-K$_2$Ti$_4$O$_9$ increased the Cr(VI) reduction efficiency of the composites under both UV and white light; this improvement was attributed to the accelerated separation of the photo-generated electrons and holes due to the rapid electron transfer between N-K$_2$Ti$_4$O$_9$ and BUC-21. Additionally, the composites exhibited good stability and recyclability after five runs of the photocatalytic reaction. Finally, mechanisms for the catalysts were proposed and confirmed.

2. Experimental

2.1. Materials and instruments

The chemicals and the characterization instruments used in this work are described in the electronic supplementary information (ESI).

2.2. Preparation of photocatalysts

2.2.1. Synthesis of BUC-21, K$_2$Ti$_4$O$_9$, and N-K$_2$Ti$_4$O$_9$

BUC-21, K$_2$Ti$_4$O$_9$, and N-K$_2$Ti$_4$O$_9$ were prepared according to previous reports [43,49,50]. Detailed preparation procedures are given in the ESI.

2.2.2. Preparation of BUC-21/N-K$_2$Ti$_4$O$_9$

The BUC-21/N-K$_2$Ti$_4$O$_9$ composites were fabricated by ball-milling treatment of mixtures of BUC-21 and N-K$_2$Ti$_4$O$_9$ at 30 Hz for 20 min. The ratios of BUC-21 and N-K$_2$Ti$_4$O$_9$ in the various composites are listed in Table 1.

2.3. Photocatalytic activity of B1NX

The photocatalytic performances of the B1NX composites were assessed via the photoreduction of Cr(VI) to Cr(III). A 200 mL of an aqueous solution of K$_2$Cr$_2$O$_7$ (10 mg L$^{-1}$) containing 0.175 g L$^{-1}$ photocatalyst was irradiated with either UV light (Hg lamp with an optical power of 153.5 mW, Beijing Aulight Co., Ltd) and white light (Xe lamp with an optical power of 598 mW, Beijing Aulight Co., Ltd). The spectra of the UV lamp and white lamp are shown in Fig. S1. Before illumination, the suspension was continuously stirred in the dark to achieve adsorption-desorption equilibrium. During illumination, 1.5 mL of the solution was extracted every 10 min using a 0.22 µm filter for subsequent detection. The Cr(VI) concentration was measured using the diphenylcarbazide (DPC) method with an AutoAnalyzer 3 instrument. The pH values of the suspension were adjusted from 2.0 to 8.0 using 0.1 M H$_2$SO$_4$ and 0.1 M NaOH solutions.

The apparent quantum efficiencies (AQEs) of B1NO.5 and B1N3 toward Cr(VI) reduction upon illumination with various frequencies of monochromatic light were calculated according to Eqs. 1 and 2, as described in previous studies [23,51,52]. The average irradiance values were measured using a cell-np2000-2 optical power meter.

\[
\text{AQE (Cr)} = \frac{\text{number of reduced Cr (VI)}}{\text{incident photons}}
\]  
\[
N_p = \frac{\lambda A R E}{hc}
\]

where $N_p$ is the number of incident photons; $\lambda$ is the irradiation wavelength (m); $t$ is the irradiation time (s); $A$ is the light-receiving area of the reactor (m$^2$); $E$ is the average irradiance (W·m$^{-2}$); $h$ is the Planck constant, and $c$ is the speed of light.

Table 1: Ratios of BUC-21 and N-K$_2$Ti$_4$O$_9$ used to prepare the BUC-21/N-K$_2$Ti$_4$O$_9$ composites.

<table>
<thead>
<tr>
<th>No.</th>
<th>BUC-21/mg</th>
<th>N-K$_2$Ti$_4$O$_9$/mg</th>
<th>Code name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>166.7</td>
<td>33.3</td>
<td>B1N0.2</td>
</tr>
<tr>
<td>2</td>
<td>133.3</td>
<td>66.6</td>
<td>B1N0.5</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>100</td>
<td>B1N1</td>
</tr>
<tr>
<td>4</td>
<td>66.7</td>
<td>133.3</td>
<td>B1N2</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>150</td>
<td>B1N3</td>
</tr>
<tr>
<td>6</td>
<td>40</td>
<td>160</td>
<td>B1N4</td>
</tr>
</tbody>
</table>
light in a vacuum (m/s).

2.4. Electrochemical test

The electrochemical tests of B1N0.5 and B1N3 were carried out with reference to previous works [38,53], as described in the ESI.

3. Results and discussion

3.1. Characterizations

The PXRD patterns of BUC-21, N-K2Ti4O9 and the series of BUC-21/N-K2Ti4O9 (B1NX) composites are depicted in Fig. 1a. All composites showed peaks at 10.2°, 14.8°, 15.9°, and 24.5° originating from BUC-21 [43,44]. Additionally, the PXRD patterns of the synthesized N-K2Ti4O9 matched well with those previously reported [54], in which the characteristic diffraction peaks at 10.9°, 13.7°, 24.3°, 28.7°, 30.3°, 31.2°, 33.6°, 43.1°, and 48.1° were attributed to the (2 0 0), (2 0 1), (1 1 0), (3 1 1), (0 0 4), (2 0 5), and (0 2 0) planes of N-K2Ti4O9 [55]. To prove the structural stability of the composites, both BUC-21 and N-K2Ti4O9 were characterized before and after ball milling by PXRD. The ball milling treatments did not bring about any noticeable changes to the crystal phase of BUC-21 (Fig. S2a). However, ball milling induced the exposure of additional crystal facets such as (–6 0 3) for N-K2Ti4O9 (Fig. S2b), which were observed in the B1NX composites and were similar to a previous report [56]. The FTIR spectra also demonstrated the successful fabrication of the B1NX composites. As shown in Fig. 1b, the characteristic peaks of both BUC-21 and N-K2Ti4O9 were observed in the spectra of the B1NX composites.

The particle sizes of the pristine BUC-21 ranged from 300 to 900 nm (Figs. 2a and S3a), and the pure N-K2Ti4O9 exhibited a rod-like structure with a length of a few micrometers [46,57] (Figs. 2b and S3b). After ball-milling treatment, the BUC-21 particles were randomly distributed over the rod-like N-K2Ti4O9 which can be observed by TEM (Figs. 2c and 2d) rather than SEM (Figs. S3c and S3d). TEM-EDS analysis was performed on selected regions of certain composites. The results showed that the B1N0.5 and B1N3 composite photocatalysts contained the elements Zn, N, K, and Ti; the presence of N, K, and Ti was attributed to N-K2Ti4O9 and the Zn was introduced by BUC-21. The interaction between BUC-21 and N-K2Ti4O9 was further affirmed by HRTM observation (Fig. 4), in which the d spacings of 3.71, 2.95, and 3.18 Å corresponded to the (1 1 0), (3 1 1), and (3 1 0) planes of N-K2Ti4O9.

As depicted in Fig. 5, obvious signals of the elements Zn, Ti, O, and N were observed in the XPS spectra of B1N0.5. The two obvious N 1s and Zn 2p peaks in the XPS survey spectrum in Fig. 5a were attributed to N-K2Ti4O9 and BUC-21, respectively. The peaks at 1045.3 and 1022.3 eV (Fig. 5b) were ascribed to Zn 2p1/2 and Zn 2p3/2 of BUC-21 in B1N0.5, respectively [44]. The peaks at 464.0 and 458.2 eV (Fig. 5c) were assigned to Ti 2p1/2 and Ti 2p3/2 [58]. Three O 1s peaks with different binding energies (Fig. 5d) were observed, which were attributed to...
O–H (532.0 eV), O–Zn (531.5 eV), and lattice oxygen (529.6 eV). Notably, the lattice oxygen peak (529.6 eV) was indicative of the existence of a Ti–O–Ti structure in N–K₂Ti₄O₉ [44,45]. The N 1s spectrum for B1N0.5 is presented in Fig. 5e; the 399.4 and 400.0 eV peaks revealed the presence of O–Ti–N and Ti–N–O or Ti–O–N, respectively [59,60]. Identical chemical composition and chemical states were observed in the XPS characterization of B1N3 (Fig. 6). In B1N3, the redistribution of additional electrons between BUC-21 and N–K₂Ti₄O₉ led to decreased binding energies for the lattice oxygen and O–Ti–N [44].

The UV-vis DRS spectra of the BUC-21, N–K₂Ti₄O₉, and B1NX composites are shown in Fig. 7a; the light absorption behavior of the B1NX composites approached that of N–K₂Ti₄O₉. The band-gap energy (E_g) of BUC-21, N–K₂Ti₄O₉, and the B1NX composites can be estimated according to the expression $\alpha h\nu = A(h\nu - E_g)^n$, as described in previous publications [61]. The results showed that the E_g values of the B1NX composites ranged from 2.91 to 2.99 eV. Based on the diffuse reflectance spectra, the band-edge wavelengths of the B1NX composites were at the junction of the ultraviolet absorption and visible absorption ranges, implying that the B1NX composites could be irradiated using both UV light and visible light.
3.2. Photocatalytic performance of B1NX

The adsorption of Cr(VI) by the composites under dark conditions was tested before carrying out photocatalytic reduction experiments. As shown in Figs. 8a and 8d, the adsorption of Cr(VI) on the BUC-21, N-K2Ti4O9, and series of B1NX composites was so weak as to be negligible. Under UV light irradiation, the optimal composites B1N0.5 and B1N1 accomplished 100% Cr(VI) reduction within 40 min, which surpassed that of bare BUC-21 (94% within 40 min). The kinetics of the Cr(VI) reduction rate followed the order B1N0.5 > B1N1 > BUC-21. Under white light, the pristine BUC-21 and N-K2Ti4O9 reduced less than 10% of the Cr(VI) after 130 min. The B1NX composites demonstrated superior photocatalytic Cr(VI) reduction capability, with the B1N3 composite showing the highest Cr(VI) reduction activity (99% within 100 min). This indicated that the introduction of N-K2Ti4O9 into BUC-21 not only broadened the light absorption region to white light, but also promoted the transfer of photo-generated electrons and inhibited the recombination of electrons and holes. The acidity and alkalinity of the reaction solution was expected to strongly affect the Cr(VI) removal performances of the catalysts. As shown in Figs. 8c and 8f, the photocatalytic Cr(VI) reduction efficiencies did indeed vary significantly under different pH conditions. Under UV and white light irradiation, the photocatalytic performances of B1N0.5 and B1N3 decreased gradually with increasing pH. At lower pH conditions, the reaction proceeded in accordance with Eqs. 3, 4, and 5, in which the high availability of H+ ions enhances the conversion of Cr(VI) to Cr(III). In contrast, at higher pH, the reaction proceeded via Eqs. 3, 5, and 6, in which the formed Cr(III) was declined to form precipitates that covered the active sites of B1N0.5 and B1N3 and inhibited further Cr(VI) reduction.

Fig. 6. (a) XPS survey spectrum, (b) Zn 2p spectrum, (c) Ti 2p spectrum, (d) O 1s spectrum, and (e) N 1s spectrum of B1N3.

Fig. 7. (a) UV-vis DRS spectra and (b) E\textsubscript{g} plots of BUC-21, N-K2Ti4O9, and the series of B1NX composites.
B1NX + hv → B1NX (h+ + e–)  

14H+ + Cr₂O₇²⁻ + 6e– → 2Cr³⁺ + 7H₂O

2H₂O + 2h+ → H₂O₂ + 2H⁺

CrO₄²⁻ + 4H₂O + 3e– → Cr(OH)₃(s) + 5OH⁻

The effective hole consumption could quickly capture photo-generated holes and enhance the utilization of electrons to

Fig. 8. (a) and (d) Photocatalytic Cr(VI) removal efficiencies of BUC-21, N-K₂Ti₄O₉, and the B1NX composites under UV and white light irradiation, respectively. (b) and (e) Reaction rate constants (k) of the different photocatalysts. (c) and (f) Effect of the initial pH on Cr(VI) removal under UV and white light irradiation, respectively. Conditions: photocatalyst = 0.175 g L⁻¹, Cr(VI) = 10 mg L⁻¹, 200 mL, pH = 2.0.

Fig. 9. (a) and (c) Photocatalytic Cr(VI) elimination over B1N0.5 and B1N3 in the presence of various hole scavengers under UV and white light irradiation, respectively. (b) and (d) Influence of water quality on Cr(VI) removal over B1N0.5 and B1N3. Conditions: Photocatalyst = 0.175 g L⁻¹, Cr(VI) = 10 mg L⁻¹, 200 mL, pH = 2.0.
achieve efficient removal of Cr(VI). Oxalic acid (H$_2$C$_2$O$_4$), citric acid (C$_6$H$_8$O$_7$), and tartaric acid (C$_4$H$_6$O$_6$) were selected to study the influence of different hole trapings on the reduction of Cr(VI) at pH 2.0. As shown in Figs. 9a and 9c, the addition of these small-molecule organic acids greatly improved the Cr(VI) reduction efficiencies of B1N0.5 and B1N3, with the enhancement following the order tartaric acid > citric acid > oxalic acid, which corresponded to the number of α-hydroxyl groups [53,62]. The depletion of the holes provided more photo-induced electrons to reduce Cr(VI), which led to the higher reduction efficiency and reaction rate.

In order to investigate the impact of co-existing ions, the wastewater stock solution with the same Cr(VI) concentration simulated from real lake water and tap water (collected from Daxing Campus, BUCEA) were used to explore the photocatalytic Cr(VI) removal performance of B1N0.5 and B1N3 under UV and white light irradiation, respectively. The parameters of the simulated wastewater are listed in Table S1. As shown in Fig. 9b, the presence of co-existing inorganic ions had a negligible effect, as demonstrated by the Cr(VI) removal efficiencies after 30 min, decreasing from 100% for the pure water solution to 90% and 86% for the tap water and lake water solutions, respectively. When the reaction time was prolonged to 40 min, Cr(VI) was completely reduced for all water quality conditions under UV irradiation, indicating that the co-existing ions had a negligible impact on the photocatalytic performance of B1N0.5. The same phenomenon could be observed under white light (Fig. 9d).

Photocatalysts for practical applications must also be recyclable and stable. B1N0.5 clearly maintained a 100% Cr removal rate after five experimental runs (Fig. 10a), and the PXRD patterns (Fig. 10b) and SEM and TEM images (Fig. S4) of the used B1N0.5 corresponded perfectly with those of the composites before reaction, implying that B1N0.5 possessed excellent stability, recyclability, and reusability. The recyclability and stability of B1N3 were also explored. As shown in Fig. 10c, the photocatalytic Cr(VI) reduction ability of B1N3 did not decline evidently after five recycles, indicating that B1N3 could be used repeatedly. Moreover, the PXRD pattern (Fig. 10d) of B1N3 before and after the photocatalytic processes demonstrated that the structure of B1N3 was not damaged even after the five cycles, which was further affirmed by TEM and SEM (Fig. S5).

3.3. Photocatalytic mechanism

Measurement of the AQEs of Cr(VI) reduction using light with specific wavelengths is important to evaluating the photocatalytic ability of a catalyst [63]. As illustrated in Fig. 11a and b, the AQEs of both B1N0.5 and B1N3 exhibited a positive correlation with the curves of their UV-vis DRS spectra, demonstrating that the Cr(VI) reduction was photo-induced. Furthermore, the AQE of B1N0.5 was much higher than that of B1N3 in the ultraviolet wavelength range. However, as the wavelength was gradually increased into the visible region, B1N3 achieved superiority; this fact helped to explain the different optimal catalyst compositions (B1N0.5 and B1N3) under UV irradiation and white light irradiation, respectively. Moreover, although the AQE of B1N3 decreased at 420 nm (Fig. 11b),
it still exhibited an efficiency of 0.2% at this frequency. The results proved that the removal of Cr(VI) over BIN3 upon white light irradiation could be attributed to both ultraviolet light and white light, resulting from the combination of BUC-21 and N-K2Ti4O9.

Based on previous work, a lower PL signal implies lower recombination efficiency of photo-generated carriers [64]. As shown in Fig S5a, the PL intensities of B1N0.5 and BIN3 were lower than that of pure N-K2Ti4O9 indicating that the BUC-21 and N-K2Ti4O9 composites exhibited superior separation of the photo-generated electrons and holes than N-K2Ti4O9 alone. Moreover, time-resolved photoluminescence analysis (Fig S6b) demonstrated that the average PL lifetimes of B1N0.5 and BIN3 were longer than that of pure BUC-21, which also proved the above point. Additionally, EIS plots for both B1N0.5 and BIN3 are depicted in Fig S6c and d. B1N0.5 and BIN3 demonstrated greater photocurrent responses than BUC-21 or N-K2Ti4O9 alone under identical conditions, confirming that B1N0.5 and BIN3 accomplished superior charge separation efficiencies.

To investigate their photocatalytic mechanisms, ESR experiments using the DMPO technique were conducted to determine the active species formed over BUC-21, N-K2Ti4O9, B1N0.5, and BIN3. As expected, no signals were detected in the dark. However, upon the illumination with UV and white light for 5 min or 10 min, •O2‒ signals were clearly observed over N-K2Ti4O9, B1N0.5, and BIN3. Longer irradiation time led to stronger signal intensity, confirming that •O2‒ radicals were produced during the photocatalytic procedure [65]. Because BUC-21 could be excited by UV irradiation, an obvious DMPO •O2‒ signal was observed after 5 or 10 min under UV exposure; however, under white light irradiation, only a weak intensity signal was observed after 10 min. This was attributed to the fact that the white light covered only part of the UV light range.

Different types of photocatalysts produce different main active species because of the differences in their band structures.
or phase compositions [66]. To explore the roles of various active substances in the photocatalytic Cr(VI) removal processes in this work, a set of capture experiments were conducted, in which e\(^{-}\), •OH, and h\(^{+}\) were captured using AgNO\(_{3}\), IPA, and EDTA-2Na, respectively. Nitrogen gas was pumped into the reaction system to remove dissolved oxygen to prevent the formation of •O\(_{2}\)\(^{-}\). As illustrated in Fig. 13a and b, e\(^{-}\)-capture clearly inhibited the reduction of Cr(VI), revealing that Cr(VI) was mainly reduced to Cr(III) by continuous single electron transfer steps on N-K\(_{2}\)Ti\(_{4}\)O\(_{9}\) (Eq. 7) [67]. Eqs. 8 and 9 demonstrate that •O\(_{2}\)\(^{-}\) could also participate in Cr(VI) reduction [68]. This participation of •O\(_{2}\)\(^{-}\) was confirmed by the fact that the Cr(VI) reduction performance also decreased after nitrogen gas was pumped into the reaction system. The •O\(_{2}\)\(^{-}\) radicals could also generate •OH through a series of reactions (Eqs. 8, 10 and 11). When •OH was captured, it promoted the reaction in Eq. 11, thereby inhibiting the elimination of Cr(VI) [69]. The addition of EDTA-2Na promoted the Cr(VI) removal; this effect was attributed to the enhanced separation of the photo-induced electrons/holes and the adverse reaction illustrated in Eq. 13.

\[
\begin{align*}
\text{Cr(VI)} & \rightarrow \text{Cr(V)} \rightarrow \text{Cr(IV)} \rightarrow \text{Cr(III)} \quad (7) \\
\text{O}_2 + e^- & \rightarrow \text{•O}_2^- \quad (8) \\
\text{•O}_2^- + \text{Cr(VI)} & \rightarrow \text{Cr(V)} + \text{O}_2 \quad (9) \\
2\text{O}_2 + 2\text{H}^+ & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (10) \\
\text{H}_2\text{O}_2 + \text{Cr(III)} + \text{H}^+ & \rightarrow \text{Cr(VI)} + \text{H}_2\text{O} + \text{•OH} \quad (11) \\
2\text{H}_2\text{O} + \text{h}^+ & \rightarrow 2\text{•OH} + \text{H}_2\text{O} \quad (12) \\
\text{Cr(V)} + \text{h}^+ / \text{•OH} & \rightarrow \text{Cr(III)} + \text{OH}^- \quad (13)
\end{align*}
\]

To further explore the reaction mechanism, the valence band (VB) of N-K\(_{2}\)Ti\(_{4}\)O\(_{9}\) was determined using valence band XPS (VB-XPS). As shown in Fig. 13c, the valence band (VB) energy level was found to be 2.57 eV for N-K\(_{2}\)Ti\(_{4}\)O\(_{9}\). Using Eqs. 14 and 15 [70], the VB and CB positions of N-K\(_{2}\)Ti\(_{4}\)O\(_{9}\) were calculated to be 2.43 eV vs NHE and -0.53 eV vs NHE, respectively. The HOMO (2.19 eV) and LUMO (-1.21 eV) positions of BUC-21 matched well with our previous work [44]. A possible mechanism is shown in Fig. 13d. In the photocatalysis process, BUC-21 and N-K\(_{2}\)Ti\(_{4}\)O\(_{9}\) are excited under UV or white light irradiation and produce photo-generated electrons and holes. Because of the difference between the E\(_{\text{LUMO}}\) of BUC-21 (-1.21 eV) and the E\(_{\text{CB}}\) of N-K\(_{2}\)Ti\(_{4}\)O\(_{9}\) (-0.53 eV), the photo-generated electrons tend to move from the LUMO of BUC-21 to the CB of N-K\(_{2}\)Ti\(_{4}\)O\(_{9}\) which facilitates the separation of the photo-generated electrons and holes of BUC-21 and promotes the reduction of Cr(VI) to Cr(III) via the electrons accumulated in the CB of N-K\(_{2}\)Ti\(_{4}\)O\(_{9}\). Since the E\(_{\text{LUMO}}\) of BUC-21 and the E\(_{\text{CB}}\) of N-K\(_{2}\)Ti\(_{4}\)O\(_{9}\) were more positive than the redox potential of O\(_2)/\text{•O}_2^-\) (-0.33 eV), the photo-generated electrons could react with dissolved oxygen (DO) to produce •O\(_{2}\)\(^{-}\), which exerted a
positive effect on Cr(VI) reduction. However, the rate of O₂-production was slow for the LUMO of BUC-21 due to the fact that the white light covered only part of the ultraviolet light range capable of exciting BUC-21, which could also explain the slower Cr(VI) reduction rate over B1N3 under white light compared to that of B1N0.5 under UV light.

\[ E_{\text{HSE}} = \Phi + E_{\text{VL}} - 4.44 \quad (14) \]

\[ E_{g} = E_{\text{VB}} - E_{\text{CB}} \quad (15) \]

\[ E_{\text{HSE}} \] is the potential of the normal hydrogen electrode; \( \Phi \) is the electron work function of the analyzer (4.30 eV); \( E_{\text{VL}} \) is the potential of the vacuum level; \( E_{g} \) is the band-gap energy.

4. Conclusions

BUC-21/N-K₂Ti₄O₉ (B1N) composites that could rapidly achieve Cr(VI) reduction under both UV and white light irradiation were easily prepared via ball milling. The obtained composites B1N0.5 and B1N3 displayed outstanding photocatalytic activity toward Cr(VI) reduction (100%) under UV and white light; the reduction was 1.4- and 14.3-fold quicker than that over pure BUC-21, respectively, as electron transfer between BUC-21 and N-K₂Ti₄O₉ decreased the chance of electron-hole pair recombination. Furthermore, experiments in the presence of co-existing ions and recycling experiments also demonstrated the good reusability and stability of B1N0.5 and B1N3, which could make them suitable for iterative processing. This study shows that N-K₂Ti₄O₉/MOF composite photocatalysts would be useful for the remediation of Cr-contaminated wastewater. BUC-21, with its two-dimensional crystal structure, should also provide further possibilities to accomplish the elimination of environmental pollutants with the aid of various nano-materials.

References


Graphical Abstract


Photocatalytic Cr(VI) elimination over BUC-21/N-K₂Ti₄O₉ composites: Big differences in performance resulting from small differences in composition

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BUC-21/N-K₂Ti₄O₉ composites show high photocatalytic activity under UV and white light, which can be used to reduce Cr(VI) to Cr(III) effectively.
采用简单的机械球磨法制备了一系列BUC-21/N-K2Ti4O9复合材料，其中X = 0.2, 0.5, 1, 2, 3和4，代表N-K2Ti4O9在复合物中的比例。本文采用简单的机械球磨法制备了一系列BUC-21/N-K2Ti4O9复合材料。
(XPS)等技术对UAC-X复合物的形貌和结构进行了表征。研究了B1NX在紫外光和白光照射下光催化还原六价铬(Cr(VI))的性能。探究了不同pH (pH = 2–8)、不同小分子有机酸(柠檬酸、酒石酸和草酸)及共存离子(自来水和湖水中的离子)对光催化还原Cr(VI)的影响。结果表明, PXRD谱图显示B1NX的衍射峰位置分别与BUC-21和N-K2Ti4O9峰位置完全吻合。SEM、TEM、EDS和HRTEM图片证明在B1NX复合物中BUC-21附着在N-K2Ti4O9表面。在紫外光照射下40 min后, B1N0.5的光催化活性最高, 还原效率达到100.0%, 且还原速率是BUC-21的1.42倍。而在白光照射下, 随着N-K2Ti4O9含量的增加, 复合物的光催化活性先增后减。最佳比例B1N3可100 min时还原99.0%的Cr(VI), 远远优于对Cr(VI)几乎无还原能力的BUC-21和N-K2Ti4O9。这是因为N-K2Ti4O9的含量的增加不仅有利于电荷的转移, 也有利于白光的利用。在紫外光和白光照射下, 随着溶液pH值从2提高到8, 还原效率逐渐降低。这是因为在酸性条件下H⁺浓度高有利于Cr(VI)还原为Cr(III), 而当pH>6时, Cr³⁺与OH⁻形成Cr(OH)₃沉淀附着在催化剂表面, 影响对光的吸收, 降低了光催化效率。当反应体系中加入草酸、柠檬酸和酒石酸等小分子有机酸时, 光催化速率得到显著提高, 这是由于小分子链烃有机物容易捕捉光生空穴。共存离子实验表明, 虽然湖水和自来水中的共存离子对B1N0.5和B1N3的还原性能稍有抑制, 但当反应时间延长时, 这种影响可忽略不计。表观量子效率实验证明B1NX还原Cr(VI)是光诱导过程。光致发光分析、时间分辨光致发光分析、电化学分析、电子自旋共振(ESR)和活性物质捕获实验显示, B1N0.5和B1N3中BUC-21最低未占轨道(LUMO)上的光生电子转移至N-K2Ti4O9导带, 提高了光生电子和空穴的分离效率, 最终增强了光催化还原Cr(VI)的活性。N-K2Ti4O9的引入也使得BUC-21的光吸收区域拓展至白光, 实现了其实际应用的潜力。同时, B1N0.5在紫外光照射下和B1N3在白光照射下经过5次光催化循环实验后其还原Cr(VI)效率仍然可达99%, 且PXRD谱图、SEM和TEM图像未见明显变化, 表明其具有稳定性和重复利用性。综上, BUC-21/N-K2Ti4O9是一种具有应用前景的高效复合型光催化剂。

关键词: BUC-21; N-K2Ti4O9; 光催化; 六价铬; 紫外光和白光