

Original Research

Performance of a Kind of Novel Z-scheme Photocatalytic Catalysts: CdMoO₄/CNTs/g-C₃N₄

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Abstract

Facial mixing preception method was used to prepare the CdMoO₄/CNTs/g-C₃N₄. The novel Z-scheme samples were characterized by using XRD, SEM, FT-IR, XPS, UV-vis, PL, EIS and photocurrent response. The photocatalytic activity of the catalyst was measured by degradation of tetracycline hydrochloride (TCH) under visible light. The optimal photocatalytic degradation efficiency of 10 wt% CdMoO₄/CNTs/g-C₃N₄ was up to 85.3%, which was higher than CdMoO₄, CdMoO₄/CNTs and g-C₃N₄. The enhanced photocatalytic performance of the heterojunction was attributed to the highly separation efficiency of photogenerated electron-hole pairs. A Z-scheme system was produced in CdMoO₄/CNTs/g-C₃N₄ with the doping of CNTs.

Keywords: photocatalytic, Z-scheme, TCH (tetracycline hydrochloride) degradation, CdMoO₄/CNTs/g-C₃N₄ heterojunction

Introduction

Semiconductor photocatalytic technology was an effective way to solve the problem of energy shortage and environmental pollution [1]. It was widely used in the degradation of pollutants and hydrogen production. There were some common materials like TiO₂ and ZnO, which could only absorb the ultraviolet light because the high recombination of photogenerated electron and hole pairs [2]. In order to expand the use of photocatalysts, it was essential to develop their visible ability. In the

past years, a Z-scheme photocatalytic mechanism caused concern for its high efficiency of quantum, deep oxidation power and excellent electrons separation efficiency [3-4]. In the all solid Z-scheme photocatalysis mechanism system, solid electron mediator played an important role in charge migration. Nowadays, there were more than two kinds of semiconductor, metal and non-metal oxides and valuable materials for all solid state Z-type photocatalysis system. Most of them, such as CdS/Bi₃O₄Cl [5], CdS/WO₃ [6], ZnO/Pt/CdZnS [7], Ag@AgCl/RGO [8] and g-C₃N₄/C/Bi₂MoO₆ Z-Scheme composites [9], had been synthesized successfully and applied in photocatalytic degradation pollutants and water splitting.

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For its advantages of cheap, available and environmental friendly, the graphite-like carbon nitride ($g\text{-C}_3\text{N}_4$) had showed outstanding performance of photocatalytic [10]. However, the fast recombination of photoinduced electrons and holes and the low surface area influenced the photocatalytic performance of bare $g\text{-C}_3\text{N}_4$. Therefore, there were varieties of catalysts based on $g\text{-C}_3\text{N}_4$ had been explored such as $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{VO}_2\text{PO}_4$ [11], $\text{Bi}_2\text{O}_3/\text{GCN}$ [12], $\text{CQDS}/g\text{-C}_3\text{N}_4$ [13] and $\text{Ag}/\text{AgBr}/g\text{-C}_3\text{N}_4$ [14] in order to avoid the above limitation. Meanwhile, novel and more efficient $g\text{-C}_3\text{N}_4$ -based catalysts still need to be developed.

Cadmium molybdate (CdMoO_4) is one of the interesting materials due to its excellent optical and chemical properties [15]. However, the photocatalytic activity was limited with pure CdMoO_4 for low visible light response and wide band gap. As a kind of carbonaceous material [16] multi-walled carbon nanotubes (CNTs) possessed great electrons transferring ability and large surface area [17]. Most importantly, CNTs include many active pots; and it could achieve the fast separation of photo-generated electron-hole pairs and enhance the photoactivity. In the past researches, the CNTs had excellent photoactivity in the application of photocatalysis, such as $g\text{-C}_3\text{N}_4/\text{CNTs}/\text{Ag}_3\text{PO}_4$ [18] and $g\text{-C}_3\text{N}_4/\text{CNTs}/\text{Bi}_2\text{WO}_6$ [19].

In order to obtain an efficient photocatalyst, CNTs was induced in CdMoO_4 and $g\text{-C}_3\text{N}_4$ by facial mixing preception method to construct a ternary heterojunction. The samples were characterized by using XRD, SEM, FT-IR, XPS, UV-vis, PL, EIS and photocurrent response. The photocatalytic activity of the catalyst was measured by degradation of tetracycline hydrochloride (TCH) under the visible light.

Experiments

Preparation of $g\text{-C}_3\text{N}_4$

The $g\text{-C}_3\text{N}_4$ was prepared through thermal condensation method [20]. 5 g melamine was put in a crucible with a cover and heated to 550°C with a heating rate of $10^\circ\text{C}/\text{min}$, then maintained at that temperature for 4 h. After natural cooling to room temperature, the obtained products were grounded to powders with the agate bowl and yellow $g\text{-C}_3\text{N}_4$ particles were collected.

Preparation of CNTs/ CdMoO_4

The CNTs/ CdMoO_4 composite was prepared by a hydrothermal method [16]. Firstly, 0.617 g $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ were dissolved in 40ml distilled water and 50 mg CNTs were subsequently added into the above solution and the mixed solution were sonicated processed for 1h. 0.484 g $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in 40ml ethylene glycol to form transparent solution. Then, the sodium molybdate solution was added slowly into $\text{Cd}(\text{NO}_3)_2$ -CNTs suspended solution.

Finally, the mixed solution was stirred for 30 min and the pasty mixture was sealed into a 100 ml Teflon-lined autoclave and maintained at 160°C for 6 h. The as-prepared composites were washed by centrifugation for several times with water and absolute ethanol respectively, and desiccation at 60°C for 8 h under vacuum. Meanwhile, the bare CdMoO_4 without CNTs was prepared in the same process.

Preparation of $\text{CdMoO}_4/\text{CNTs}/g\text{-C}_3\text{N}_4$ Composite Photocatalyst

Different ratios of $\text{CdMoO}_4/\text{CNTs}/g\text{-C}_3\text{N}_4$ composite photocatalysts were fabricated by a facile precipitation and mixed heating method. In a typical procedure, 0.1 g $g\text{-C}_3\text{N}_4$ were dispersed into 20 ml methanol and sonicated for 30 min. A certain amount of CNTs/ CdMoO_4 was added into the above suspension slowly under violent stirring, and the mixture was under subsequent continuous stirring at room temperature until the methanol was vaped. Then, the precipitate was collected and dried at 60°C for 5 h. Finally, the composite was heated at 400°C for 2 h in muffle furnace after grounded. The different weight ratios photocatalysts were prepared successfully, and the weight percentage ratios of CNTs/ CdMoO_4 to $g\text{-C}_3\text{N}_4$ were 3%, 7%, 10%, 20%, 30%, 40%, 50% in the precursors, respectively. The obtained different ratio $\text{CdMoO}_4/\text{CNTs}/g\text{-C}_3\text{N}_4$ composites were marked as 3MCN, 7MCN, 10MCN, 20MCN, 30MCN, 40MCN and 50MCN, respectively.

Characterization

The crystal structures of the as-obtained samples were determined using X-ray diffract meter (XRD, Bruker/D8-advance). The microscopic morphology and size were observed by scanning electron microscopy (SEM, Hitachi FESEM-4800). The optical absorption range was investigated through diffuse reflectance spectra using a UV-vis spectrophotometer (UV-vis, Evolution 220) with white BaSO_4 as a reference sample. The functional groups were analyzed by fourier transformation infrared spectroscopy (FT-IR) spectrometer (Spectrum Two). X-ray photoelectron spectroscopy (XPS) was conducted to analyze the chemical elements and atoms states of the samples. Electrochemical impedance spectroscopy (EIS) and photocurrent response were obtained to realize the electrochemical property with a CHI660 D electrochemical workstation (Chen Hua Instruments, Shanghai, China). Photoluminescence (PL) was also carried out to test the charge transfer efficiency.

Photocatalytic Experiment

The photocatalytic performance of the catalysts was measured by photocatalytic degradation of 15 mg/L TCH solution under visible light irradiation.

Firstly, 25 mg samples were added into 50 mL tetracycline hydrochloride (TCH) solution with violently magnetically stirring in a glass vessel. Then the mixture was placed in a dark room for 30 minutes to reach adsorption-desorption equilibrium between photocatalysts and TCH. Subsequently, the photocatalytic experiment was carried out under a 350W Xe light irradiation with filtering short wavelength light ($\lambda < 420$ nm). Compared to the catalyst, the blank sample was treated in the same condition to study the self-decomposition performance of TCH solution. The visible light catalytic experiment was continued for 120 min and 5 ml of suspended solution was collected every 20 min, and the mixture was centrifuged for 5 min at 12000r/min to separate the residual photocatalyst. The concentration of TCH solution was measured by a UV-vis spectrophotometer featuring at 356 nm (the largest absorption wavelength of the target contaminant).

Results and Discussions

Structure and Morphology Characterization

XRD diffraction results of $g\text{-C}_3\text{N}_4$, CdMoO_4 and different MCN composites were shown in Fig. 1. The diffraction of $g\text{-C}_3\text{N}_4$ showed two different peaks, the weaker one at 13.1° and the stronger one were at 27.4° . The diffraction peaks were in accordance in the (100) and (002) characteristic patterns of $g\text{-C}_3\text{N}_4$, respectively [21]. The characterized peaks of CdMoO_4 were corresponding to the tetragonal phase of CdMoO_4 (JCPDS NO:07--0209) [22], whose the peaks were observed at about 29.24° , 32.0° , 34.8° , 47.98° , 50.0° , 55.3° , 58.98° and 60.6° . Furthermore, that both peaks of $g\text{-C}_3\text{N}_4$ and CdMoO_4 was obvious in the all MCN composites characteristic patterns. It was notable that

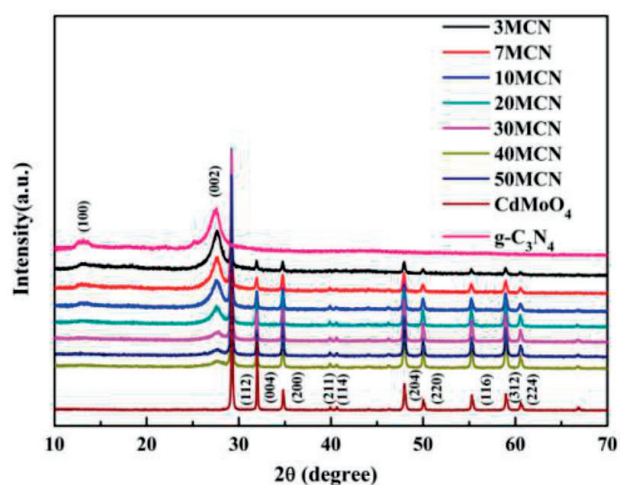


Fig. 1. The characterized patterns of $g\text{-C}_3\text{N}_4$, CdMoO_4 and MCN composites.

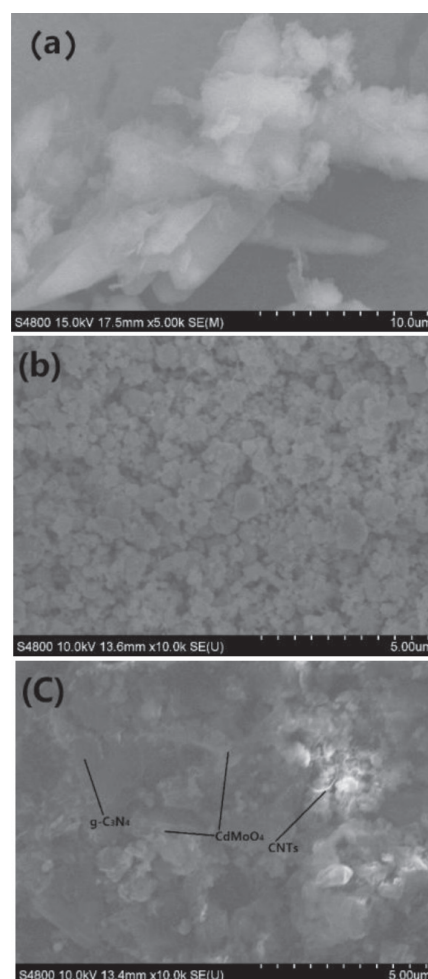


Fig. 2. SEM images of $g\text{-C}_3\text{N}_4$ a), CdMoO_4 b) and 10MCN c).

the peaks of $g\text{-C}_3\text{N}_4$ became weaker in the composites as the ratio of $\text{CNTs}/\text{CdMoO}_4$ increased.

The microstructure and morphology of $g\text{-C}_3\text{N}_4$, CdMoO_4 and 10MCN composite was shown in Fig. 2. Pure $g\text{-C}_3\text{N}_4$ exhibited folded sheet shape in Fig. 2a). Spherical shape of CdMoO_4 was dispersed

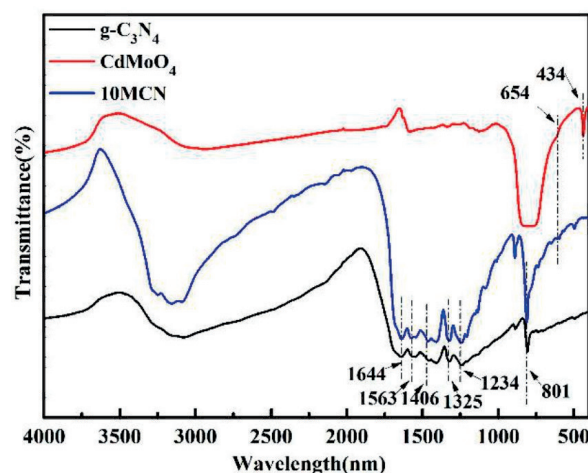


Fig. 3. FT-IR spectrums of $g\text{-C}_3\text{N}_4$, CdMoO_4 and 10MCN.

with a micro-nano meter level in Fig. 2b). And the CdMoO₄/CNTs/g-C₃N₄ scanning image was shown in Fig. 2c), cube-like CNTs were combined with CdMoO₄ particles and dispersed in the g-C₃N₄ surface. It was clearly that the g-C₃N₄ sheet became thicker in the composite, which indicated the great interaction between the two semiconductors.

FT-IR Results

FT-IR results of g-C₃N₄, CdMoO₄ and 10MCN were shown in Fig. 3. For bare g-C₃N₄, distributions of

main characteristic peaks were at 1234, 1325, 1406 and 1563 cm⁻¹, which were corresponding to the aromatic C–N stretching vibration modes. The peak related to C–N stretching vibration modes was appeared at 1644 cm⁻¹, another peak at 808 cm⁻¹ could be observed that represented the out-of-plane bending modes of heterocyclic C–N [23]. The spectrum pattern of CdMoO₄ showed two absorption peaks at 654 cm⁻¹ and 434 cm⁻¹, which corresponded to the O–Mo–O stretching vibration mode and Mo–O–Mo stretching vibration mode, respectively [24]. For 10MCN, the absorption peak of g-C₃N₄ could be obviously observed, and the

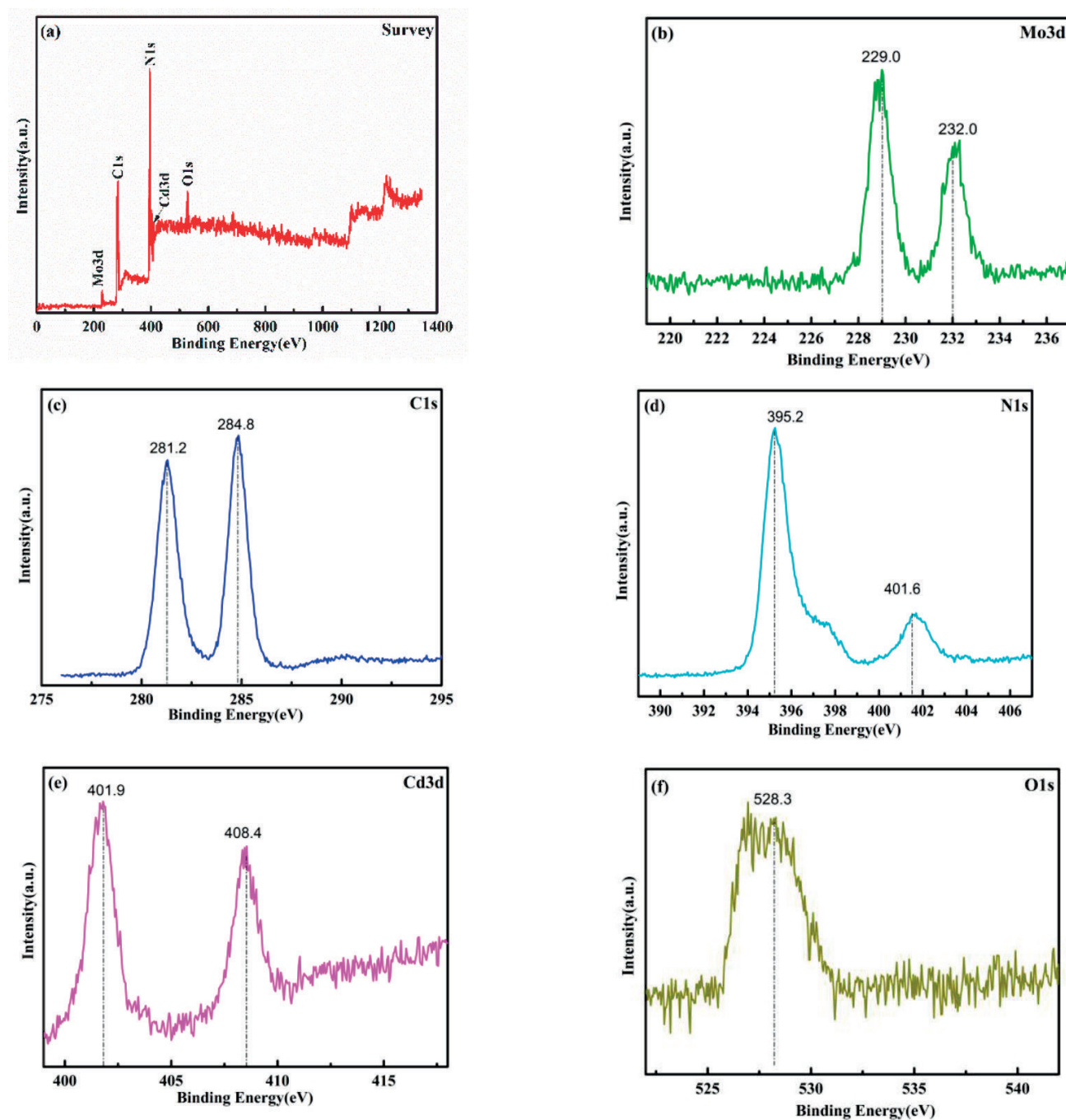


Fig. 4. XPS spectrum of 10 MCN: survey a), Mo3d b), C1s c), N1s d), Co3d e) and O1s f).

O-Mo-O expansion bond corresponding to 654 cm^{-1} could be seen. The peak corresponding to the Mo-O-Mo expansion bond was weak, which may be due to the low content of CdMoO_4 in the heterojunction and the weak strength of this peak. The above results proved the existence of $\text{g-C}_3\text{N}_4$ and CdMoO_4 characteristics bonded in heterogeneous junction and the two materials were recombined successfully.

XPS Analysis

XPS analysis of 10MCN was conducted and the results were shown in Fig.4. According to the Fig. 4a), the composition elements of heterojunction included Mo, C, N, Cd and O. In the Mo3d spectra (Fig. 4b), binding energy were at 229.0 and 232.0 eV [25]. The binding energy at 401.9 and 408.4 eV were in accordance with the Cd symmetric peaks, which corresponded to the previous report [22]. The spectra peak of C1s at 281.2 and 284.8eV [16] corresponded to the C=N-C bond from $\text{g-C}_3\text{N}_4$, and C-C bond from CNTs respectively. From the Fig. 4d), the N1s peak at 395.2eV attributed to the N-C-N bond [21]. The XPS analysis results were in good agreement with the XRD patterns.

UV-vis Analysis

UV-vis spectra of $\text{g-C}_3\text{N}_4$, CdMoO_4 , CNTs/ CdMoO_4 and 10MCN were measured in the range of 200-800 nm and all the results were presented in Fig. 5a). Based on the previous report [26], it showed that $\text{g-C}_3\text{N}_4$ could absorb the UV strongly, and the absorption spectrum edge was about 470 nm. For the pristine CdMoO_4 , the absorption edge was blown 365 nm which indicated CdMoO_4 only absorbed the UV light [27]. As the introduction of CNTs, CNTs/ CdMoO_4 had stronger absorption in all light regions. As for 10MCN heterojunction, the visible light absorption edge got red shifted and it can utilize more range light. It proved that the visible light response was enhanced after introducing the CNTs into the 10MCN heterojunction.

The Kubelka-Munk equation could be used for calculating band gap (E_g) to evaluate the light utilization ability of the samples further, the equation are as following formula (1) [28].

$$\alpha(h\nu) = A(h\nu - E_g)^{n/2} \quad (1)$$

In here, α , h , ν , A , E_g and n present the absorption coefficient, Planck constant, incident light frequency, a constant, band gap and an integer, respectively.

The value of n mainly depends on the electronic transition structure of different semiconductors, where $n = 1$ if the band gap is a direct transition and $n = 4$ if the band gap is an indirect transition. After the calculation, the detailed E_g values of $\text{g-C}_3\text{N}_4$ and CdMoO_4 were obtained, which were about 2.65eV and 3.58eV, respectively (shown in Fig. 5b).

What is more, the edge potential of the valence band (VB) and conduction band (CB) could be calculated by following equation (2) and (3) [29] with the known E_g .

$$E_{CB} = X - E^e - 0.5E_g \quad (2)$$

$$E_{VB} = E_{CB} + E_g \quad (3)$$

In these equations, E_{CB} and E_{VB} represents CB and VB edge potentials of semiconductor, respectively. X is the absolute electronegativity of semiconductor that is estimated by the geometric mean of the electronegativity of the constituent atoms. Furthermore, E^e is the energy of free electrons on the hydrogen scale ($\sim 4.5\text{ eV}$). According to the Ref [30-31], the X value of CdMoO_4 and $\text{g-C}_3\text{N}_4$ were 6.16eV and 5.64eV, respectively. After the above calculations, we could see the E_{CB} of CdMoO_4 and $\text{g-C}_3\text{N}_4$ were -0.13 eV and -1.2 eV ; and the E_{VB} of them were 3.45 eV and 1.45 eV , respectively.

According to these results, it was obvious that the visible light absorption performance of 10MCN was considerably enhanced compared with pure CdMoO_4 and $\text{g-C}_3\text{N}_4$, it showed the heterojunction could utilize more visible light. The enhanced visible light absorption performance involved high separation efficiency

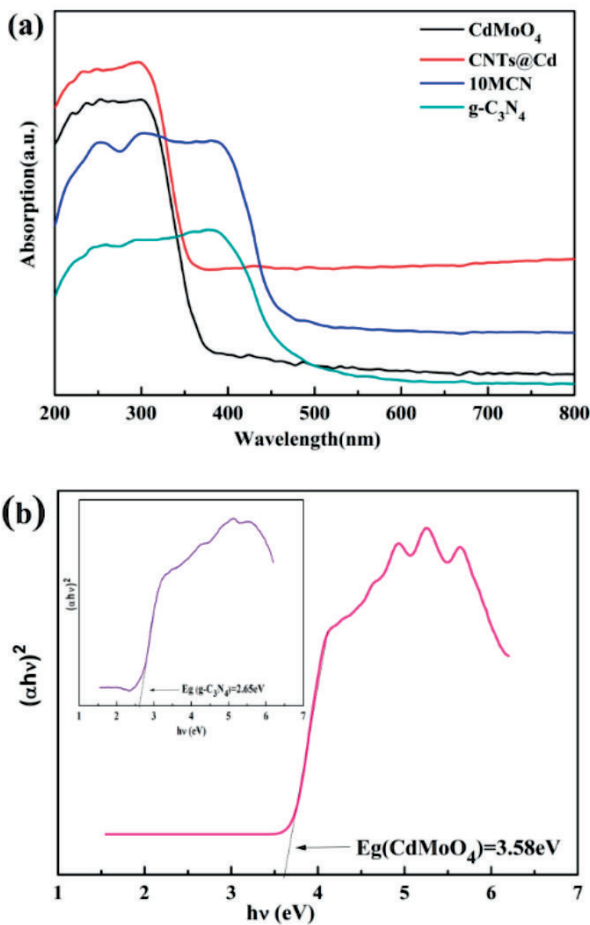


Fig. 5. UV-vis absorption spectra a) and band gap values b) of $\text{g-C}_3\text{N}_4$, CdMoO_4 and 10MCN.

between photogenerated electron-hole pairs by the introducing of CNTs.

Electrochemical Analysis

The photocurrent response of $g\text{-C}_3\text{N}_4$, CdMoO_4 and 10MCN were displayed in Fig. 6. The high photocurrent response intensity represented rapid separation of photogenerated electron-hole pairs [23]. From the Fig. 6(a), the photocurrent response of 10MCN showed the higher intensity than bare $g\text{-C}_3\text{N}_4$ and CdMoO_4 . It indicated the high separation efficiency of photogenerated electron-hole pairs with

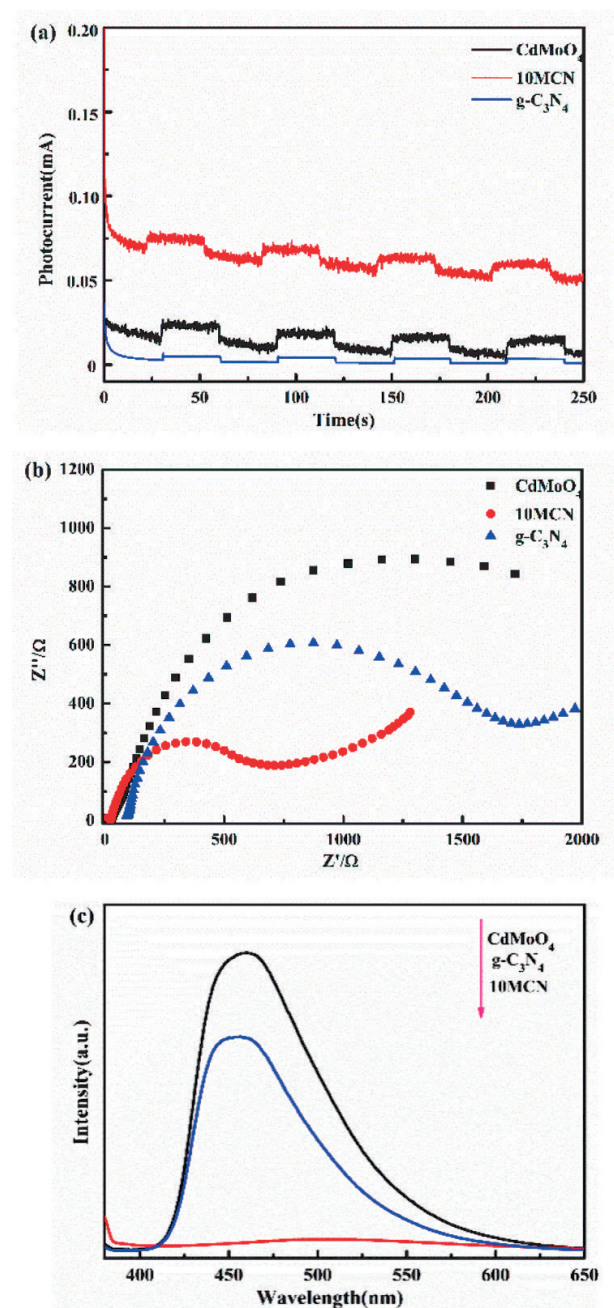


Fig. 6. Photocurrent response EIS of $g\text{-C}_3\text{N}_4$, CdMoO_4 a) and 10MCN b) of $g\text{-C}_3\text{N}_4$, CdMoO_4 and 10MCN c).

the heterojunction. The electrochemical impedance spectroscopy (EIS) of $g\text{-C}_3\text{N}_4$, CdMoO_4 and 10MCN were characterized, Nyquist plots of these samples were shown in Fig. 6(b). It was known that the smaller arc radius represented a lower electron transfer resistance and the charge transfer efficiency was improved in the process of photocatalytic degradation [32]. It was seen that the interfacial charge-transfer resistance of 10MCN was greatly decrease than the bare LaCoO_3 and $g\text{-C}_3\text{N}_4$, and it would enhanced the carrier transport efficiency that was attributed to the formation of the heterojunction.

To further certify the electrochemical property, photoluminescence (PL) was tested and the result was shown in Fig. 6(c). The PL spectra results displayed the separation of charge and the recombination of electron-hole pairs. Higher spectra peaks usually represented higher recombination of electron-hole pairs and a lower photocatalytic activity [33]. The absorption intensity of 10MCN is lower than that of the two pure semiconductors, indicating that the suppression of electron-hole recombination has occurred in the heterojunction.

The above measured results revealed the high charge separation efficiency and more suppression of electron-hole pairs from the recombination in the $\text{CdMoO}_4/\text{CNTs}/g\text{-C}_3\text{N}_4$ heterojunction. It was proved that the CNTs-inserted heterojunction could improve the quantum efficiency and had an influence on the charge transferring, and enhanced photocatalytic activity further.

Photocatalytic Activity Analysis

The photocatalytic performances of the as-prepared samples were measured by degradation of TCH solution under visible light, the experimental results was shown in Fig. 7. These could be concluded that (i) TCH contaminant was stable. It is too hard for them to self-decompose under visible light irradiation without any photocatalysts from the blank experiment. (ii) For pure CdMoO_4 and $g\text{-C}_3\text{N}_4$, the degradation rate was unsatisfied with 8.15% and 17.4% of TCH was degraded respectively. While, $\text{CNTs}/\text{CdMoO}_4$ had stronger photodegradation efficiency that was 30.4%, which indicated the introduction of CNTs played an important role in catalytic activity. (iii) $\text{CdMoO}_4/\text{CNTs}/g\text{-C}_3\text{N}_4$ heterojunction showed higher catalytic activity than $\text{CNTs}/\text{CdMoO}_4$ and $g\text{-C}_3\text{N}_4$, the photocatalytic rate was enhanced gradually with $\text{CNTs}/\text{CdMoO}_4$ loading ratio from 3% to 10%. The optimal degradation rate was up to 85.3% with 10MCN. (iv) The photocatalytic activity decreased with further increasing the doping ratio of $\text{CNTs}/\text{CdMoO}_4$, which could lead the contacted area decreased and the charge transferring restrained.

To further confirm the photocatalytic activity was improved efficiently heterojunction, the kinetic constant [34] was introduced that calculated by the pseudo-first-order reaction rate equation of $-\ln(c/c_0) = kt$, where c_0

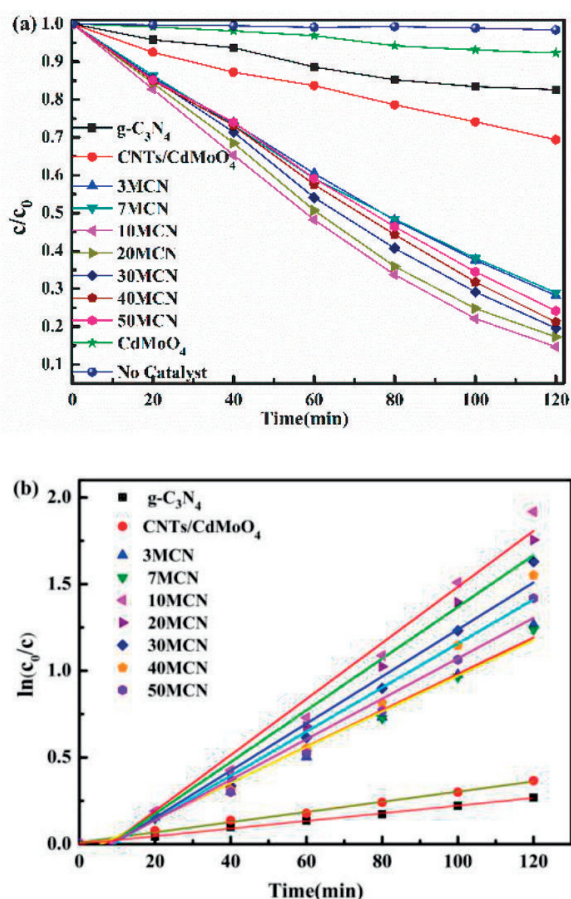


Fig. 7. Photocatalytic degradation efficiency of TCH with $g-C_3N_4$, CNTs/CdMoO₄ and MCN composites a), the first-order kinetics of photodegradation with $g-C_3N_4$, CNTs/CdMoO₄ and MCN composites b).

represents the initial concentration of TCH, c is the TCH concentration at the time t , and κ is the kinetic constant. From the calculation results, it was shown that the heterojunction had prominent photocatalytic degradation performance compared with pure catalysts. The kinetic constant of TCH degradation of 10MCN ($\kappa = 0.01617 \text{ min}^{-1}$) was about 10.43 times of pure $g-C_3N_4$ ($\kappa = 0.00155 \text{ min}^{-1}$) and about 5.39 times of pure CNTs/CdMoO₄ ($\kappa = 0.003 \text{ min}^{-1}$), which could be inferred the modification with CNTs/CdMoO₄ improved the photocatalytic performance dramatically under light irradiation. The specific results were shown in Fig. 7b).

To explore the stability and recyclable use of the heterojunction, cycling degradation experiments including using, recovering, washing and reusing for 5 times were carried out, and the results showed that photocatalytic activity of 10MCN was deteriorated after 5 cycling due to the occurrence of light corrosion, but the heterojunction still exhibited high photocatalytic activities. After 5 cycles of experiments, the 10MCN heterojunction was still displayed excellent catalytic activity (TCH degradation was over 80%), which proved that the heterojunction had relatively high stability against light corrosion reaction.

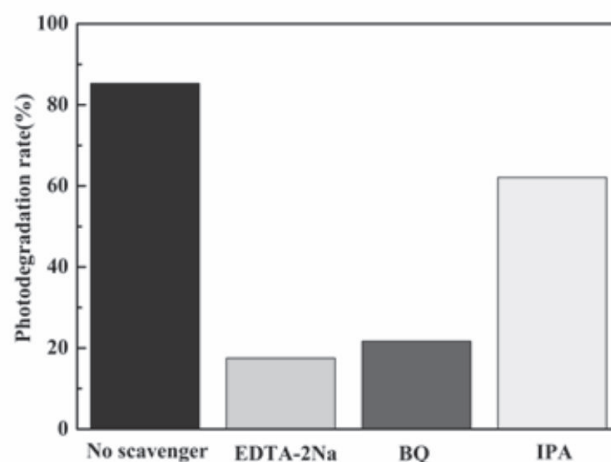


Fig. 8. Active species trapping experiment of 10MCN.

Active Species Trapping Experiment

In order to explore the main active materials at the photocatalytic degradation process of 120 CL heterojunction, the trapping experiment was carried out. The scavengers include 1, 4-benzoquinone (BQ), disodium ethylenediamine tetraacetic acid (EDTA) and 2-propanol (IPA), which were used to scavenge the superoxide radicals ($\bullet O_2^-$), holes (h^+) and hydroxyl radicals ($\bullet OH$), respectively. The details were adding 0.5 mmol scavengers to test how scavengers influenced the quality of photocatalytic under the same experiment condition. The experiment result was shown as Fig. 8. It was concluded that the photo degradation efficiency of TCH decreased remarkably with the addition of BQ and EDTA. In addition, it changed with the addition of IPA. When IPA was added to the reaction system, the degradation rate of TCH was about 60%, while, when EDTA-2Na and BQ were added in the system, respectively, the degradation rate of TCH reached about 15% and 20%, respectively. Therefore, the main active species were h^+ and $\bullet O_2^-$, and the $\bullet OH$ was the secondary active species.

Photocatalytic Mechanism Discussion

The CdMoO₄/CNTs/ $g-C_3N_4$ photocatalytic mechanism could be concluded according to the above the result of the experiment. The Z-scheme photocatalytic system was formed due to the insertion of CNTs. The difference of VB and CB edge potentials between $g-C_3N_4$ and CdMoO₄ could offer the condition to achieve the separation of photo-generated electron-hole pairs. At the same time, the recombination of both could be restricted by the existence of heterojunction. In the system, the charge transfer and separation were faster in the occurrence of CNTs. When light irradiated to the heterojunction, both $g-C_3N_4$ and CdMoO₄ absorbed photon powder and they were excited rapidly themselves to produce e^- and h^+ . As an important

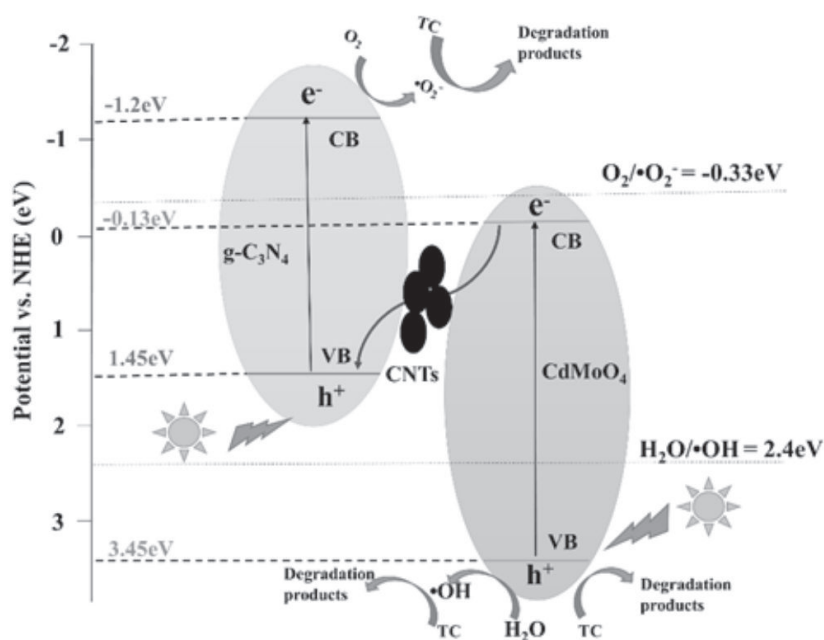


Fig. 9. Z- scheme photocatalytic mechanism of CdMoO₄/CNTs/g-C₃N₄ heterojunction.

bridge, CNTs had an important influence on the charge migration. The e^- in the CB of CdMoO₄ could move quickly to the VB of g-C₃N₄ by the electron transfer bridge. As a result, e^- was reserved in the CB surface of g-C₃N₄, h^+ was reserved in the VB of CdMoO₄. Subsequently, the CB edge potential of g-C₃N₄ was more negative than the standard redox potential E^0 ($O_2/\bullet O_2^-$) (-0.33 V vs. NHE), which could react with O₂ to generate $\bullet O_2^-$ by this channel. At the same time, the VB edge potential of CdMoO₄ was less positive than the standard redox potential E^0 ($H_2O/\bullet OH$) (2.4 eV vs. NHE), which could react with H₂O to $\bullet OH$. Rely on the oxidation activity of $\bullet O_2^-$, $\bullet OH$ and h^+ , TCH molecules could be easily oxidized into CO₂, H₂O and other simple products. Corresponding Z-scheme photocatalytic mechanism in CdMoO₄/CNTs/g-C₃N₄ heterojunction was displayed in Fig. 9.

Conclusions

A novel Z-scheme CdMoO₄/CNTs/g-C₃N₄ heterojunction was obtained by facile mixed precipitation method. CNTs were successfully introduced to enhance the charge transferring efficiency. The elements compose analysis indicated the heterojunction included CdMoO₄, CNTs, and g-C₃N₄ without any impurity. SEM images showed the interaction was achieved and great crystallization in the heterojunction. The optimal photocatalytic degradation rate of TCH was up to 85.3% with 10MCN under visible light irradiation. It was explored that the kinetic constant of TCH degradation by 10MCN photocatalyst was about 5.39 times of that by CNTs/CdMoO₄ and about 10.43 times of that by pure g-C₃N₄, and the heterojunction

still showed highly photocatalytic performance after 5 cycle using. The mechanism study revealed that the inserted-CNTs had an important influence on charge migration as a transferring bridge. It was concluded that the Z-scheme photocatalytic system in the CdMoO₄/CNTs/g-C₃N₄ heterojunction improved its photocatalytic activity under visible light. This work would provide a facile and effective approach for fabricating a high efficiency photocatalyst.

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Conflict of Interest

The authors declare no conflict of interest.

References

1. NI M., LEUNG MKH., LEUNG DYC. A review and recent developments in photocatalytic water-splitting using TiO₂ for hydrogen production. *Renewable and Sustainable Energy Reviews* **11** (3), 401, **2007**.
2. CHEN Z.L., WANG W.L., ZHANG Z.G. High-Efficiency Visible-Light-Driven Ag₃PO₄/AgI Photocatalysts: Z-Scheme Photocatalytic Mechanism for Their Enhanced Photocatalytic Activity. *The Journal of Physical Chemistry C* **117** (38), 19346, **2013**.

3. CHEN B.C., SHEN Y., WEI J.H. Research progress on g-C₃N₄-based Z-scheme photocatalytic system. *Acta Phys. Chim. sin.*, **32** (6), 1371, **2016**.
4. ZHOU P., YU J.G., JARONIEC MIETEK All-solid-state Z-scheme photocatalytic systems. *Adv Mater* **26** (29), 4920, **2014**.
5. CHEN H.N., CHE G.B., JIANG E.H. A novel Z-Scheme CdS/Bi₃O₄Cl heterostructure for photocatalytic degradation of antibiotics: Mineralization activity, degradation pathways and mechanism insight. *Journal of the Taiwan Institute of Chemical Engineers*, **91**, 224, **2018**.
6. ZHANG L.J., LI S., LIU B.K. Highly Efficient CdS-WO₃ Photocatalysts Z-Scheme Photocatalytic Mechanism for Their Enhanced Photocatalytic H₂ Evolution under Visible Light. *ACS Catal.* **4** (10), 3724, **2014**.
7. ISIMJAN T.T., MAITY P., LLORCA J. Comprehensive Study of All-Solid-State Z-Scheme Photocatalytic Systems of ZnO/Pt/CdZnS. *ACS Omega.* **2** (8), 4828, **2017**.
8. MIN U.L., HE G.Q., XU Q.J. Self-assembled encapsulation of graphene oxide/Ag@AgCl as a Z-scheme photocatalytic system for pollutant removal. *J. Mater. Chem. A* **2** (5), 1294, **2014**.
9. MA T.J., WU J., MI Y.D. Novel Z-Scheme g-C₃N₄/C@Bi₂MoO₆ composite with enhanced visible-light photocatalytic activity for β-naphthol degradation. *Separation and Purification Technology.* **183**, 54, **2017**.
10. WANG X.C., MAEDA KAZUHIKO, THOMAS AREN, A metal-free polymeric photocatalyst for hydrogen production from water under visible light. *Nat Mater* **8** (1), 76-, **2009**.
11. ZHANG T.T., SHAO X., ZHANG D.F., Synthesis of direct Z-scheme g-C₃N₄/Ag₃VO₂ PO₄ photocatalysts with enhanced visible light photocatalytic activity. *Separation and Purification Technology*, **195**, 332, **2018**.
12. ZHANG L., WANG G., XIONG Z. Fabrication of flower-like direct Z-scheme β-Bi₂O₃/g-C₃N₄ photocatalyst with enhanced visible light photoactivity for Rhodamine B degradation. *Applied surface science*, **436**, 162, **2018**.
13. HONG Y.Z., MENG Y.D., ZHANG G.Y. Facile fabrication of stable metal-free CQDs/g-C₃N₄ heterojunctions with efficiently enhanced visible-light photocatalytic activity. *Separation and Purification Technology* **171**, 229, **2016**.
14. YANG Y.X., GUO W., GUO Y.N. Fabrication of Z-scheme plasmonic photocatalyst Ag@AgBr/g-C₃N₄ with enhanced visible-light photocatalytic activity. *J Hazard Mater* **271**, 150, **2014**.
15. XU J.J., WU M.M., CHEN M.D. A one-step method for fabrication of CdMoO₄-graphene composite photocatalyst and their enhanced photocatalytic properties. *Powder Technology.* **281**, 167, **2015**.
16. WANG S.H., ZHOU S.Q. Photodegradation of methyl orange by photocatalyst of CNTs/P-TiO₂ under UV and visible-light irradiation. *J Hazard Mater* **185** (1), 77, **2011**.
17. ADEL A ISMAIL, Mesoporous PdO-TiO₂ nanocomposites with enhanced photocatalytic activity. *Applied Catalysis B: Environmental*, **117-118**, 67, **2012**.
18. WANG W.W., WANG L., LI W.B. Fabrication of a novel g-C₃N₄/Carbon nanotubes/Ag₃PO₄ Z-scheme photocatalyst with enhanced photocatalytic performance. *Materials Letters.* **234**, 183, **2019**.
19. JIANG D.L., MA W.X., XIAO P. Enhanced photocatalytic activity of graphitic carbon nitride/carbon nanotube/Bi₂WO₆ ternary Z-scheme heterojunction with carbon nanotube as efficient electron mediator. *J Colloid Interface Sci* **512** 693, **2018**.
20. CHEN F. DI, Two-dimensional heterojunction photocatalysts constructed by graphite-like C₃N₄ and Bi₂WO₆ nanosheets: Enhanced photocatalytic activities for water purification. *Journal of Alloys and Compounds*, **694**, 193, **2017**.
21. OU M., ZHONG Q., ZHANG S.L. Synthesis and characterization of g-C₃N₄/BiVO₄ composite photocatalysts with improved visible-light-driven photocatalytic performance. *Journal of Sol-Gel Science and Technology*, **72** (3), 443, **2014**.
22. ADHIKARI RAJESH, MALLA SHOVA, GYAWALI GOBINDA Synthesis, characterization and evaluation of the photocatalytic performance of Ag-CdMoO₄ solar light driven plasmonic photocatalyst. *Materials Research Bulletin* **48** (9), 3367, **2013**.
23. XIU Z.L., BO H., WU Y.Z. Graphite-like C₃N₄ modified Ag₃PO₄ nanoparticles with highly enhanced photocatalytic activities under visible light irradiation. *Applied Surface Science.* **289**, 394, **2014**.
24. EGHBILL-ARANI MOHAMMAD, POURMASOUD SAEID, AHMADI FARHAD Optimization and detailed stability study on coupling of CdMoO₄ into BaWO₄ for enhanced photodegradation and removal of organic contaminant. *Arabian Journal of Chemistry*, **2018**.
25. LIU Y.D., REN L., QI X. One-step hydrothermal fabrication and enhancement of the photocatalytic performance of CdMoO₄/CdS hybrid materials. *RSC Advances* **4** (17), 8772, **2014**.
26. LV J., DAI K., ZHANG J. Facile synthesis of Z-scheme graphitic-C₃N₄/Bi₂MoO₆ nanocomposite for enhanced visible photocatalytic properties. *Applied Surface Science*, **358**, 377, **2015**.
27. MOSTAFA H.M., MADDAHFAR MAHNAZ., SOBHANI-NASAB A. Novel silver-doped CdMoO₄ synthesis, characterization, and its photocatalytic performance for methyl orange degradation through the sonochemical method, *J Mater Sci: Mater Electron.* **27**, 474, **2016**.
28. HAO R., XIAO X., ZUO X.X. Efficient adsorption and visible-light photocatalytic degradation of tetracycline hydrochloride using mesoporous BiOI microspheres. *J Hazard Mater* **209-210**, 137, **2012**.
29. SONG S., HONG F.Y., HE Z.Q. AgIO₃-modified AgI/TiO₂ composites for photocatalytic degradation of p-chlorophenol under visible light irradiation. *J Colloid Interface Sci* **378** (1), 159, **2012**.
30. MOUSAVI MITRA, HABIBI-YANGJEH AZIZ, Novel magnetically separable g-C₃N₄/Fe₃O₄/Ag₃PO₄/Co₃O₄ nanocomposites: Visible-light-driven photocatalysts with highly enhanced activity. *Advanced Powder Technology*, **28** (6), 1540, **2017**.
31. ZHANG H., CHENG G. Enhanced visible light photocatalytic activity of CdMoO₄ microspheres modified with AgI nanoparticles. *Catalysis communication*, **86**, 124, **2016**.
32. XU L., LI H.N., YAN P.C. Graphitic carbon nitride/BiOCl composites for sensitive photoelectrochemical detection of ciprofloxacin. *J Colloid Interface Sci*, **483**, 241, **2016**.
33. WANG R.L., XIE T., SUN Z.Y. Graphene quantum dot modified g-C₃N₄ for enhanced photocatalytic oxidation of ammonia performance. *RSC Advances*, **7** (81), 51687, **2017**.
34. GUO W.Y., WU P., JIANG D.M. Synthesis of AgBr@Bi₂O₃ composite with enhanced photocatalytic performance under visible light. *Journal of Alloys and Compounds*, **646**, 437, **2015**.

