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Photocatalytic Properties of Copper Nitride/Molybdenum Disulfide Composite Films Prepared by Magnetron Sputtering

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Abstract: Cu₃N/MoS₂ composite films were prepared by magnetron sputtering under different preparation parameter, and their photocatalytic properties were investigated. Results showed that the composite films surface was uniform and had no evident cracks. When the sputtering power of MoS₂ increased from 2 W to 8 W, the photocatalytic performance of the composite films showed a trend of increasing first and then decreasing. Among these films, the composite films with MoS₂ sputtering power of 4 W showed the best photocatalytic degradation performance. The photocatalytic degradation rate of methyl orange at 30 min was 98.3%, because the MoS₂ crystal in the films preferentially grew over the Cu₃N crystal, thereby affecting the growth of the Cu₃N crystal. The crystallinity of the copper nitride also increased. During photocatalytic degradation, the proper amount of MoS₂ reduced the band gap of Cu₃N, and the photogenerated electron hole pairs were easily separated. Thus, the films produces additional photogenerated electrons and promotes the degradation reaction of the composite films on methyl orange solution.

Keywords: Cu₃N/MoS₂ composite films; photocatalysis; magnetron sputtering; methyl orange

1. Introduction

With the rapid development of global industry, the environmental pollution problem caused by industrial processing has become a new challenge. Among these problems, the degradation of pollutants of aromatic and azo structures has attracted attention, and the use of photocatalytic technology to degrade dyes has emerged as a promising technology [1–6]. Photocatalysts, on the basis of semiconductor materials, such as TiO₂ [7–9], ZnO [10–14], CdS [15–19], and WO₃ [20–24], have caused a new upsurge in the degradation of methyl orange structure pollution due to their simplicity, high efficiency, low energy consumption, and mild reaction conditions [25]. Although these conventional semiconductor photocatalysts substantially affect the degradation of methyl orange, they also have limitations [17,20,26,27]. TiO₂ and ZnO photocatalysts are direct bandgap wide bandgap semiconductor materials with short response bands to light and have high semiconductor carrier recombination rate and low photon efficiency [2,9,28,29]. Although CdS has a narrow band gap and a suitable band structure, the electron–hole pair recombination rate is fast, the photocatalytic activity is low, and the material is unstable, which causes photocorrosion that is harmful to the environment and human body [15,30–32]. WO₃ has a small band gap and thus has a good response in the visible range, but its photocatalytic activity is low [23,24]. Given that Cu₃N and MoS₂ have an adjustable bandgap structure, the photocatalytic performance can be improved by adjusting the size of the band gap, which is a promising photocatalytic material. Therefore, we conducted research in this area.

Cu₃N has become a research topic for new generation photocatalysts due to its excellent physical and chemical properties, large reserves, and no pollution [33–35]. Although the Cu₃N film alone has better photocatalytic performance, it still has some shortcomings, so researchers often dope or recombine Cu₃N with other materials. Cu₃N has a ReO₃ structure, and the eight corners of the cubic crystal are occupied by N atoms; each side of the unit cell has a Cu atom, and many vacancies are present in the center of the unit cell [36–39]. These vacancies can be filled by other atoms (e.g., Pb [40], Ag [33], and Sc [41]), thereby changing the Cu₃N band gap width and consequently its electrical and optical properties. Among them, there are few reports on Cu₃N and MoS₂ composite films. MoS₂ is a typical layered 2D material, in which Mo and S are covalently bonded, and layers are connected by van der Waals force [42–45]. As the number of layers increases, the band gap also varies, and the band gap width gradually changes from 1.29 eV to 1.80 eV [43,46–49]. The tunable optoelectronic properties of Cu₃N and MoS₂ provide additional options for the study of photocatalysts [50,51].

Most studies on the photocatalytic performance of Cu₃N are focused on doping modification. Composite films need further research. Considering the good band gap controllability of MoS₂, we combined Cu₃N and MoS₂ to study its photocatalytic performance. In addition, compared to some preparation methods that require multiple steps, highly toxic precursors, and pretreated substrates as growth templates, films prepared by magnetron sputtering have high purity, good uniformity and repeatability. Cu₃N/MoS₂ composite films with different sputtering powers were prepared through magnetron sputtering. The effects of power on the crystal structure, chemical composition, surface morphology, and photocatalytic properties of Cu₃N/MoS₂ composite films were investigated. The mechanism of the photocatalytic degradation of methyl orange by composite films was analyzed.

2. Experimental

In this experiment, a Cu₃N/MoS₂ composite films was prepared on a single crystal (100) substrate and a quartz substrate by RF magnetron sputtering (JGP-450a, Chinese Academy of Sciences Shenyang Scientific Instrument Co., Ltd., Shenyang, China). First, the silicon and quartz wafer substrates were separately sonicated in acetone and ethanol solution for 15 min, rinsed with deionized water, dried, and placed in a substrate holder for further use. The sputtering chamber was evacuated to bring the vacuum to 1×10^{-4} Pa. The surface of the target was cleaned by pre-sputtering for 10 min in an Ar atmosphere before the experiment. A Cu₃N/MoS₂ composite films was deposited on the substrate in a gas atmosphere of Ar and N₂ at room temperature using a high degree of MoS₂ target (99.99%) and a Cu target (99.99%). The total gas flow rate was set to 40 Sccm, the N₂ and Ar flow ratio = 4:1, and the vacuum chamber pressure was 1.0 Pa. The sputtering power on the Cu target was fixed at 100 W, and those of the MoS₂ target were 2, 4, 6, and 8 W. Both targets were simultaneously sputtered for 5 min.

Films surface morphology was characterized by a field emission scanning electron microscope (S-4800, Hitachi, Tokyo, Japan). The crystal structure of the films was characterized by an X-ray diffractometer (X'Pert PRO, Panalytical, Almelo, The Netherlands). Its light absorption characteristics were investigated by ultraviolet (UV)–visible (vis) spectrometer (UV-2600/2700, Shimadzu, Tokyo, Japan).

The photocatalytic performance of the composite films was investigated by degrading the methyl orange solution. First, in a dark environment, the sample was immersed in a 10 mg/L methyl orange solution for 1 h to avoid interference of the physical adsorption with the experimental results. With a high-pressure Hg lamp as a light source, the sample was exposed to UV light for 30 min, the power was set to 500 W (voltage of 100 V, current of 5 Å), and the methyl orange solution was collected every 3 min. The absorbance of the solution was measured by an UV-vis spectrophotometer. The absorption spectrum of the methyl orange solution as a function of photocatalytic time was obtained.

3. Results and Discussion

The XRD test pattern of different MoS₂ sputtering power composite Cu₃N films is shown in Figure 1. The films had the crystallization peaks of Cu₃N and MoS₂, of which the 2θ values of 23.3° ,

33.1°, and 47.6° corresponded to Cu₃N (100), (110), and (200) crystal faces, respectively [52,53]. The peak of $2\theta = 62.02^\circ$ corresponded to the MoS₂ (107) crystal plane. Comparison of the diffraction patterns of different composite films showed that when the emission power of MoS₂ was 2 W, the films appeared to be bulging at 23.3°, which was not a sharp peak. No diffraction peak was observed at 47.6°, indicating that sputtering MoS₂ under power affects the crystal growth of Cu₃N [41]. This phenomenon occurred because the entropy of Cu₃N was high, causing it to lag behind the growth of MoS₂ crystals. At low power, the nucleation rate of MoS₂ was low, and the crystallinity was poor, which resulted in Cu₃N to have a small growth probability along the grain boundary of MoS₂. The nucleation process is difficult. Thus, the crystallinity of Cu₃N is also relatively poor. When the sputtering power of MoS₂ increased, the diffraction peak of the MoS₂ (107) crystal plane in the films became increasingly sharp, the corresponding Cu₃N half-width was gradually reduced, and the diffraction peak was enhanced. When the sputtering power of MoS₂ was 8 W, the MoS₂ (107) crystal plane had the strongest diffraction peak, its half width was the smallest, and the crystallization was the best. Owing to the influence of MoS₂, the diffraction peak of Cu₃N crystal was the sharpest, and the crystallinity was also the largest. The crystallization of different phases in the composite membrane had a considerable influence on the photocatalytic degradation effect. The presence of MoS₂ crystals adjusts the band gap of the Cu₃N matrix and finally changes the photocatalytic degradation performance of the films.

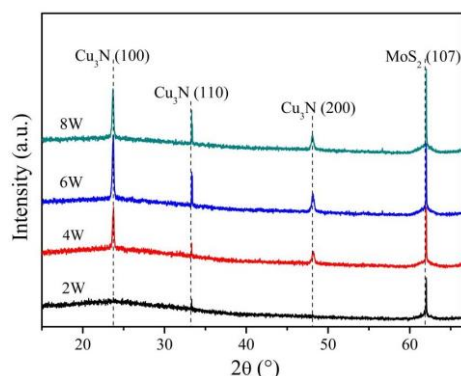


Figure 1. XRD spectra of Cu₃N/MoS₂ composite films with different sputtering powers.

The surface and cross-sectional morphologies of the Cu₃N/MoS₂ composite films are shown in Figure 2. Figure 2a shows that the surface of the films sample was rough overall and consisted of spherical particles of uniform size without evident cracks. The rough surface of the films can provide a large specific surface area, which was favorable for the catalytic degradation reaction. Figure 2b shows that the deposited films has a thickness of approximately 50 nm.

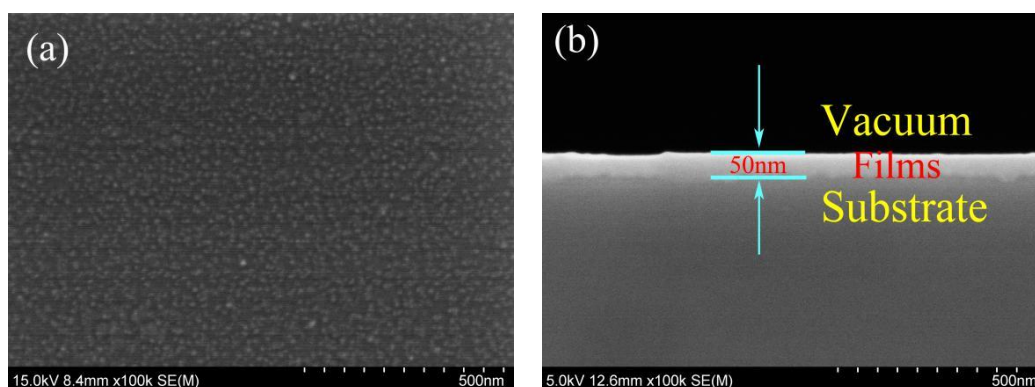


Figure 2. SEM image of the Cu₃N/MoS₂ composite films: (a) surface and (b) cross section.

The chemical composition of the $\text{Cu}_3\text{N}/\text{MoS}_2$ composite films with different sputtering powers was characterized by XPS. The test results are shown in Figure 3. The four samples in the XPS total spectrum (Figure 3a) had the same high intensity peaks corresponding to the S 2p, Cu 2p, N 1s, O 1s, and Mo 3d peaks, respectively. Among these peaks, the O 1s peak appeared at a binding energy of 532.2 eV [54] mainly because of the trace amount of air remaining in the vacuum chamber during the sputtering process, and the oxidation and physical adsorption of the surface of the films exposed to the atmosphere during the test. Figure 3b shows the high-intensity peaks of the Cu 2p spectra at 932.4 and 952.3 eV, which corresponded to the Cu 2p_{3/2} and Cu 2p_{1/2} orbital peaks, respectively [54,55]. Considering the spin-orbit coupling, the splitting energy spacing was approximately 20 eV. The two peaks were attributed to Cu (I), and the figure shows that no peaks were associated with Cu (II) (933.6 and 953.5 eV). The deposited films was a Cu (I) nitride compound having a high purity. The spectrum of N 1s is shown in Figure 3c. The characteristic peak at approximately 397.5 eV can be attributed to be the Cu-N hybrid bond structure in Cu_3N , which was consistent with the analysis results in XRD. The weaker characteristic peak at approximately 398.7 eV is due to the physical adsorption of N atoms between grains during deposition [54,55]. Figure 3d shows the XPS spectrum of S 2p in the composite films with the binding energies of the two main peaks of 162.7 and 163.8 eV, thereby corresponding to the S 2p_{3/2} and S 2p_{1/2} orbital peaks, respectively [56]. The Mo 3d peak appears at a binding energy of approximately 220 eV, but the Mo content in the films was extremely small, and the peak shape trend was not evident. Combining the results of XRD spectrum analysis, we know that MoS_2 has been successfully composited with Cu_3N to form a composite film. Cu_3N as a host in the composite films provided a large number of photoelectrons to participate in the catalytic reaction. The addition of MoS_2 promoted the growth of copper nitride and also changed the photocatalytic effect of the composite films.

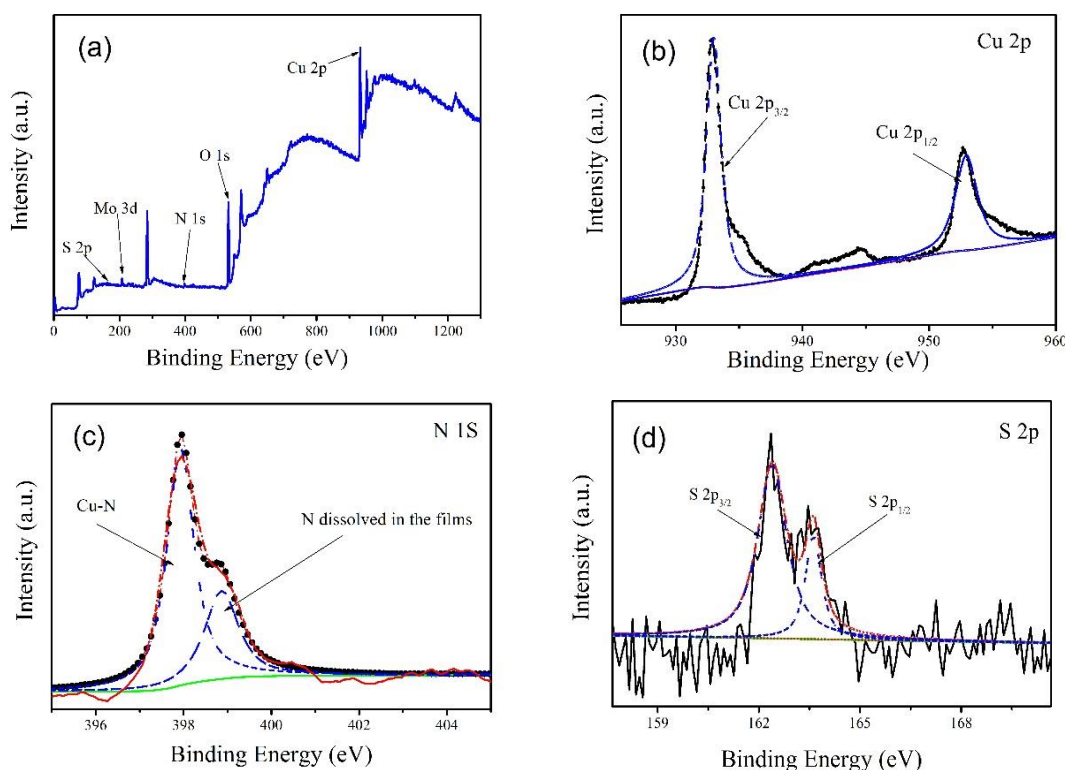


Figure 3. XPS diagram of $\text{Cu}_3\text{N}/\text{MoS}_2$ composite films: (a) total spectrum, (b) Cu 2p peak fitting, (c) N 1s peak fitting, and (d) S 2p peak fitting.

Figure 4 shows the change trend of the absorption spectrum and color of methyl orange dye solution with time. The figure shows that in the first 15 min, the absorbance of methyl orange decreases rapidly because the concentration of highly active electrons generated by UV light irradiation on the films surface was high, and photogenerated electrons had strong redox ability, which can rapidly react with methyl orange and reduce the methyl orange content. As the degradation reaction continued, the content of methyl orange in the solution decreased, and the color of the solution became gradually light. Thus, the rate of the decrease in absorbance also slowed down. When degraded for 30 min, the solution became almost transparent. The illustrations reflected the color change of methyl orange during photocatalytic degradation, and the overall degradation and fading process was consistent with the change in absorbance.

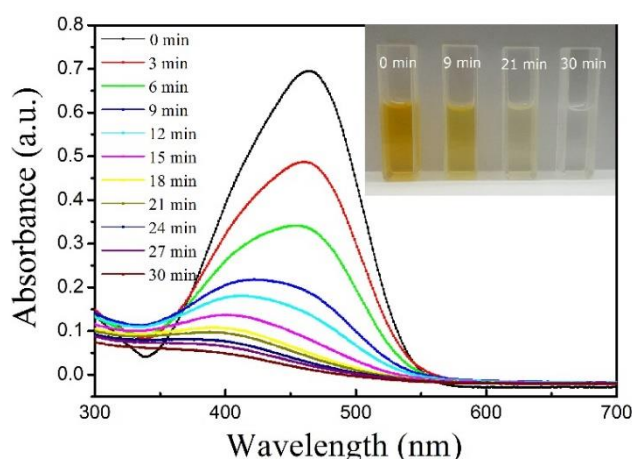


Figure 4. Change in absorbance and color of methyl orange solution with photocatalytic degradation time.

Figure 5a shows the UV–Vis transmission spectra of $\text{Cu}_3\text{N}/\text{MoS}_2$ composite films prepared with different power values. The film showed good transmittance in the infrared region. With the increase of the MoS_2 compounding amount, the transmittance of the film gradually increases. According to the transmission spectrum curve of the film and the law of optical constants (1), the absorption coefficient of the film can be calculated as follows.

$$\alpha = \ln(100/T)/d \quad (1)$$

Among them, T represents transmittance, and d represents film thickness. Using the Tauc Equation (2), the E_g of the film can be calculated:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (2)$$

where α , $h\nu$, and A represent the absorption coefficient, photon energy, and constant, respectively.

From the relationship curve of $(\alpha h\nu)^2$ and $h\nu$, calculate the band gap E_g by extrapolation, as shown in Figure 5b. The E_g range of $\text{Cu}_3\text{N}/\text{MoS}_2$ composite films is between 2.05 and 2.10 eV. As the power increases, the E_g of the composite film decreases first and then increases. When the deposition power is 4 W, the E_g of the film is the smallest, which is 2.05 eV. This may be because after MoS_2 is recombined with Cu_3N , Mo atoms replace Cu vacancies in the Cu_3N lattice to act as donors, thus providing carriers to reduce the optical band gap; It is also possible that the film produced at a lower power has more defects. With the increase of power, the MoS_2 content increases, and the optical band gap increases due to the hole filling effect in the valence band or the free carriers occupying the bottom of the conduction band.

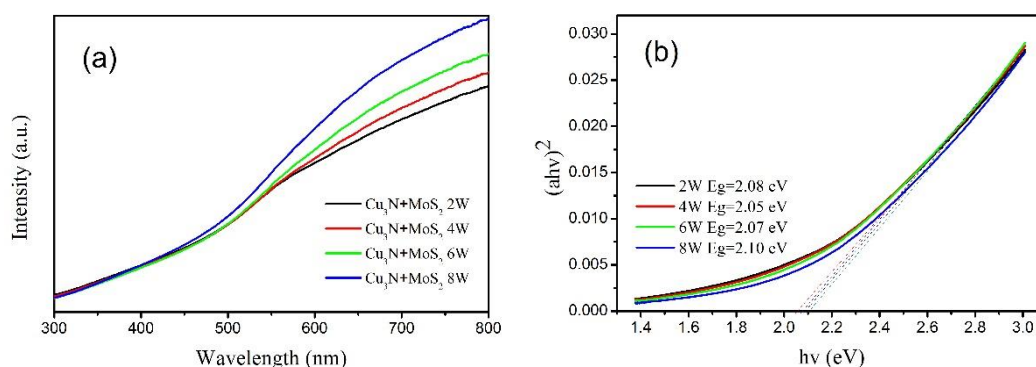


Figure 5. (a) UV-Vis transmission spectrum of the $\text{Cu}_3\text{N}/\text{MoS}_2$ composite films, (b) determination of optical band gap of the $\text{Cu}_3\text{N}/\text{MoS}_2$ composite films.

The change in concentration in the catalytic degradation of methyl orange solution by composite films with different sputtering power is shown in Figure 6. The figure shows that the composite films had a catalytic degradation effect on methyl orange. With the increase of MoS_2 power in the composite films, the concentration of methyl orange first decreased and then increased. When the deposition power was 4 W, the concentration of methyl orange solution was the smallest. At this time, the photodegradation of methyl orange was the most thorough, and then the degradation was weakened with the increase in MoS_2 sputtering power. Within 30 min, the MoS_2 sputtering power of 2, 4, and 6 W on the films' samples had improved degradation effect on methyl orange. Among the films samples, the films sample with the MoS_2 sputtering power of 4 W had a fast degradation rate and a thorough degradation.

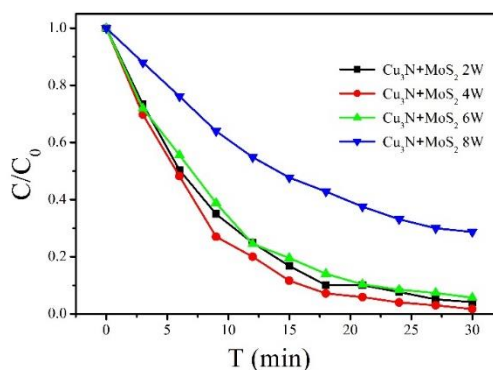


Figure 6. Change in concentration in photocatalytic degradation of methyl orange solution by $\text{Cu}_3\text{N}/\text{MoS}_2$ composite films with different sputtering powers.

A schematic diagram of the experimental process is shown in Figure 7. A $\text{Cu}_3\text{N}/\text{MoS}_2$ composite film was prepared on a silicon wafer by sputtering Cu target and MoS_2 target simultaneously. Then, under the ultraviolet light irradiation, the composite orange film was used for catalytic degradation of the methyl orange solution. The illustration shows the principle of photocatalytic degradation of methyl orange solution by $\text{MoS}_2/\text{Cu}_3\text{N}$ composite film. When irradiated by UV light, the electrons of the low energy valence band of Cu_3N absorbed enough energy to be excited and entered the high energy conduction band beyond the forbidden band. Negatively charged high activity electrons are produced on the conduction band, thereby leaving positively charged holes on the valence band and resulting in highly active photoelectron-hole pairs. After the electrons and holes are separated, they migrated to the Cu_3N surface and combined with O_2 and OH^- in the solution to form $\text{O}_2^{\cdot-}$ ions and $\cdot\text{OH}$ with strong oxidizing properties. These highly reactive particles undergo redox reactions with methyl orange, which in turn degrade methyl orange [3].

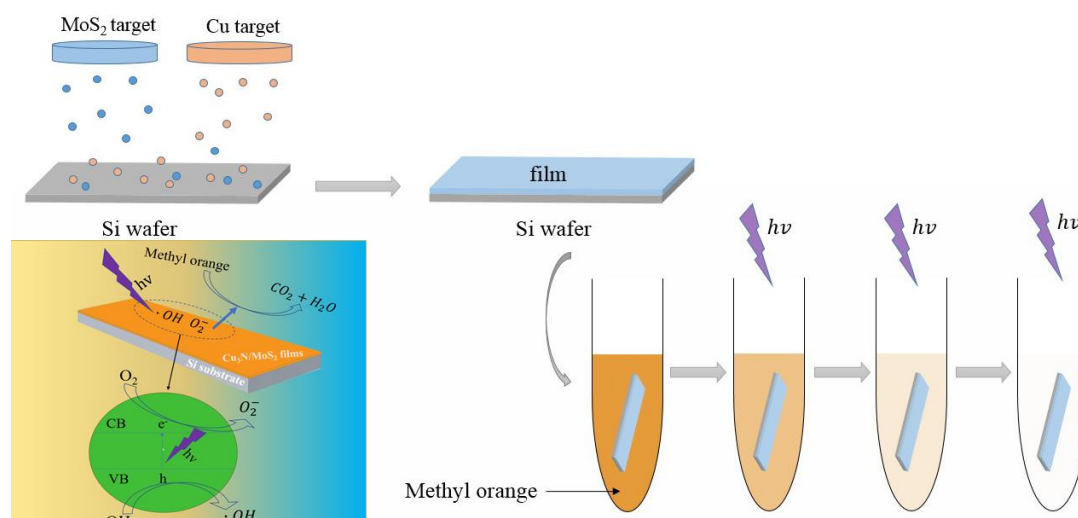


Figure 7. Scheme of photocatalytic degradation of methyl orange solution by $\text{Cu}_3\text{N}/\text{MoS}_2$ composite films.

After MoS_2 was combined with Cu_3N , the band gap of Cu_3N was adjusted to change the rate of producing photoelectron–hole pair, thereby resulting in a change in degradation effect. When the sputtering power of MoS_2 was 2 W, the crystallinity of Cu_3N was relatively poor. Thus, the effect of the thin films catalytic degradation of methyl orange was poor. When the power of MoS_2 increased to 4 W, the crystallinity of Cu_3N was affected by MoS_2 . After Cu_3N was combined with MoS_2 , the band gap of Cu_3N was reduced due to the regulation of a small amount of MoS_2 , which was beneficial to the separation of photogenerated electron–hole pairs and promoted the catalytic degradation of methyl orange. At the same time, MoS_2 can also directly participate in the catalytic degradation reaction. Thus, the sample has a good catalytic degradation effect on methyl orange. With the further increase in MoS_2 power, the MoS_2 content was also increased. The wide band gap of MoS_2 itself caused the band gap of the Cu_3N body to change directly, thereby decreasing the amount of photogenerated electrons produced by the films sample under the same conditions. Thus, the degradation effect is poor. Therefore, the composite films sample with the MoS_2 power of 4 W is likely to produce photoelectron–hole pairs, its photocatalytic degradation rate is fast, and the degree of degradation is good.

4. Conclusions

$\text{Cu}_3\text{N}/\text{MoS}_2$ composite films with different MoS_2 powers were prepared on silicon wafers and quartz wafer substrates by magnetron sputtering. Microstructure studies showed that the crystallinity of Cu_3N increased with the increase in MoS_2 power, mainly because the crystallized MoS_2 affected the crystal growth of Cu_3N . The diffraction peak of Cu_3N was the sharpest, and the crystallization was the best when the sputtering power of MoS_2 was 8 W. The composite films surface was distributed with distinct spherical grains and uniform in size, and the films thickness was approximately 50 nm. The $\text{Cu}_3\text{N}/\text{MoS}_2$ composite films had good photocatalytic activity by the UV degradation of methyl orange solution, and the photodegradation effect varied for different MoS_2 powers of the composite films. When the sputtering power of MoS_2 was 4 W, the catalytic degradation rate of the composite films to methyl orange solution is faster and the degree of degradation was thorough. This phenomenon was due to the effect of MoS_2 on the band gap of Cu_3N in the films, which caused the films to generate additional photogenerated electrons to promote the catalytic degradation of the films sample to methyl orange solution. In general, the $\text{Cu}_3\text{N}/\text{MoS}_2$ composite films with a sputtering power of 4 W have a good photocatalytic degradation effect on methyl orange, and the photocatalyst prepared by magnetron

sputtering has the advantages of nontoxicity, high efficiency, and easy recycling, which provides additional options for the photocatalytic degradation of methyl orange.

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