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# RESEARCH PROCRESS OF P-TYPE CUPROUS OXIDE IN THE FIELD OF LIGHT ENERGY UTILIZATION

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#### ПРОГРЕСС ИССЛЕДОВАНИЙ ЗАКИСИ МЕДИ Р-ТИНА В ИСПОЛЬЗОВАНИИ ЭНЕРГИИ СВЕТА

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Abstract. Cuprous oxide (Cu<sub>2</sub>O), as a representative intrinsic p-type inorganic semiconductor material, has been widely used in the field of optical energy utilization, such as photovoltaic, photocatalysis, photodegradation and other fields, and has an extremely important position. For a long time, the literature on Cu<sub>2</sub>O's application technology in the field of light energy utilization is relatively scattered and independent, resulting in a certain degree of obstacles and difficulties to obtain relevant technical knowledge and have a deep understanding of its internal principles. According to the application of Cu<sub>2</sub>O in the field of light energy utilization in recent years, it is mainly divided into three modules (photovoltaic, photocatalysis, photodegradation), and mainly summarizes the classification, principle and characteristics of Cu<sub>2</sub>O application in the field of light energy and prospects the optimization method and development direction of the application in the field of Cu<sub>2</sub>O light energy. This review aims to provide reference and guidance for the optical energy applications of Cu<sub>2</sub>O and other related inorganic oxide semiconductors.

Аннотация. Закись меди (Cu<sub>2</sub>O), как типичный неорганический полупроводниковый материал р-типа, широко используется в области использования оптической энергии, такой как фотоэлектрика, фотокатализ, фотодеградация и другие области, и занимает чрезвычайно важное положение. Долгое время литература по технологии применения Cu<sub>2</sub>O в области использования световой энергии была относительно разрозненной и независимой, что определенной степени препятствий И трудностей для приводит к получения соответствующих технических знаний и глубокого понимания его внутренних принципов. В соответствии с применением Cu<sub>2</sub>O в области использования световой энергии в последние годы, он в основном разделен на три модуля (фотоэлектрический, фотокатализ, фотодеградация) и в основном обобщает классификацию, принцип и характеристики применения Cu<sub>2</sub>O в области световой энергии, и перспективы метода оптимизации и направления развития применения в области световой энергии Cu<sub>2</sub>O. Цель этого обзора предоставить справочные материалы и рекомендации по применению Cu<sub>2</sub>O и других родственных неорганических оксидных полупроводников в оптической энергии.

Keywords: cuprous oxide, inorganic oxide, light energy utilization, research progress.

Ключевые слова: закись меди, неорганический оксид, использование световой энергии.

 $Cu_2O$  is a promising p-type semiconductor material, with a direct bandgap structure of 2.17eV, high electrical conductivity, high carrier mobility, non-toxic and rich content and other properties that make  $Cu_2O$  is widely used in various industries [1-6].

In the photovoltaic field,  $Cu_2O$  is mainly used as the hole transmission material and light absorption material in solar cells [7-12]. Due to the direct band-gap structure of  $Cu_2O$ ,  $Cu_2O$  can effectively absorb in the visible light range of the solar spectrum. At the same time [13], compared with the side effects of dilution, transfer, transformation, oxidation and ozone treatment measures of traditional pollution treatment measures, nano copper oxide in photocatalysts that degrade organic pollutants has been attracting attention to in the field of photocatalysis industry due to its strong oxidation ability [14-18], high catalytic activity and good stability. Photodegradation refers to the phenomenon of pollutant decomposition caused by the action of light. These include photochemical degradation, polymer photodegradation, photodegradable plastics, and photodegradable photosensitive polymers. However,  $Cu_2O$  is mainly used in [19-23] photochemical degradation and polymer photodegradation.

As a traditional inorganic oxide semiconductor material proposed and applied as early as 1926 [24], although the previous literature has been introduced and summarized to a certain extent, but the content is relatively scattered and independent, and the explanation of the process and mechanism is relatively simple. This paper will systematically classify, summarize and summarize the various kinds of  $Cu_2O$  in the field of light energy utilization, and advance the various technical schemes. Line analysis and summary, aiming to play a enlightening and synergistic role in the application of  $Cu_2O$ .

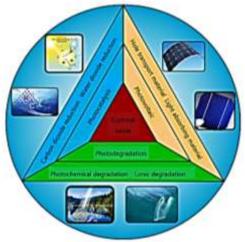


Figure 1. Application neighborhood of cuprous oxide

## Photovoltaic Field

Solar photovoltaic effect, hereinafter referred to as photovoltaic (PV), refers to the phenomenon of potential difference between uneven semiconductor or semiconductor and metal combination during light. Photovoltaic technology has many advantages, such as no mechanical operating parts; except sunlight; working in both direct and oblique sunlight. Among them, nano-copper oxide has the advantages of rich raw materials, high theoretical conversion efficiency and direct energy band structure, which has become a relatively potential solar cell material in recent years [25-27].

## Cave Transmission Material

Cu<sub>2</sub>O, as a hole transmission material, can improve the open circuit voltage, short circuit current and photocurrent of solar cells, thus improving the efficiency and stability of solar cells by [8, 28]. In 2015, Hossain [29] used wxAMPS and SCAPS software to calculate key features of

CH3NH3PbI3-based solar cells. The results showed that solar cells containing  $Cu_2O$  as the HTM outperformed all other organic or inorganic HTM devices tested to date. The obtained power conversion efficiency exceeded 24%. Moreover, the use of  $Cu_2O$  is expected to provide moisture protection for perovskite, thus improving the performance of the device. These results suggest that, by replacing the expensive and water-sensitive spiro-OMETAD with  $Cu_2O$ , it promises to further improve the performance of perovskite cells and reduce their cost. In the same year, Yu [1] prepared perovskite layers with 11.0% PCE under AM1.5G nano-Cu<sub>2</sub>O film (5 nm) HTM illumination.

In addition, the ultra-thin properties of Cu<sub>2</sub>O films help reduce the material consumption and manufacturing costs of large-scale production of perovskite solar cells. The thickness and performance of the Cu<sub>2</sub>O layer must be precisely adjusted to achieve optimal solar cell performance. I n 2016, Nejand [30] introduced inorganic sandwich perovskite solar cells, with a PCE value of 8.93%. The use of Cu<sub>2</sub>O as the HTM on the pinhole and needle-free perovskite layers yields high values of power conversion efficiency, especially when the pinhole-free perovskite layers are used. According to photoluminescence studies, Cu<sub>2</sub>O shows better hole pumping capacity (hole-extraction) com- pared to Spiro-OMeTAD, proving that it is a promising candidate for alternatives to expensive organic HTMs in perovskite solar cells.

Moreover, in 2017, Guo [31] et al. synthesized  $Cu_2O$  films through reactive magnetron sputtering at room temperature (Figure 2a). The maximum power conversion efficiency of the OSCs based on the classic PTB7: PC71BM active layer is 8.61% (Figure 2b), 15% higher than the OSCs (solar cell) in the standard PEDOT: PSSHTM layer. Devices based on Cu oxide HTM exhibit better energy level alignment, reduced series resistance, and therefore improved charge extraction capab- ility. The results show that high mobility, low series resistance and better band energy alignment are related to improving the pumping capacity of the device, improving the performance of the short-circuit current density and filling factor in the Cu oxide solar cells.

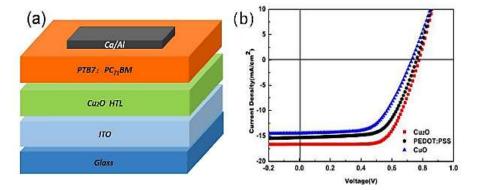


Figure 2. (a) Schematic diagram of planar body heterojunction solar cell, (b) OsCS power conversion efficiency diagram based on PTB7:PC71BM system [31]

Later, in 2019, Elseman [32] provided a p-type hole transport layer (HTL) for a regularly structured nano-Cu<sub>2</sub>O (p-i-p) perovskite solar cell. This work is the first to use this treated Cu<sub>2</sub>O nanocubic solution as a top layer in perovskite solar cells. He prepared (100) crystal surfaces of 60 to 80 n m without surfactant and template and found that Cu<sub>2</sub>O nanocrystalline were not easy to reunite. The synergistic effect of different Cu<sub>2</sub>O nanocubic concentrations on the photovoltaic performance was investigated, and the optimized Cu<sub>2</sub>O-based PSC was 17.23% higher than the device PCE where P3HT is HTL. The Cu<sub>2</sub>O nanocubes showed more stability at room temperature compared to P3HT.The results show that the Cu<sub>2</sub>O nanocubes can be used to prepare highly efficient and stable PSCs, and they are a very promising hole transport layer.

The Absorption Layer

Cu<sub>2</sub>O began to be studied as a photoelectric conversion material in the 1970s. At present, many heterojunction solar cells combined with n-type semiconductors such as ZnO, CdO, and ITO have been reported, among which the theoretical conversion efficiency of Cu<sub>2</sub>O/ZnO solar cells can reach 20% [33]. The conversion efficiency of Cu<sub>2</sub>O/ZnO heterojunction solar cells is significantly improved by doping and interface control, but the current experimental data only show a conversion efficiency of about 2% [34]. Meanwhile, different thicknesses also affect the optical response properties of Cu<sub>2</sub>O films. In 2012, Gershon [35] proposed a new approach to overcome the limitations of low long-wavelength absorption and short charge transport length in electrodeposited bilayer ZnO/Cu<sub>2</sub>O solar cells. Here, the Gershon reduces the thickness of the Cu<sub>2</sub>O to the transport length of about a few charge carriers, and covers a thin film of a semiconductor polymer between the Cu<sub>2</sub>O and the top electrode. Experiments show that the ZnO/Cu<sub>2</sub>O photoabsorption layer of 2.7 m thickness shows the best light absorption to film thickness is a promising way to overcome the charge transport difference and low-wavelength absorption in copper oxide electrodeposited films.

In 2015, Soundaram [34] successfully prepared the ZnO/Cu<sub>2</sub>O/ITO heterostructures deposited by SILAR. The study showed that the SITAR method improved Voc and reached 0.297 and 4.841, respectively. It is also demonstrated that the maximum transmittance of ZnO films is 80% as the Cu<sub>2</sub>O film thickness increases. The solar cell efficiency of the Cu<sub>2</sub>O/ZnO structure was measured and found to increase with the Cu<sub>2</sub>O membrane thickness.

In the same year, Yu [36] used electrochemical deposition method to synthesize Cu<sub>2</sub>O films with high electron and optical properties with different fluorine (F) content on ITO glass (Figure 3A), especially when the molar ratio of F/Cu was 1:2. The sample has a unique mesh microstructure, with the optimal visible light absorption performance (Figure 3C), and its electron concentration (Figure 3B) is more than 10 times that of pure Cu<sub>2</sub>O.Moreover, it has the lowest resistivity (Figure 3D), which favors the light-generation charge transfer and a reduction of the electron-hole pair composite-doped Cu<sub>2</sub>O films were prepared into Cu<sub>2</sub>O homogeneous junction solar cells by continuous electrochemical deposition. The conversion efficiency of F-doped Cu<sub>2</sub>O in homogeneous junction solar cells (Figure 3E) is nearly 8 times that of pure Cu<sub>2</sub>O as the n-type layer. The application of F-doped Cu<sub>2</sub>O to homogenous junction solar cells will provide inspiration for the development of another cheap, environmentally friendly solar cell.

## Photocatalysis

The photocatalytic technology using solar energy is a new technology and has a broad application prospect, which is very suitable for physical adsorption, chemical oxidation and other traditional methods that cannot degrade or degrade inefficient organic matter. Among them, Cu<sub>2</sub>O is favored by [37, 38] in the field of photocatalysis. Usually, Cu<sub>2</sub>O and other inorganic semiconductor electrons are coupled to make the photocatalytic material [39-41].

## The Reduction Reaction of CO2

The release of  $CO_2$  into the environment is one of the worst problems caused by the greenhouse effect. Photocatalytic reduction of  $CO_2$  using solar energy is a promising approach to address the problem of greenhouse gases and to convert  $CO_2$  into a reusable hydrocarbon resource [42, 43].

When two semiconductor electrons are coupled, their photocatalytic properties can greatly improve the [44-47]. In 2020, Ojha [48] used a solvent thermal reactor to form heterostructures between Cu<sub>2</sub>O and SnS<sub>2</sub>/SnO<sub>2</sub> nanocomposites, which generate CO<sub>5</sub> H<sub>2</sub> and CH<sub>4</sub> by H<sub>2</sub>O-reducing CO<sub>2</sub> at room temperature. With the addition of Cu<sub>2</sub>O, the apparent quantum yield for measuring the photoactivity was increased from 7.16% to 8.62%. Meanwhile, the selectivity of CH<sub>4</sub> for CO was about 1.8-fold higher than that for SnS<sub>2</sub>/SnO<sub>2</sub>. The resultant catalyst is capable of fixing N<sub>2</sub> to the

NH3 under light conditions. In the absence of the sacrificial agent, the  $NH_4^+$  generation rate of  $Cu_2O/SnS_2/SnO_2$  of 66.35 molg<sup>-1</sup>h<sup>-1</sup> was 1.9 times that of  $SnS_2/SnO$ . The p-n heterojunction formed between the  $Cu_2O$  and the  $SnS_2/SnO$  nanocomposites has a good photoreduction potential and a high stability.

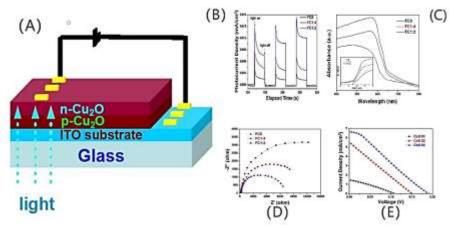


Figure 3. (A) Assembly schematic diagram of P-N Cu<sub>2</sub>O homogeneous junction solar cell (B) Photocurrent density of the sample doped with F Cu<sub>2</sub>O under visible light irradiation and optical switching cycle(C) UV-Vis diffuse reflectance spectra of Fe-doped Cu<sub>2</sub>O samples with different molar ratios of Fe/Cu (D) Electrochemical Impedance Spectrometry of F-doped Cu<sub>2</sub>O electrode measured in Na<sub>2</sub>SO<sub>4</sub> aqueous solution (0.02 M) under dark conditions.(E) I-V curves of three kinds of p-N Cu<sub>2</sub>O homojunction solar cells under AM 1.5 illumination [36]

As early as 2014, Li [49] prepared cuprous oxide/red iron nanotubes (Cu<sub>2</sub>O/ Fe<sub>2</sub>O<sub>3</sub>NTs) by using the constant potential electrodeposition method. Among them, materials with a double-layer copper oxide sphere (Cu<sub>2</sub>O/Fe<sub>2</sub>O<sub>3</sub>NTs-30) show excellent PEC performance, with a suitable band gap (1.96eV) and a minimum superpotential (180mV). In addition, Cu<sub>2</sub>O/Fe<sub>2</sub>O<sub>3</sub>NTs-30 shows two synergies in CO<sub>2</sub> reduction by PEC: (i) between electrocatalysis and photocatalysis, and (ii) between cuproxide and Fe<sub>2</sub>O<sub>3</sub>NTs. After 6 hours, the efficiency and methanol yield of the Faraday method reached 93% and 4.94 mmol L-1cm2, respectively.

In 2018, in order to achieve 24-hour photocatalysis, Lu [50] successfully designed and built a  $Cu_2O$  nanocryststal/TiO<sub>2</sub> microsphere ( $Cu_2O$  NCs/M-TiO<sub>2</sub>) rotating disk reactor assisted by long afterglow phosphobodies, with the mechanism diagram shown in Figure 4. Experiments show that the composite expands the light response region and improves the quantum efficiency.

It improves the light utilization yield of the photocatalytic system by keeping the catalyst hovering and avoiding the solution shading effect. Finally, 24h photocatalysis was achieved with the help of long afterglow phosphoomes.

In addition, in 2018, Li [51] synthesized the  $Cu_2O/TiO_2$  complex by rapid chemical reduction. Use as a thin-film electrode raw material for carbon dioxide photoreduction. The composite was then tested as a thin film electrode in the photoreduction of  $CO_2$  in the cathode chamber in different fresh solutions (250mL) at different pH values of 2.0,7.0, and 12.0.  $CO_2$  photoreduction and visible photoactivation of  $Cu_2O/TiO_2$  composite showed excellent performance at pH of 12. The methanol yield was 1.635 mg/L after 4 h of  $CO_2$  reduction, and  $CO_2$  passed through formaldehyde intermediates. The surface properties of the  $Cu_2O/TiO_2$  composite have good effects on the band coupling to obtain efficient photocatalytic properties.

Also in 2018, Kulandaivalu [52] synthesized blue, fluorescent carbon quantum dots (CQDs) through a simple top-down hydrothermal method, using biochar as the carbon source. The synthetic CQD is combined with the commercial copper (I) oxide (ferrous copper oxide) nanoparticles to form the CQD/Cu<sub>2</sub>O nanocomposites. The CQD, Cu<sub>2</sub>O, and CQD/Cu<sub>2</sub>O nanocomposites were then

applied for gas-phase photocatalytic  $CO_2$  reduction. The experimental results showed that the photocatalytic activity of the CQDs/Cu<sub>2</sub>O nanocomposite photocatalysts was increased by 54% when compared to the original Cu<sub>2</sub>O.

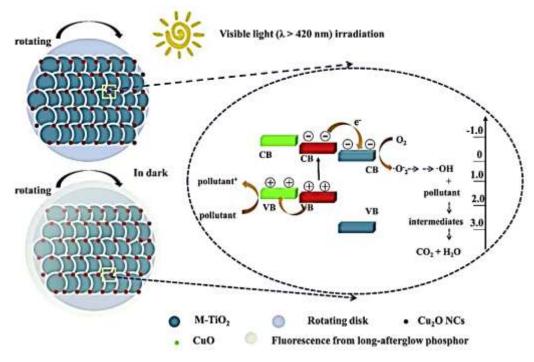


Figure 4. Degradation mechanism of pollutants in  $Cu_2O$  NCS /M-TiO<sub>2</sub> rotating disc reactor assisted by long-afterglow phosphor [50]

### Oxidation Reaction of the $H_2O$

Some advanced oxidation processes (AOP) are characterized by a special chemical feature: the ability to use the high reactivity of the OH free radicals in driving the oxidation processes. These free radicals are suitable for achieving complete emission reduction, including even mineralized [53-55] with less reactive contaminants. In 2005, Carrier [56] used a photocatalytic process to degrade imazapal, a herbicide of the imimazolinone family. It has been shown to rapidly and extensively photodegrade in aqueous solutions. The effect of dissolved metal ions on the photocatalytic degradation rate of titanium dioxide powder is investigated. The results can be summarized as follows: For low concentrations of  $Cu^{2+}$  and  $Ni^{2+}$ , the rate constant decreases. At higher concentrations, the plateau was reached. Phototon reactions at higher concentrations reduced negative effects such as photodeposition of CuO and Cu<sub>2</sub>O and recombination of  $h^+/e^-$ . In 2020, Omrani [3] demonstrated that for individual Cu<sub>2</sub>O or CdS semiconductors, the coupling of Cu<sub>2</sub>O and CdS nanoparticles (NPs) showed enhanced photocatalytic activity in the degradation of sulfamalazine (SSZ) in aqueous solution. Experiments show that the improved photocatalytic activity of the Cu<sub>2</sub>O-CdS composite is associated with a better charge transfer between the charge carriers in the composite.

As early as 2013, Wang [57] deposited  $Cu_2O/TiO_2p$ -n heterojunction photoelectrodes on ntype titanium dioxide nanotubes (Figure 5A.C.D). Loading of copper oxide nanoparticles enhanced the visible light response of titanium dioxide NTAs. The photocatalysts with a small amount of copper oxide nanoparticles loaded on Ti 2 nanotubes showed the maximum photo flow and photoconversion efficiency under both UV and visible light irradiation, as well as the highest visible photocatalytic degradation rate of RhB, and the degradation mechanism diagram is shown in Figure 5B. In particular, when the 0.5V bias potential is applied, the  $Cu_2O/TiO_2NTA$  photoelectrode has a superior photocatalytic efficiency due to the synergistic effect of electrical and visible light irradiation, and thus it is one of the candidates for environmental applications of wastewater treatment and water light-induced splitting into hydrogen.

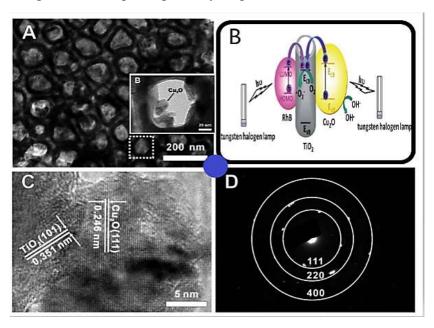


Figure 5. (A) Low magnification TEM image of  $Cu_2O/TiO_2$  NTAS prepared by ultrasound-assisted S-CBD for 4 min (top view). (B) Schematic diagram of photocatalytic degradation of RHB by  $Cu_2O/TiO_2$  NTAS under visible light (C) High-resolution TEM images of  $Cu_2O/TiO_2$  NTAS.(D)  $Cu_2O$  is selected from the Region Electron Diffraction (SAED) mode of (C) nanoparticles [57]

Later, by 2020, Wang [58] prepared the Cu<sub>2</sub>O-Pt/SiC/IrOx composite by controlled photodeposition and used the Nafion membrane as an artificial photosynthetic system to separate reduction and oxidation. To find out the optimal co-catalyst content, they tested the photocatalytic activity of the sample on the reaction of CO<sub>2</sub> with H<sub>2</sub>O under visible light irradiation and found that HCOOH was the main product of all the photocatalysts. When IrOx and Cu<sub>2</sub>O were deposited simultaneously on the optimal Pt/SiC, the HCOOH yield was highest at an IrOx content of  $\sim 2.2$ wt% and a Cu<sub>2</sub>O content of ~ 1.8 wt%, respectively. The deposition of a too-thick Cu<sub>2</sub>O layer rather than that on the surface of the Pt was unfavorable at a Cu<sub>2</sub>O content higher than 1.8 wt%. The HCOOH yield was almost 37 times more abundant than the naked SiC activity under the optimal Cu<sub>2</sub>O-Pt/SiC/IrOx conditions. This artificial system showed excellent photocatalytic performance in CO<sub>2</sub> reduction to HCOOH and the oxidation of H<sub>2</sub>O to O<sub>2</sub> under visible light irradiation. The yields of HCOOH and O<sub>2</sub> essentially coincided with the stoichiometry, being as high as 896.7 and 440.7  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>, respectively. The high efficiency of CO<sub>2</sub> reduction and H<sub>2</sub>O oxidation in the artificial system is attributed to the direct z-format electronic structure of the Cu<sub>2</sub>O-Pt/SiC/IrOx and the spatially separated indirect z-format reduction and oxidation units. This greatly extends the service life of photogenerated electrons and holes and prevents the reverse reaction of the products. This study provides an effective and feasible strategy to improve artificial photosynthetic efficiency.

### Light Degradation

In recent years, metal oxide semiconductors have received increasing attention as a catalyst for photocatalytic degradation of organic pollutants in water, which is conducive to solving environmental problems related to wastewater [59-62].

## Photochemical Degradation

Photochemical degradation refers to the reaction of organic compounds into homologues with less carbon atoms under the action of light. In 2012, An [63] used a combination of catalysts (FeCu

and  $Cu_2O$ ) to degrade five commonly used drugs and personal care products (PPCPs). The current between Cu and Fe increases the dissolution rate of the anode iron as compared to the internal microcircuit of Fe/Moreover, due to the photochemical properties,  $Cu_2O$  can accelerate the degradation process of PPCPs under visible light irradiation.

Also in 2012, Zhu [64] successfully prepared the Cu<sub>2</sub>O/AS composites by using a simple deposition method (Figure 6C). Acid-treated silica (AS) fibers are excellent carriers for Cu<sub>2</sub>O particles (Figure 6A). AS improves the optical properties of Cu<sub>2</sub>O and redshifts the band gap, thus improving the use of visible light, and thus effectively improving the photocatalytic activity of Cu<sub>2</sub>O.The Cu<sub>2</sub>O/AS composites showed excellent photo- catalytic properties in the degradation of red water (Figure 6B).The 87.0% red water can be photocatalyzed degraded by Cu<sub>2</sub>O/AS 5h after irradiation, and most of the organic components of red water were degraded except 1,3,5-trinitrobenzene.

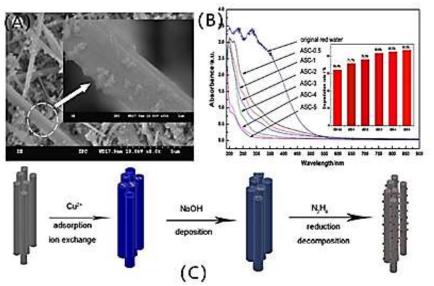
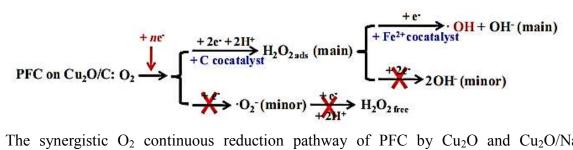


Figure 6. (A) SEM images of different  $Cu_2O/As$  samples. (B) UV-Vis spectra of residual red water treated with different photocatalysts for 5 h.(C)  $Cu_2O/As$  preparation process schematic diagram [64]

Cu<sub>2</sub>O is a low-cost semiconductor with narrow band gap, high absorption coefficient and suitable conduction band, but it has low charge mobility, poor quantum yield and poor catalytic performance. However, in 2017, Zhang [65] greatly improved the catalytic capacity of Cu<sub>2</sub>O for the degradation of fire-resistant pollutants with a simple and effective strategy. Using a synergistic effect of photocatalysis and Fenton, Scheme I propose a novel and highly efficient photocatalytic-driven Fenton system for the PFC. The Cu<sub>2</sub>O/nano C mix was used and experimentally verified. The synergistic PFC is highly dependent on nanoscale C and facilitates the wastewater removal of rhodamine B and p-nitrophenol, two typical fire-resistant contaminants.



The synergistic O<sub>2</sub> continuous reduction pathway of PFC by Cu<sub>2</sub>O and Cu<sub>2</sub>O/Nano-C complexes under visible light irradiation ( $\lambda > 420$  nm) [65].

Antibiotics and heavy metals often coexist in the polluted environment, and the harm of compound pollution is greater than that of a single pollution. In 2019, Huang [66] synthesized a series of graphene-loaded p-n heterojunction rGO@Cu<sub>2</sub>O/BiVO<sub>4</sub> composi- tes, doped with different Cu<sub>2</sub>O, for the simultaneous detoxification of Cr (VI) and antibiotics. In this study, a series of p-n heterojunction composite materials, rGO@Cu<sub>2</sub>O/BiVO<sub>4</sub>, was applied to the efficient reduction and SMZ oxidation of Cr (VI) under LED light. With the increase of the Cu<sub>2</sub>O load, the photoabsorption performance of LED improves, and the appropriate band gap of the p-n heterojunction enables its effective electron/hole separation, ensuring the photocatalytic activity of LED. This work provides a new method for the coexistence of Cr (VI) and antibiotic pollutants in wastewater treated by rGO@Cu<sub>2</sub>O/BiVO<sub>4</sub> p-n heterojunction compound synthesis.

### Polymer Photodegradation

Polymer photodegradation is one of the research advances in the field of light energy. With the deepening of the research in the field of light energy, polymer photodegradation has increasingly attracted the attention of researchers. In the process of applying this method, many problems have become highlighted, and the discussion on polymer photodegradation is becoming increasingly fierce.

Back in 2015, Falah [67] introduced the synthesis of spherical Cu<sub>2</sub>O nanoparticles and a composite of P25 TiO<sub>2</sub> with aluminsilicate inorganic polymer (ground polymer), and XRD and FTIR confirmed that the addition of Cu<sub>2</sub>O/TiO<sub>2</sub> nanoparticles had no effect on the formation of the polymer matrix. But experiments under dark conditions and under UV irradiation show that the composite removes the MB dye through a combination of adsorption and photodegradation without disrupting the structure of the polymer. The combination of nanometer Cu<sub>2</sub>O particles and photoreactive P25 titanium in an aluminosilicate inorganic polymer substrate under UV irradiation is a more effective photocatalyst than a single oxide under UV irradiation. It can effectively remove the model organic contaminant methylene blue dye in solution.

Later, in 2016, Zhang [68] synthesized a new copy oxide nanocomposite ( $Cu_2O@3D$ -rGO@NCS) by one-step in situ reduction (Figure 7a). The  $Cu_2O@3D$ -rGO@NCS has an excellent photocatalytic capability, thanks to the high porosity of the 3D-rGO, the efficient charge transfer from the Cu<sub>2</sub>O to the rGO, and the high adsorption capacity of the NCS (Figure 7d). XPS, SEM, and TEM show that Cu<sub>2</sub>O nanospheres and NCS particles are evenly distributed on 3D-rGO sheets. The porous and mesh structure of 3D-rGO not only improves the high load of Cu<sub>2</sub>O and improves the adsorption capacity of dye molecules, but also promotes the rapid transfer of optoelectronics (Figure 7b). The Cu<sub>2</sub>O@3D rGO was @ N C S improved RhB PGs efficiency compared to the Cu<sub>2</sub>O nanosphere and Cu<sub>2</sub>O@3D-rGO nanocomposites and the nanocomposites, respectively (Figure 7c.e.f). Interestingly, the simple method proposed in this study may be extended to the synthesis of other nanocomposites with various functions grown on 3D-rGO sheets.

In addition, in 2018, Anku [69] proposed the biolorization of acrylic acid (Gg) grafted acrylic acid (AA) and acrylamide (AAm) (Cu<sub>2</sub>O/Gg AAm AA) as nano Cu<sub>2</sub>O particles. The results show that Cu<sub>2</sub>O/Gg AAm AA is a good photocatalyst to effectively remove naphthol blue-black dye from water. The procedure has an optimal pH value of 6. The photodecolorization process enhanced with increasing catalyst concentration but showed a decreasing trend above 0.3 g L-1. The excellent photodegradation efficiency of the nanocomposite is attributed to the excellent dye molecule adsorption capacity of the Gg AAm AA polymer matrix, as well as the high visible photoactivity and photocatalytic properties of the Cu<sub>2</sub>O nanoparticles. The recyclability studies show that Cu<sub>2</sub>O/Gg AAm AA nanocomposites can be efficiently recycled and reused.

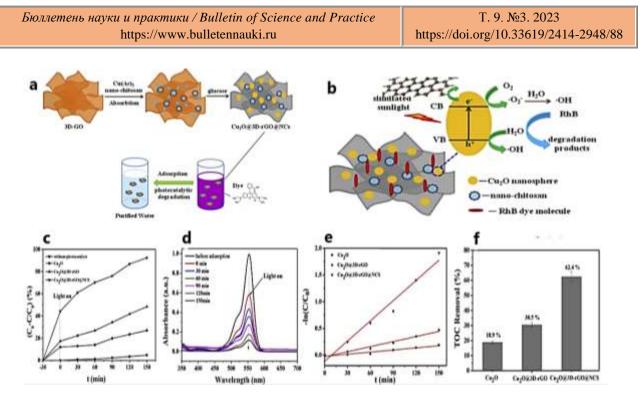


Figure 7. (a) A schematic diagram of photocatalytic degradation of RhB using the developed  $Cu_2O@3D$ -rGO@NCS nanocomposite as a photocatalyst.(b) Using  $Cu_2O@3D$ -rGO@NCS nanocomposite as photocatalyst, the schematic diagram of charge separation and photodegradation mechanism of RhB dye of @NCS nanocomposite under solar irradiation was simulated.(c) The presence of  $Cu_2O$  nanospheres,  $Cu_2O$  @3D-rGO, and Acr@NCs in simulated sunlight, and the elimination of RhB in the absence of photocatalyst.(d) UV-Vis absorption spectra of RhB in the presence of  $Cu_2O$  @3D-rGO@NCS nanocomposites.(E) The change curve of  $eln(C/C_0)$  in photodegradation of RhB aqueous solution with simulated illumination time in the presence of  $Cu_2O$  @3D-rGO and FeN@NCS.(f) The percentage of TOC in RhB aqueous solution was removed by  $Cu_2O$ ,  $Cu_2O$  @3D-rGO and NaNi@NCS [68]

In 2019, Razmara [70] synthesized the  $[Cu_2(\mu \Box ox)2(pyz)3]n$  (Pyz = pyrazine + ox = oxalate) supramolecular coordination complex under ultrasound irradiation. Studies of the complex show that the complex has good thermal stability and is a weak ferromagnet. After characterization with various techniques, octahedral Cu<sub>2</sub>O nanoparticles with edge lengths of 5-80 nm were produced by calcination at 600°C. The adsorption capacity and photocatalytic activity of octahedral Cu<sub>2</sub>O nanoparticles at room temperature were investigated. The final results indicate that octahedral Cu<sub>2</sub>O nanoparticles play an important role in the degradation and adsorption of RB, with a maximum degradation efficiency of 91.7% and a maximum adsorption capacity of 83.3mg/g at 40min.

Also in 2019, Xu [71] prepared Cu<sub>2</sub>O/ PLA composite nanofibers through surface modification induced by electron beam irradiation by using PLA fibers as a carrier for Cu<sub>2</sub>O nanoparticles. Based on the FTIR spectroscopy, the binding of the Cu<sub>2</sub>O nanoparticles and the PLA particles can be attributed to the strong hydrogen bonds between them, so that the Cu<sub>2</sub>O nanoparticles can be uniformly dispersed on the PLA fragments to form a composite membrane. The obtained Cu<sub>2</sub>O/PLA nanofibers showed excellent photocatalytic properties in the organic pollutants of soil and water systems (e. g., MO and bran ether). Antimicrobial tests show that the prepared composites can enhance the antimicrobial properties. This provides an idea to constructing bifunctional composites for effective degradation of organic pollutants in soil and water systems.

#### Conclusions and Outlook

It has abundant raw materials, high theoretical conversion efficiency, high efficiency photoelectric catalytic performance, proper band gap of p-n heterojunction, strong oxidation capacity and good stability; both as nanomaterials to improve the performance of solar cells, and as composite materials to help decompose environmental pollutants. With the deepening of relevant

research, more and more excellent properties of nano copper oxide will be explored and developed. It is believed that in the near future, these products will be widely used in real life, and they will play a decisive role in solving the problem of human living resources and living environment.

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