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Bleaching of Dyes by Using Metal Copper Oxide as Semiconductor by Spectrophotometric Methods

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ABSTRACT: The photocatalytic degradation or bleaching of different dyes on copper oxide semiconductor suspended in aqueous solution has been carried out. The progress of reaction has been studied spectrophotometrically by observing absorbance of reaction mixture at different time intervals. The effects of various parameters such as concentration of dyes, pH of reaction mixture amount of semiconductor and intensity of light on the rate of reaction have also been observed. The photocatalytic degradation or bleaching of different dyes follows pseudo first order kinetics and the rate constant has been determined. A tentative mechanism for the reaction has also been proposed. Spectrophotometric methods were utilized.

KEYWORDS: bleaching, photocatalytic degradation, spectrophotometer, absorbance, copper oxide, semiconductor, rate constant

I. INTRODUCTION

The photodegradation of dyes is regarded as a promising technology for industrial wastewater treatment. This technology demonstrates the light-enhanced generation of charge carriers and reactive radicals that non-selectively degrade various dyes into water, CO₂, and other compounds via direct photodegradation or a sensitization-mediated degradation process¹. The overall efficiency of the photocatalysis system is closely dependent upon operational parameters that govern the adsorption and photodegradation of dye molecules, including the initial dye concentration, pH of the solution, temperature of the reaction medium, and light intensity. Additionally, the charge-carrier properties of the photocatalyst strongly affect the generation of reactive species in the heterogeneous photodegradation and thereby dictate the photodegradation efficiency. The pseudo kinetics and mechanisms of the photodegradation reactions were analysed. The operational factors affecting the photodegradation of either cationic or anionic dye molecules, as well as the charge-carrier properties of the photocatalyst², are also fully explored. By further analyzing past works to clarify key active species for photodegradation reactions and optimal conditions, this review provides helpful guidelines that can be applied to foster the development of efficient photodegradation systems. Utilization of different dyes were carried out and spectrophotometric methods.

The widespread presence of dyes in industrial wastewaters from the textile, apparel, and paper industries results in significant environmental contamination. These dye-polluted effluents contain highly hazardous, carcinogenic, non-biodegradable, and colored pigments that can cause damage to humans [1,2]. Even at very low concentrations (below 1 ppm), dyes are clearly visible in water and seriously deteriorate aqueous environments [3,4,5]. Therefore, the removal of colored dyes from wastes is imperative and important. For conventional treatment on industrial wastewater, adsorption [6] and coagulation [7] are common methods used to remove the dyes. However, these processes cause secondary hazardous pollution because dyes³ are only changed from a liquid phase into a solid phase. Thus, further treatments are necessary to resolve the problem of secondary pollution [8,9]. Over the past few years, photocatalysis was regarded as a promising alternative treatment in the aspect of water purification [10]. Essentially, the photocatalytic reaction involves heterogeneous catalysis, where a light-absorbing catalyst is put in contact with the target reactants, in either a solution or gas phase. This heterogeneous approach was successfully employed as an effective tool for the degradation of various hazardous materials, including atmospheric and aquatic pollutants, and shows many advantages over traditional wastewater treatment techniques. For instance, the complete degradation of pollutants using active photocatalysts can occur within a few hours at room temperature. In addition, pollutants can be entirely mineralized to relatively non-toxic products (CO₂ and water) without the formation of secondary hazardous products [11,12].

The typical mechanism for the photodegradation of dyes is shown. Upon irradiation with incident photons, electrons are excited to the conduction band (CB) of the photocatalyst, while holes are formed in the valence band

(VB). ⁴The photoexcited electrons and holes can either recombine to generate thermal energy or diffuse to the photocatalyst surface reacting with the adsorbed molecules. The reactive radical species, such as superoxide radicals ($\cdot\text{O}_2^-$) and hydroxyl radicals ($\cdot\text{OH}$), are further derived from the photoexcited electrons and holes, respectively. Moreover, the photosensitization of dye molecules can provide photocatalysts with additional electrons, which are also capable of generating radicals like $\cdot\text{O}_2^-$. These reactive species can quickly²⁶ and non-selectively decompose pollutants. The whole photodegradation process, from the adsorption of dye molecules⁵ on the surface of the photocatalyst to the decomposition of dye molecules by reactive radicals, is affected by operational parameters such as the pH of solution, initial dye concentration, reaction temperature, and irradiation intensity. For example, that the degradation of reactive yellow 17, reactive red 2, and reactive blue 4 over Degussa P-25 followed pseudo first-order kinetics in which increasing initial dye concentration depressed the photodegradation efficiency. Also we performed photodegradation of methyl blue and methyl orange and found that the pH of solution and steric structure were highly related to photocatalytic efficiency. In addition to these operational parameters, the band position and charge-carrier utilization of the photocatalysts also have an impact on the generation of reactive radicals and the subsequent photodegradation performance. To improve the carrier utilization and thereby achieve efficient reactive radical generation, heterostructure photocatalysts with enhanced photocatalytic activity are proposed and employed using metal copper oxide as semiconductor by spectrophotometric methods.⁶

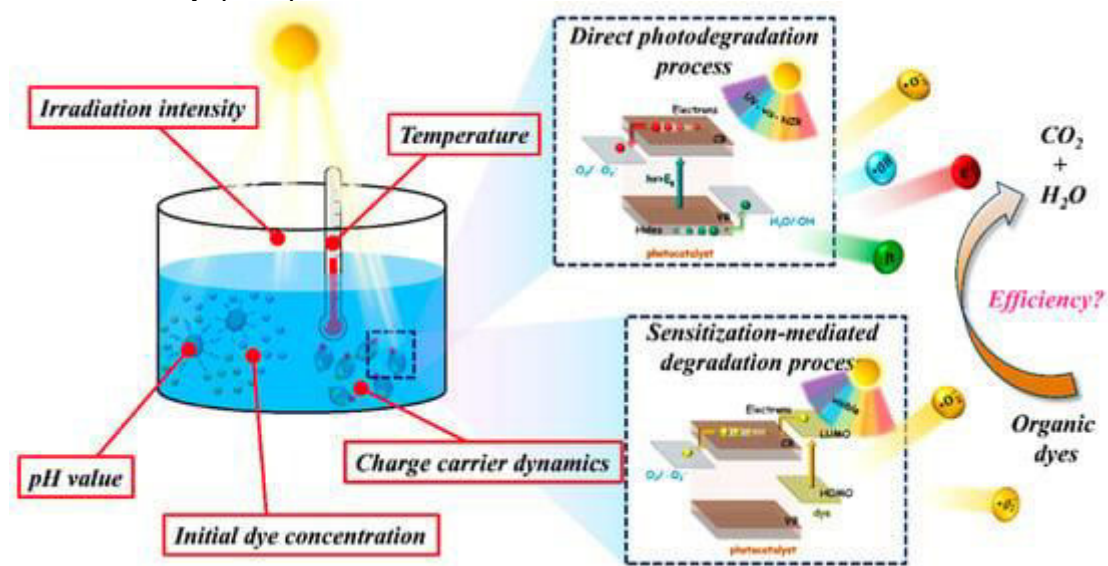


Fig. 1. Schematic illustration of operational factors affecting the photodegradation of different dyes over semiconductor photocatalysts.

$$\text{Degradation efficiency} = \frac{C_0 - C}{C_0} \times 100\%$$

II. DISCUSSION

In the textile industry, commonly used dyes include acid, basic, direct, azo, naphtha, reactive, mordant, vat, disperse, and sulfur dyes, with azo dyes being the most used at present. To study their properties with regard to photodegradation reactions, dyes are usually classified using their molecular charge upon dissociation in aqueous-based applications²⁵. According to the chemical structure, they are divided into cationic and anionic dyes. The cationic dyes, including methylene blue (MB), rhodamine B (RhB), malachite green (MG), rhodamine 6G (Rh6G), crystal violet (CV), and safranin O (SO), contain cationic functional groups that can dissociate into positively charged ions in an aqueous solution. The most common cationic functional group is the onium group and, thus, most of the cations are N^+ ions. On the other hand, the anionic dyes cover direct, acid, and reactive dyes, such as acid orange 7 (AO7), eosin Y (EY), methyl orange (MO), acid red 14 (AR14), alizarin red S (ARS), rose bengal (RB), and phenol red (PR). All anionic dyes contain anionic functional groups,⁷ e.g., sulfonic or carboxylic acid groups. These functional groups are

water-soluble and can effectively interact with photocatalysts with hydrophilic surfaces. Hence, cationic and anionic dyes are also known as basic and acidic dyes, respectively.⁸

During the photodegradation reaction, a redshift or blueshift can be sometimes seen in the characteristic absorption of dye molecules, possibly caused by the aggregation of dyes. Furthermore, the decomposition process of dye molecules could also cause an absorption peak shift. These spectral shifts bring difficulty in determining the concentration of the remaining dyes from the absorbance of the characteristic peak²⁴. Special care is, therefore, necessary in order to represent accurate photodegradation efficiency. The blueshift of the absorption band from 554 to 530 nm was caused by the de-ethylation of RhB molecules. The generation of intermediates can be further observed by steady-state photoluminescence (PL) spectroscopy⁹. The emission at 575 nm decreased, while a new emission appeared after 7 min of light illumination, confirming the formation of the de-ethylated intermediate. The de-ethylation process of RhB molecules. Upon light illumination, the four ethyl groups of RhB can be sequentially removed until it is totally converted into rhodamine without any ethyl groups. This process causes a large blueshift in absorption from 553 nm to 498 nm. The further decomposition of rhodamine with its conjugated ring structure causes a further decrease of the absorption peak without a corresponding peak shift²³. In the presence of benzoquinone (BQ) as an $\cdot\text{O}_2^-$ scavenger, the peak intensity decreases without shifting, while the peak shows a blueshift in the presence of 2-propanol (IPA) as an $\cdot\text{OH}$ scavenger, further confirming that the blueshift is caused by the attack of active oxygen species on the N-ethyl groups.¹⁰ Moreover, it was found that the formation of N-de-methylated MG products through the attack of active oxygen species accounts for the observed absorption blueshift of the MG absorption during the MG photodegradation over TiO_2 using metal copper oxide as semiconductor by spectrophotometric methods¹¹.

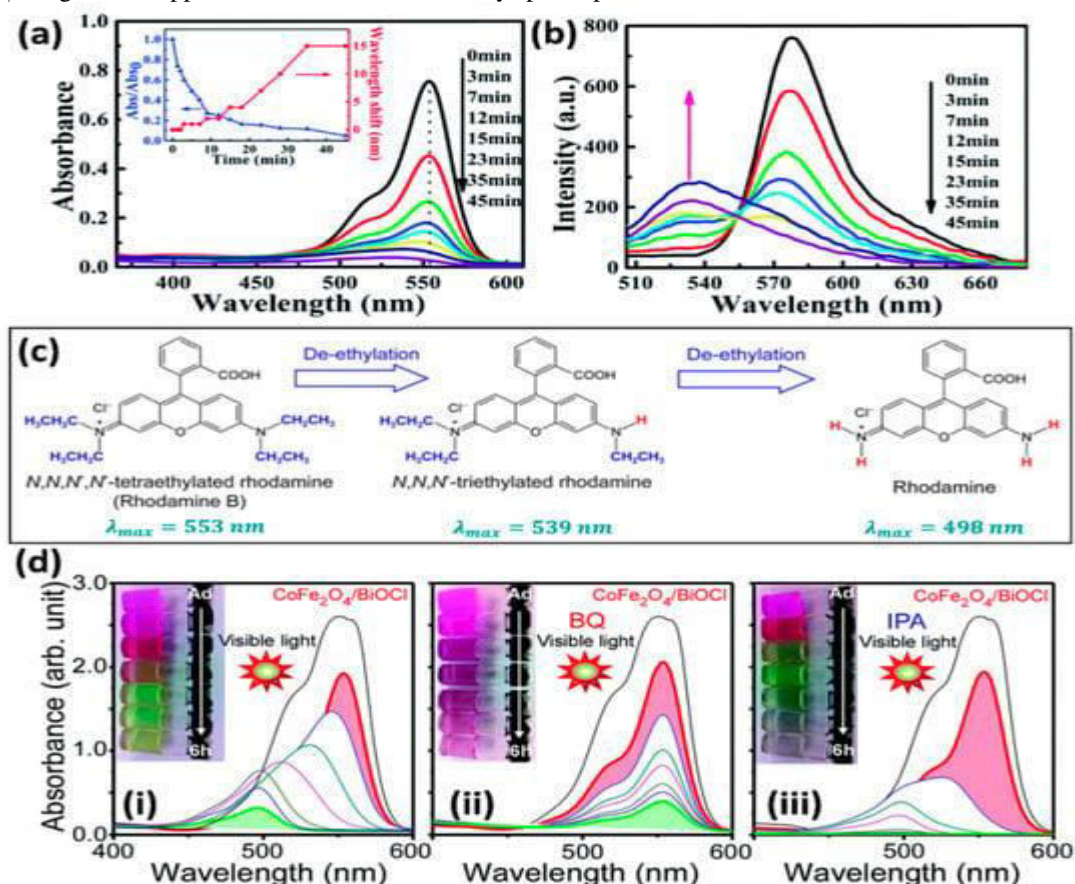


Fig.2. Photodegradation of RhB over Ag_3PO_4 nanoparticles under visible illumination recorded as (a) ultraviolet-visible light (UV-Vis) absorption spectra (inset shows the correlation between absorbance changes of maxima absorption peak (blue line) and the corresponding wavelength shifts (red curve)), and (b) steady-state PL spectra. (c) Scheme of the de-ethylation process of RhB molecules. (d) Photodegradation of RhB over $\text{CoFe}_2\text{O}_4/\text{BiOCl}$ microflowers under visible irradiation (i) without and with scavengers of (ii) BQ and (iii) IPA.

III. RESULTS

Au–CdS metal–semiconductor nanocrystals were demonstrated to photodegrade RhB molecules. Using TRPL to study the photoexcited charge transfer kinetics, the display the TRPL spectra for two Au–CdS nanocrystals with different shell thicknesses (14.0 nm and 18.6 nm). Compared with their CdS counterpart, obtained by etching Au cores, a fast decay was found in Au–CdS samples, indicating electron transfer from CdS to Au.²² This difference became more noticeable for Au–CdS with shell thickness increasing to 18.6 nm, suggesting much more pronounced electronic interaction between CdS and Au. By further analysis with biexponential kinetics, the interfacial charge transfer rate constant (k_{et}) was estimated. In addition, the photodegradation rate constant (k_{RhB}) changed with CdS thickness in the core–shell nanocrystals.¹² It was enhanced with increasing shell thickness due to the raised ratio of CdS to Au, which led to greater light absorption and, thus, generation of more charge carriers. The correlation among k_{RhB} , k_{et} , and CdS shell thickness²¹. The change in k_{et} with CdS shell thickness was consistent with the trend of k_{RhB} , revealing that efficient charge separation can provide a hole-enriched CdS shell for the photodegradation reaction and further enhance the photodegradation efficiency using metal copper oxide as semiconductor by spectrophotometric methods¹³.

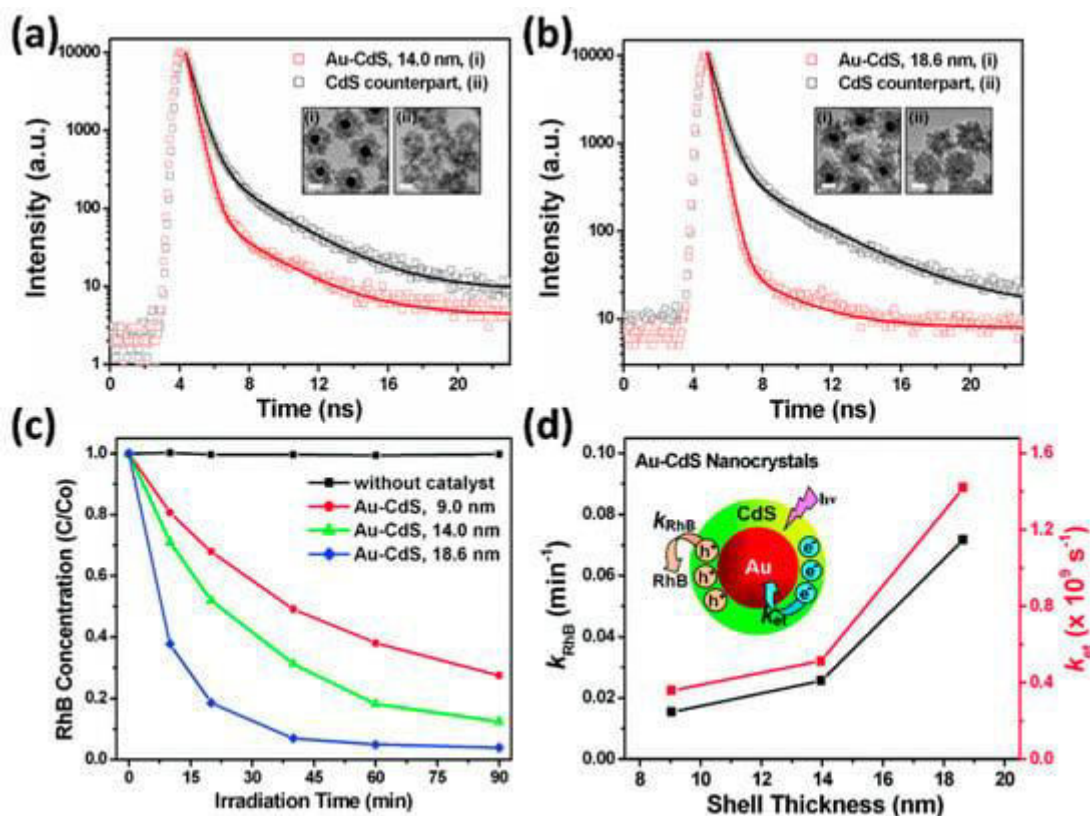


Figure 3. TRPL spectra (dots) and fitting results (solid curves) of Au–CdS and pure CdS nanocrystals with shell thicknesses of (a) 14.0 nm and (b) 18.6 nm (inset shows the corresponding TEM images, with scale bar of 20 nm). (c) RhB photodegradation under visible irradiation and (d) correlations of k_{et} and k_{RhB} for Au–CdS nanocrystals with different shell thicknesses.

IV. CONCLUSIONS

Most dyes have either a positive or a negative charge upon dissociation in aqueous solutions, characteristic of cationic and anionic dyes, respectively. The pH of the solution modifies the electrical double layer of the photocatalyst, affecting the interaction between dye molecules and photocatalysts, the charge transfer for the self-photosensitization of dyes, and the subsequent decoloration efficiency, as highlighted in this review.²⁰ The optimization of other operational factors (i.e., initial dye concentration, light intensity, reaction temperature) and charge-carrier properties of heterostructure photocatalysts can establish the most efficient photodegradation system. In addition, research on the

reactive species, as well as the photosensitization pathway of dye molecules for photodegradation, is helpful to clarify the overall decoloration mechanism,¹⁴ which is beneficial for further application to the degradation of multicomponent industrial wastewaters. With strong progress in photocatalytic techniques, more in-depth characterization and modeling of the photodegradation, and even mineralization processes for multicomponent dyes in practical applications will be possible in the near future. Unlike other heterogeneous photocatalysis, such as photoelectrochemical water splitting and CO₂ reduction in which the solar-to-hydrogen (STH) and AQY are introduced to determine the photocatalytic efficiency for comparison, a quantitative comparison with AQY is relatively unexplored for photodegradation reactions. The introduction of AQY into the photodegradation reaction provides helpful information to understand the efficiency of semiconductor photocatalysts.¹⁹ However, for visible-light-responsive photocatalysts, the feasible determination of photodegradation efficiency is especially challenging due to the relatively high photoabsorption coefficient of dye molecules, as well as the complicated mechanism of dye degradation using metal copper oxide as semiconductor by spectrophotometric methods¹⁵.

Another major concern in reactions involving self-photosensitization of dye molecules is the interactions between photocatalysts and multiple types of dye molecules, which are not always clear. Limited studies described the underlying interactions and mechanisms. By using self-photosensitization of dye molecules, both cationic and anionic dyes can be simultaneously decomposed, which has the potential to degrade multicomponent dyes¹⁸ in real wastewater systems. However, for multicomponent dye systems,¹⁶ the quantification of efficiency for each individual dye molecule is difficult to determine with simple spectrophotometric methods especially when their absorption spectra overlap. The development of a new method to easily and reliably obtain quantitative detection of dye molecules is necessary for accurate estimation using metal copper oxide as semiconductor by spectrophotometric methods¹⁷.

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