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Photodegradation of tartrazine under UV light irradiation Using Cu-modified SiNWs treated with H_2O_2 solution as photocatalyst

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Abstract**—** The application of semiconductors in heterogeneous photocatalysis to eliminate various pollutants in aqueous systems as well as in the air has gained significant attention in the last decade. In the present work, we report on the high efficiency of silicon nanowires coated with copper nanoparticles and treated with H_2O_2 for the degradation of Tartrazine under UV light irradiation. Also, the effect of catalyst reusability was study. Elaboration of silicon nanowires and their modifications were performed by Ag-metal assisted chemical etching and electroless chemical deposition, respectively. Tartrazine is used a lot of in the textile industry. Dyes are an important factor in environmental pollution and its degradation mechanism has been studied quite well.
The wavelength range was 200–600 nm. The results show that the % of degradation of azo dye (tatrazine) treated with H_2O_2 decrease slightly with the number of reusability and can be used several times for the degradation of tartrazine with good photocatalytic activity.

Keywords**—** silicon nanowires, copper, catalyst, degradation, tartrazine, H_2O_2

I. Introduction

Until 1850, color was only obtained from natural origin, vegetal or animal such as extract of plants, of trees, of lichens, or of insect. In 1856, Perkin synthesized the first dye. At the end of XIX century, more than 90 dyes were used in in textile, pharmaceutical, cosmetic and food industries [1]. Most of synthetic dyes are azo dyes and are suspected to be carcinogenic [2]. The removal of toxic pollutants from industrial wastewater would reduce their environmental impact and health effect. To this end, a variety of biological and physico-chemical methods for waste water treatment have been developed (e.g., activated carbon, reverse osmosis, and advanced oxidation) [3–6]. According to the limitations imposed by present legislation, wastewater produced by the textile industry is usually treated by physico-chemical methods [7] or, most commonly, by active sludge biochemical plants [8] before its release into the environment. Photocatalysis has been successfully used to oxidize many organic pollutants and particularly to decolorize dyes. Among the new oxidation methods or “advanced oxidation processes” (AOPs), heterogeneous photocatalysis appears as an emerging destructive technology leading to the total mineralization of many organic pollutants. Photocatalytic oxidation, in the presence of semiconducting materials such as Silicon nanowires as photocatalyst is one of the various advanced oxidation processes used nowadays, of organic compounds with environmental concern was studied extensively recently and it was demonstrated that heterogeneous photocatalysis can be an alternative to conventional methods for the removal of organic pollutants from water and wastewater [9].

The dye under consideration is Tartrazine is an acidic azo dye with a sulfonic group as an auxochrome that is highly water soluble and polar. It is widely used in cosmetics, drugs, electroplating, pharmaceuticals and textile industry and also as food colorant [10-11]. Tartrazine seems to cause the most allergic and intolerance reactions, particularly among asthmatic patients, migraines, eczema, thyroid cancer, and lupus [10].

In the present work, we use silicon nanowirs coated with copper nanoparticles and treated with H_2O_2 as phototcatalyst for the degradation of Tartrazine under UV light irradiation. Effect of catalyst reusability is also study.

II. EXPRIMRNTAL

A. *Copper nanoparticles modified silicon nanowires*

Silicon nanowire was formed by electroless etching of p-type Si (100) with resistivity 7.7-8.66 Ohm.cm. The silicon wafers were cut up in samples of 10x10 mm2 size. The cleaning of the samples, elaboration of silicon nanowires and modified with copper nanopartcles were made according the processes reported in our previous report [12]. Also, the oxidation of copper with H_2O_2 and the catalyst reusability was studied.

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B. *Morphological study*

The modification of silicon nanowires with Cu nanoparticles was performed by an electroless deposition (EMD) process in aqueous HF solutions containing the copper sulfate. The electroless deposition of Cu occurs according to the following cathodic reactions [13]:

$$Cu^{2+} \rightarrow Cu + 2h^{+} \qquad (I)$$

Fig. 1a and b depicts typical cross-section SEM images of the Cu-modified SiNWs in the solution 0.14M $CuSO_4$-1.35M HF for 2 min at room temperature. It can be seen that the CuNP are deposited onto nanowire walls reaching a depth of about 8 µm. They are of spherical shape with a diameter in the range 46–110 nm.

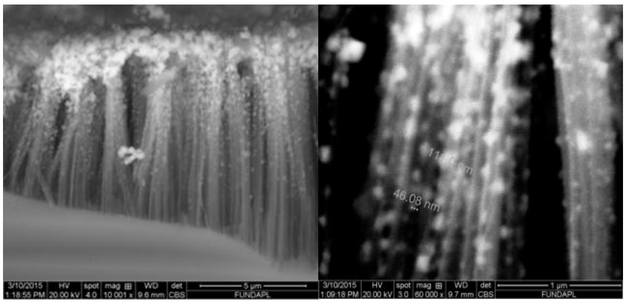


Fig. 1 Cross-sectional view SEM images of SiNWs modified with copper nanoparticles.

C. *Procedure for photocatalytic studies*

In this application of photocatalysis, we used silicon nanowires sample and modified with copper nanoparticles of surface about 1.5cm x 0.7cm as catalysts. The photocatalyst was immersed in a quartz cuvette containing a 4 mL aqueous solution of tartrazine with an initial concentration C0= 1.035x10-5 mol/l. The solution were irradiated with UV light (λ = 365 nm) at room temperature for 200 min as shown in figure 2. The progress of the degradation of tartrazine was monitored every 20 min by UV-Vis spectroscopy. This photocatalyst is used several times in order to studya number of uses of its effectiveness for the degradation of tartrazine.

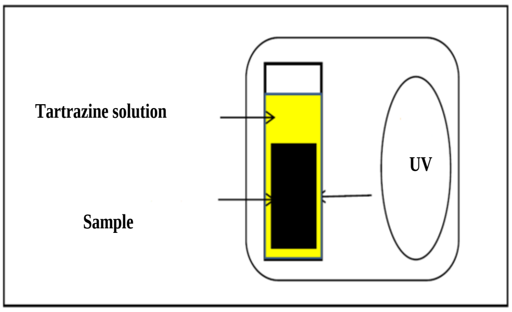


Fig. 2 Schematic experimental of photodegradation

D. *Instrumentation*

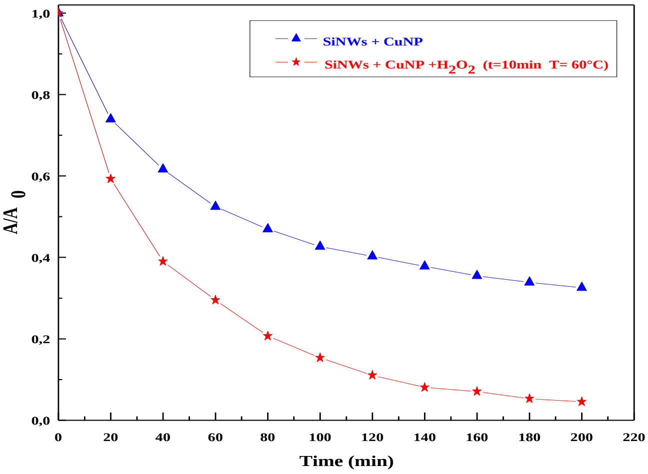
The morphology of silicon nanowires modified with copper nanoparticles was examined by scanning electron microscopy (SEM) Philips (XL30). The absorption spectra of the tartrazine solutions in quartz cuvettes with an optical path of 10 mm were recorded using a CARY 500 “VARIAN” UV–vis spectrophotometer. The wavelength range was 200–600 nm.

III. RESULTS AND DISCUSSION

A. *Photocatalytic degradation of tartrazine*

We noted that the storage of the sample of silicon nanowires decorated with copper nanoparticles in the open air for three months, increased efficiency do the oxidation of surface. It was in this context that chemical oxidation was carried out in order to improve the efficiency of the photocatalytic activity of silicon nanowires decorated with copper nanoparticles for the degradation of tartrazine; we immersed this catalyst in a solution of H2O2 in order to oxidize chemically.

Fig 3, indicated degradation of 95.48% after 200min of irradiation under UV light, this value is greather than the catalyst not treated with H2O2 (67.45%). it is well known that copper oxide phases promote the production of hydroxyl radicals OH•, which are strong oxidizing agents for organic pollutants. [12-14].



. the
presence of silicon nanowires decorated with copper nanoparticles (SiNFs / CuNPs) before and after treatment with H_2O_2.

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The photocatalytic degradation of the dyes show

that the degradation rate follows the law of La Hinshelwood for low initial concentration of dyes (C_0 (pseudo-first-order kinetics) [15-16]. For stud photocatalytic degradation kinetics in this case, we ha Ln (A_0/A) as a function of time. The rate const photocatalysis treated with H_2O_2 is (17.04±0.49) x10^{-3} this constant is more important than photocatalysis not with H_2O_2 (6.76±0.44) x10^{-3}min-1 (table 1).

This confirms that the silicon nanowires modified with nanoparticles and treated with H_2O_2 is the most ef catalyst for the degradation of tartrazine under UV irrad

Table 1

Pseudo-first-order apparent constant values for catalysts.

catalyst	**k ($min^{-1}.10^{-3}$)**	**R^2**
SiNWs/CuNPs not treated with H_2O_2	6.76±0.44	0.96
SiNWs/CuNPs treated with H_2O_2	17.04±0.49	0.99

B. Effect of catalyst reusability

The study of effect of catalyst reusability is very important for a slow cost of the treatment of dye effluent. It is for this reason we are interested to study this parameter.

Figure 4 illustrates the kinetics of degradation of tartrazine under UV irradiation, in presence of silicon nanowires modified with copper nanoparticles, treated in the solution H_2O_2 and used several times under the same conditions. The first experiment (test 1), the degradation reaches a value of 95.48% after 200 min of irradiation; the second test (test 2) indicates a slight decrease in the rate of degradation 88.96%. Beyond that, we notice a significant decrease in the degradation rate of 62.76%, 60.66% and 38.34% respectively for tests 3, 4 and 5. However, oxidation of the same sample a second time in the H_2O_2 solution (30%) for 10 min at 60 ° C. gives a degradation rate of 91.07% (test 6).

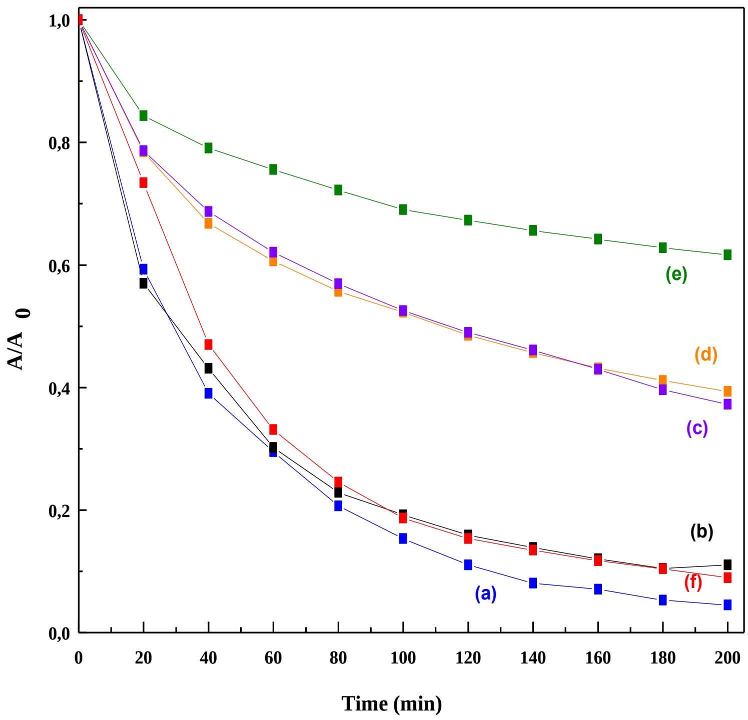

Fig. 4 Kinetics degradation of tartrazine under UV irradiation, in the presence of silicon nanowires decorated with copper nanoparticles (SiNFs / CuNPs) and treated with H_2O_2, **used several times**: (a) test1, (b) test2, (c) test3, (d) test4, (e) test5 et (f) test 6 the sample treated a second time in the solution H_2O_2.

IV. CONCLUSION

A detailed feasibility study has been carried out on photocatalytic degradation of Tartrazine using silicon nanowires treated and not treated with H_2O_2. It was observed that a significant improvement in photocatalytic activity of this catalyst (SiNFs / CuNPs), when treated with H_2O_2, generates a level of photodegradation of 95.48% obtained after 200 min of UV irradiation. This improvement is due to the formation of the CuO phase on the nanoparticles of copper, which favors the separation of charge carriers (electron-hole), and play an important role in the degradation of the organic dye (tartrazine). The decolorization of tartrarine using silicon nanowires modified with copper nanoparticles followed pseudo first-order kinetics. However, the rate of disappearance of color was more important for silicon nanowires modified with copper nanoparticles and treated with H_2O_2. Finally, it may be noted that the sample of nanowires modified with copper nanoparticles and treated with the H_2O_2 solution, can be used several times for the degradation of tartrazine with good photocatalytic activity.

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