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Synthesis of copper oxide nanoparticles, characterization and photocatalytic applications

K. Lakshmi[1,2], V. RajaRajeswari[2] and R.R. MuthuChudarkodi*[3]

[1] Research scholar, Reg. No. 17222232032005, PG & Research Department of Chemistry, V.O. Chidambaram College, Thoothukudi-628008, Tamilnadu, India

[2]Department of Chemistry, Sri Sarada College for women, Tirunelveli-62701, Tamilnadu, India
[3]PG & Research Department of Chemistry, V.O. Chidambaram College, Thoothukudi-628008, Tamilnadu, India.
(Affiliated to Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli-627012, Tamilnadu, India)

Abstract

Copper oxide nanoparticles (CuO NPs) have been produced employing the precipitation technique and a copper nitrate ($Cu(NO_3)_2$) substrate. X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), Fourier transform infrared (FTIR) Spectroscopy, and transmission electron microscopy, or TEM, were used for examining relevant parameters and required properties of as-synthesized nanoparticles. Overall, the results indicate that this process can effectively form CuO nanostructures of varying shapes, sizes, and morphological characteristics. Copper oxide is an effective antibacterial agent against both gramme positive and gramme negative organisms, and CuO NPs have demonstrated exceptional photocatalytic activity against Methylene Blue.

Keywords: ***Copper oxide****, XRD, TEM, FESEM,* ***photocatalytic activity, Methylene Blue***

1. Introduction

Materials' characteristics transform as the material's thickness approaches the Nano scale level. Nanoparticles have the same size as most molecules in life and structures to use. This makes them an appealing candidate for in vivo and in vitro biomedical research [1]. When coated on surfaces, metal nanoparticles with antimicrobial activity have enormous applications in synthetic textiles, biomedical and surgical devices, water treatment, food processing, and packaging [2]. Copper oxide is a compound of two elements, copper and oxygen, which are in the structure of the periodic table as d and p block elements, respectively. Four oxygen ions are used to coordinate the copper ion in a crystal. Small copper oxide outperforms widespread copper oxide powdered in terms of catalytic activity as well as selectivity. CuO nanoparticles are widely used in superconducting materials optical equipment, electricity, tiny fluids, catalysts, photocatalytic breakdown, detectors for gases, as well as biological sensors [3-5]

The relationship of tiny particles with cells that are alive is influenced by factors such as shape, composition, and size. Antimicrobial compounds are now being investigated in depth due to a huge rise in resistant bacteria due to the overbearing and recited use of antibiotics [6]. The resistance to antibiotics have been linked to the excessive use and abuse of these medications, as well as a lack of innovation in drugs by pharmaceutical companies because of reduced economic incentives and difficult regulatory requirements. There have been only a few investigations on the antimicrobial properties of nanoCuO. As a result, an attempt was made to examine the antibacterial activity and minimum inhibitory concentration of Cuo nanoparticles synthesized using the co-precipitation technique [7-10].

The industrial uprising has raised the danger of contamination to the surroundings [11]. Different kinds of trash can endanger lakes and rivers. Organic dyes constitute major contaminants emitted by many different sectors, such as medicine, food, leather goods, clothing, textile, colors, beauty products, and so on [12]. Tonnes of complicated dyes are formed

and discharged into their bodies of water each year, causing adverse impacts on aquatic organisms. Investigators face difficulties when creating methods for demeaning dyes. Ion exchange, organic oxidation, ozonolysis, photocatalytic degradation, and clotting cascade-based methods are some of these techniques [13-16].

Adsorption is frequently used to remove a variety of pollutants from water. However, photocatalytic degradation using a semiconductor photocatalyst is regarded as a cost-effective and environmentally friendly method of successfully degrading dyes [17]. Organic dyes must be degraded using light active materials with large surface areas [18]. Because of their small band gap, multiple states metal oxides or electronic components are active photo catalysts in sunlight. CuO is a p-type semiconductor with a 2.1 to 2.71 eV band gap. CuO nanoparticles (NPs) perform well in optical, mechanical, and photolytic applications [19]. Sol-gel, solvothermal, microwave irradiation, hydrothermal, arc discharge, and other techniques are employed to synthesize CuO NPs [48,49]. To our knowledge, the co-precipitation synthesis of CuO NPs has not been reported in the literature. In this study, we construct a simple method for synthesizing CuO NPs using a battery-operated mortar grinder mill. Additionally, we looked at the antimicrobial capacity as well as the degradation effectiveness of water-soluble dyes like methyl blue [20].

2. Materials and Methods

For this synthesis, all chemicals and materials were purchased from Sigma-Aldrich. De ionized water used for the entire synthesis.

CuO NPs were characterized using the following instruments UV–Vis spectral analysis was performed on a JASCO, V-600 Diffuse Reflectance spectrophotometer. FTIR measurements of samples prepared as KBr disks were performed on a Thermo Scientific Nicolet iS5 FTIR spectrometer. XRD Measurements carried out using a Gonio radius 240 with Cu (λ= 1.54060 Á) in the range of [10°–80°]. FE-SEM investigation done through a high performance TESCAN MIRA3. The Atomic force microscopy study by the Nano surf easy 2 scan BT02218 is profilometer – a sharp cantilever tip interacts with the sample surface sensing the local forces between the molecules of the tip and sample surface. Electrochemical works carried out in CHI instruments.

Simple metal oxide of Copper oxide nanoparticles are the most promising materials have been synthesized by co-precipitation methods by 50 ml of 0.1 N precursors with alkaline solution. In Mixed metal oxides 50 ml 0.1 N of each chemicals with alkaline chemicals, with the synthesis were carried out in different parameters, such as temperature heated to boil (25 and 80℃), adding a base to the reactants and the opposite process, and using nitrogen as an inert gas. After ensured the formation of CuO NPs, then precipitates centrifuged. The residues washed deionized water several times and dried at 220 ºC in an oven. The dried powdered mixture crushed using mortar – pestle, after it was calcinated in muffle furnace at 900ºC for 2 h and finally powdered.

3. Results and Discussion

3.1. Ultra violet spectroscopy

Optical absorption properties of the synthesized CuO-NPs are investigated by UV–visible spectroscopy. UV–visible spectra of samples exhibit a broad absorption peak in the range of 200–1200 nm as shown in Fig1. The surface plasmon resonance (SPR) of the CuO-NPs shows an excitonic absorption at 342 nm [22].

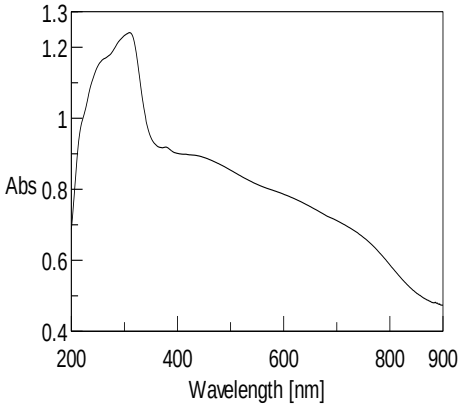

Fig. 1. UV-VIS behavior of CuO nanoparticles

3.2.Fourier transforms infrared spectroscopy

Figure 2 shows the CuO-NPs show absorption peak at 3434.68, 1489.21, 1033.63 and 779.17 cm−1. The band around 1489.21 cm−1 confirms the deformation vibration of the C–H of alkane group. The bands around 1072.94 cm−1 is attributed OH bending vibration and C–H stretching, indicates the existence of a large number of hydroxyl groups. FT-IR spectra show characteristic absorption bands around 3400–3450 cm−1, 1600–1636 cm−1, 1430–1450 cm−1, 860–880 cm−1, 590–620 cm−1 and 470–490 cm−1. The bands around 3400–3450 cm−1 may be to C=O stretch of carboxylic acids. The bands around 1430–1450 cm−1 are corresponding to aliphatic C–H bending and stretching vibrational modes. The band around 860–880 cm−1 can be assigned to the aromatic bending vibration of C–H group. The two important characteristic bands appeared at 590–620 cm−1 and 470–490 cm−1 are assigned to the Cu–O stretching vibrational mode [23-24].

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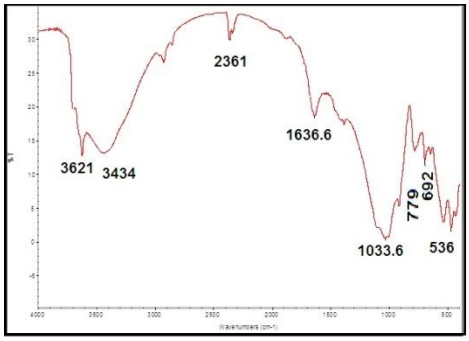

Fig.2. FTIR spectrum of CuO nanoparticles

3.3. X- Ray Diffraction

Powder XRD was a rapid analytical technique primarily used for phase identification of a crystallite material and can provide information on unit cell dimensions. The XRD pattern of the CuOnanopowderwas in monoclinic phasewasshown in the Fig. 3. The average crystallite size was calculated using Debye Scherrer's formula:

$$D = 0.9\lambda/\beta\cos\theta \text{ ---------- (1)}$$

Where D is the crystallite size, λ is the wavelength (1.5406 A ° for Cu Kα) of the X-ray radiation, β is the full width at half maximum of the peaks at the diffracting angle θ. Crystallite size wascalculated to be 19 nm [25].

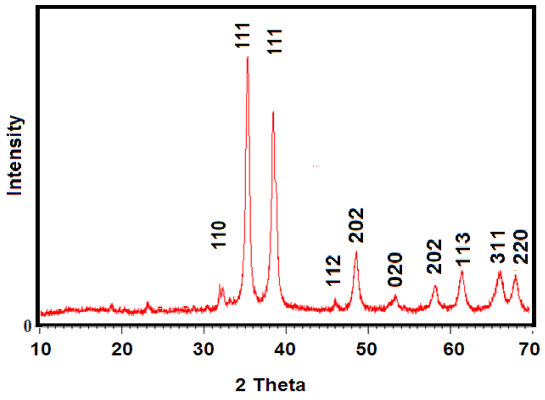

Fig. 3 XRD behavior of CuO nanoparticles

According to JCPDS data (80-0076), the exhibited diffraction peaks at 2θ = 32.51 ° (1 1 0), 35.53 ° (-1 1 1), 38.75 °(111), 46.28 ° (-1 12), 48.76 ° (-2 02), 53.58 ° (0 2 0), 58.31 ° (2 0 2), 61.58 ° (-1 1 3), 66.24 ° (-311) and 68.08 ° (2 2 0) corresponds to different planes ofmonoclinic phase of CuOnano particles(table 1). The lattice parameters of CuO sample were calculated from the XRD data. The evaluated cell parameters were a = 0.46891 nm, b = 0.34214 nm, and c = 0.51276 nm in agreement with the reported values.

3.4. FESEM

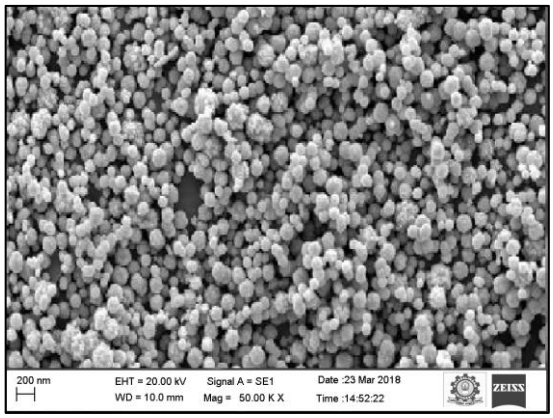

Fig.4 FESEM image of CuO nanoparticles

Field emission scanning electron microscopy (FE-SEM) is an advanced technology used to capture the Nanostructured image of the materials. Figure 4 shows the FESEM image of copper oxide nanoparticles. From the obtained results, it looks like spherical or ball like structures. It shows particles are in the nano meter region; its size is range 10 to 40 nm with smooth surfaces, and is uniform. This uniformity proves the formation of effective copper oxide nanoparticles. FESEM is similar with XRD data

3.5. EDAX

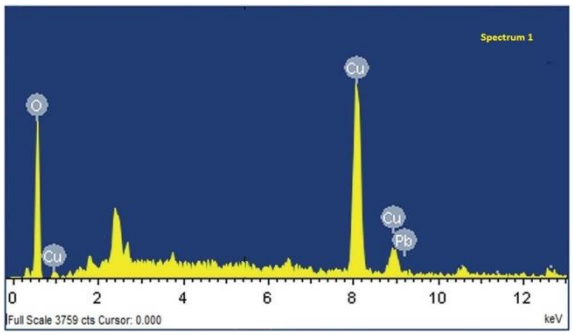

Figure 5 EDAX spectrum of CuO Nanoparticles

Table 1. EDAX data of CuO NPs

S. No	Element	Weight %
1	Cu	67.4
2	O	28.14
3	Pb	4.46
4	Total	100

EDAX analysis was employed to confirm the elemental composition of the synthesized Copper oxide NPs. The synthesized Copper oxide NPs has been proven by the peaks of Cu, and O in the figure

5. Elemental ratio of Cu, O, and Pb obtained from EDAX spectrum data in Table 1. From the Figure and Table were the witnessed of the formation copper oxide Nanoparticles.

3.6. TEM analysis

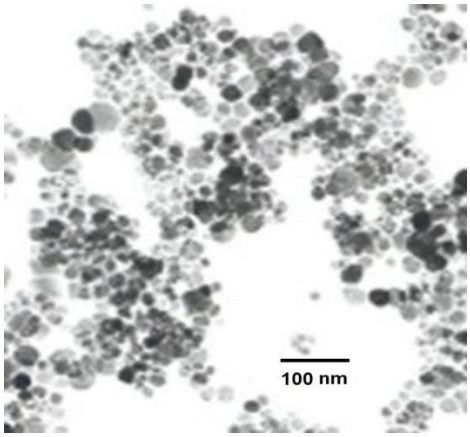

Figure 6 TEM images of CuO Nanoparticles

In the Figure 6 shows the tiny nano particles, as fine CuO NPs about 10 to 30nm in size, serves as one of the most commonly utilized Nanoparticles. Ceramics, glass, electronics, sensor device, and the propellant sectors utilize copper oxide nanoparticles. It is frequently dealt with as a mixture that dissolves inside a suitable financially sound, as are many nanomaterials. These To learn more about ordering, handling, storing, and using copper oxide nanopowder, visit CuO nanopowder.CuO NPs play an essential role in producing high-tech superconducting materials and superconductive substances in optical-electronic applications, as well as photoconductive, photothermal, and semiconductor applications.

3.7. Atomic force microscopy

AFM is the best surface scanning technique to detect the nano sized materials. It is mostly used to analysis the topography and surface morphology of the particles. A topographical image of Copper oxide nano particles was taken through the AFM instrument Nanosurf easy 2 scan. Figure 7 topographical images seem like spherical size like structure and 3 – D images observed were mountain like nature. The size of the particle are in nanometer region. The average size of particles is 70 – 100 nm and 3-D images show that the materials have inter particles gap and depths, it may increase the rate of reaction in the electro and photo catalytic applications. The high roughness value 6.4252 calculated from particle size distribution data for copper oxide nano particles.

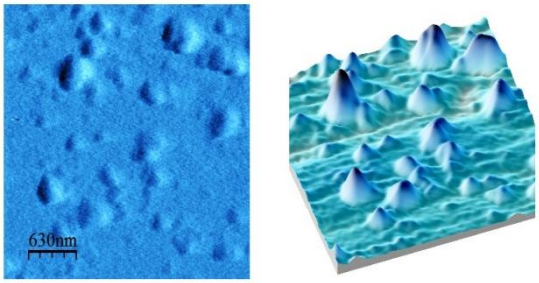

Figure 7AFMimages of CuO Nanoparticles

3.8. Electrochemical analysis

Fig 8 shows the performance of electrochemical study recorded the Cyclic Voltammograms of Copper oxide nanoparticles in the potential range from -0.8 to 0.8 V at 100 mV/s in pH 7.0. Nano sized Copper oxide nanoparticles were coated on glassy carbon electrode (GCE), Ag/AgClandplatinumwireelectrodewereusedaswor kingelectrode,referenceelectrodeand counter electrode respectively. Figure 8 shows cyclic voltammetry behavior of copper oxide nano particles in pH 7.0. The voltrammogram shows one oxidation peak and reduction peak at 0.56 mV and 0.22 mV respectively. The good reversible redox behavior confirmed formation of copper oxide nanoparticles.

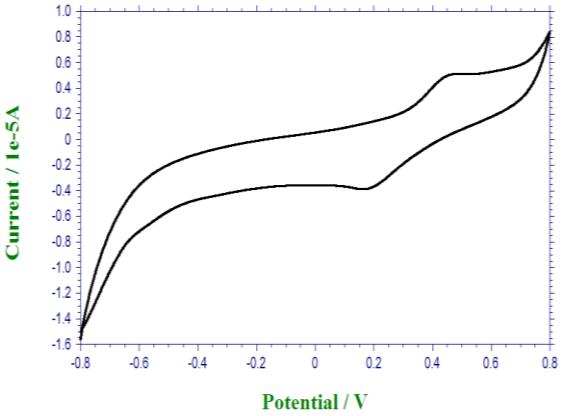

Fig. 8 Cyclic voltammetricbehaviour of CuO nanoparticle on GCE at 100 mV/s in pH 7.0

3.9. Photo catalytic studies

Figure 9 shows the dye degradation mechanism followed by CuO NPs. Researchers were reported that hydroxyl radicals were the most important reactive oxygen species that caused degradation when CuO NPs were used. CuO NPs have been widely used as catalysts in photo catalytic degradation and reduction of impurities. In fact, dark adsorption is an initial step and one of the most critical aspects of the photo catalysis mechanism. CuO NPs were used to study the photo degradation of cationic dyes like MB when exposed to sunlight. In the presence of light radiation, the MB solutions

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were stirred in the dark for 1 h to establish adsorption–desorption equilibrium between the CuO NPs and dye molecules. The UV–Visible spectrum was then used to estimate the MB concentrations. Within 75 min, the photo catalytic activity of CuO NPs and the absorption peaks significantly decreased. The morphology, crystalline structure, and dimensions of NPs all play a role in photo catalytic activity.

MB were nearly fully degraded under direct sunlight in the presence of catalyst. Sunlight is a very important factor from an industrial perspective. The degradation was 55%, for MB dye, respectively within 30 min of photo irradiation. While it was 67% for MB dye within 75 min of photo irradiation. After 1.15 h of irradiation, an efficiency of 81% is obtained, indicating that integrating CuO NPs species into the solution serves a primary function in the improvement of photo degradation shown in the Figure. The CuO NPs are degradation of MB dye was observed higher [26-27].

The photo-removal efficiency percentage was calculated from the equation given below;

% Photo-removal efficiency = $C_0 – C/C_0 \times 100$

Where C0 is the initial concentration of dye and C is the concentration of dye after photo-irradiation.

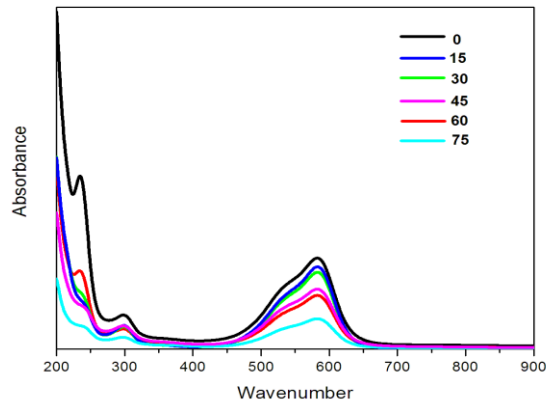

Fig. 9 Dye degradation of MB in Sun light

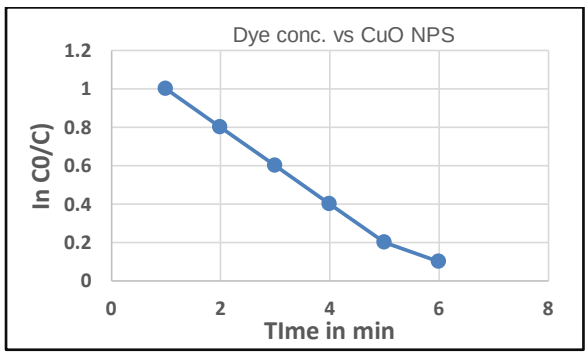

Fig. 10 Dye degradation concentration vs CuO NPs

Table 2 Concentration vs Time

OD (Min)	Test sample concentration (µg/ml)					
	Control	500	250	100	50	10
0	0.145	0.126	0.131	0.136	0.140	0.143
15	0.145	0.121	0.125	0.130	0.132	0.142
30	0.145	0.118	0.123	0.127	0.129	0.138
45	0.145	0.109	0.111	0.122	0.127	0.134
60	0.145	0.106	0.112	0.116	0.126	0.131
75	0.145	0.099	0.103	0.110	0.125	0.129

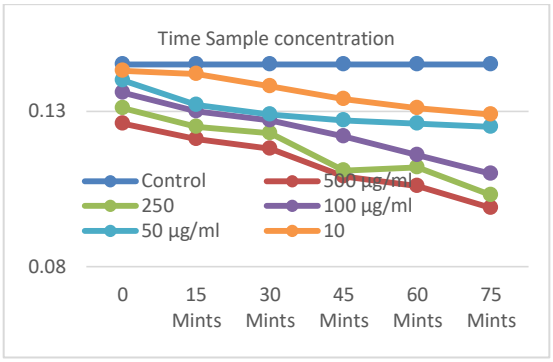

Fig. 11 Dye degradation of MB chart vs time

Based on the increasing concentration and time which leads the rate of reaction and efficiency of the degradation reaction.

3.10. Antifungal activity

The potato dextrose agar medium was prepared by dissolving 20 gm of potato influsion, 2 gm of dextrose and 1.5 gm of agar in 100ml of distilled water. The dissolved medium was autoclaved at 15 lbs pressure at 121°C for 15 minutes. The autoclaved medium was mixed well and poured onto 100mm petri plates (25-30 ml/plate) while still molten.

Petri plates containing 20ml potato dextrose agar medium were seeded with 24hr culture of fungal strain*Candida albicans*. Wells were cut and different concentration of sample KL4S (500 µg/ml, 250 µg/ml, 100 µg/ml and 50 µg/ml) was added.The plates were then incubated at 37°C for 24 hours. The anti-fungal activity was assayed by measuring the diameter of the inhibition zone formed around the wells. Amphotericin B was used as a positive control. The values were calculated using Graph Pad Prism 6.0 software (USA).

Antifungal activity of the synthesized CuO NPs was first tested in a broad range, from 50 to 500 µg/mL

shows in the Figure 12. In this assay, Candida stopped growing at a concentration of 395 µg/mL. Different a concentration range was tested to define a more specific activity. The results obtained showed that Candida grows similarly to the negative control at concentrations also. From the Figure 12, at higher concentrations, growth slowly decreases has been obtained. At concentrations of 270 to 395 µg/mL, growth is completely inhibited, and no growth was detected for after 24 hrs.

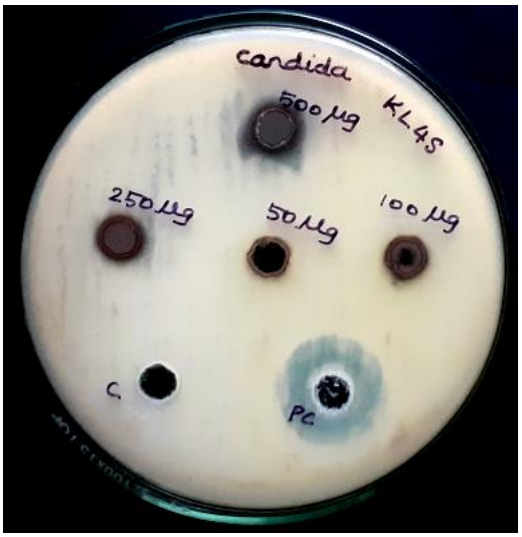

Figure 12 Growth of candida after 24 h treatment with CuONPs at different concentration

5. Conclusions

A co-precipitation approach was used to effectively for synthesize of CuO NPs in this study. A monoclinic CuO phase with a crystallite size of 19.nm was identified using XRD analysis. AFM examination deliberates the better topography and it also indicates the better activity in application part. Under sunlight illumination, the Nano sized material successfully demonstrated catalytic activity in degrading MB dye. The photo catalytic reduction had pseudo-first-order kinetics, with an 81% removal rate for MB dye. These encouraging findings provided a new avenue for researchers to develop cost-effective and environmentally friendly photo catalysts for efficiently removing dyes from water.

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