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Visible light degradation of textile effluent using nanostructured TiO_2/Ag/CuO photocatalysts

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TiO_2, Ag and CuO nanomaterials, and nanostructured TiO_2/Ag/CuO photocatalytic materials coupled in different weight percentages were synthesized. The prepared materials were characterized by XRD, SEM, EDX and UV-Vis diffuse reflectance spectroscopy. Photocatalytic degrading capabilities of the pure, as well as the nanostructured TiO_2/Ag/CuO photocatalytic materials were tested on the dye effluent collected from the textile industries. The samples collected during the photocatalytic degradation of textile dye effluent were studied with UV-Vis spectroscopy. The nanostructured TiO_2/Ag/CuO photocatalyst with the composition of 80:10:10 weight percentage exhibited remarkable performance. Coupling of Ag metal nanoparticles and narrow bandgap CuO semiconductor nanomaterial to the wide bandgap TiO_2 semiconductor nanomaterial was found to modify the operative bandgap of the system and generate electron-hole pairs under visible light irradiation. The coupled TiO_2/Ag/CuO system facilitates improved electron transfer to the adsorbed molecules, and thus the system improves the photocatalytic degradation of dyes by enhanced redox mechanism.

Keywords: Coupled TiO_2/Ag/CuO, Nanostructured photocatalysts, bandgap, degradation of textile effluents, advanced oxidation process.

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1. Introduction

In 1972, Fujishima and Honda found that TiO_2 could be used as catalytic electrode in a photo-electrolysis cell to decompose water into H_2 and O_2, without applying an external voltage [1]. Further researches established the use of TiO_2 for photo-assisted degradation of organic compounds and reduction of inorganic compounds. Researches on purification of polluted water gained greater importance with ever increasing need to purify the industrial effluents as well as the contaminated water resources by the industrial waste streams which often created serious health and environmental problems. Among the many, textile effluents play significant role in polluting the water resources and the environment. Traditional effluent purification processes often produce end products with carcinogenic compounds, which require further treatment for complete purification. The photocatalytic degradation of textile effluents using nanophotocatalysts through advanced oxidation process is one of the recent scientific explorations that gain importance mainly due to its ability to produce harmless end products [2–4].

Titania is a semiconductor with bandgap energies in the range of 3.2 – 3.4 eV, and hence could produce electron–hole pairs upon UV region photon irradiation. When these photogenerated charge carriers migrate to the surface without recombining, they could interact with the adsorbed water and oxygen molecules to produce radical species. These radicals strike any adsorbed organic dyes and lead to complete or selective degradation. Repeated efforts are being made by the researchers to trigger this degradation process under visible light irradiation, to make the process very economical by using abundantly-available solar light in various photocatalytic applications. Efficient photogeneration of electron – hole pairs, prevention of their recombination and reduction of specific surface area of the particles of the photocatalysts are the key factors in increasing the efficiency of photocatalytic activity. Several researchers have proven that coupling of semiconductors with noble metals and other semiconductor materials at nanoscales plays significant role in modifying the above factors [5–9].

In this exploration, TiO_2, Ag and CuO nanomaterials, and nanostructured TiO_2/Ag/CuO photocatalysts coupled in different weight percentages were synthesized under optimized conditions [10,11] and tested for their degradation efficiency on a model dye and also on an effluent collected from textile industries in Tamil Nadu, India.

2. Experimental methods

Titania was synthesized using the sol-gel method, by dissolving the precursor titanium (IV) isopropoxide in isopropanol under continuous stirring at room temperature, and then by adding citric acid as the chelating agent mixed with deionized water. Ag and CuO were synthesized via thermal decomposition method by heat treatment

of silver acetate and copper acetate, separately in alumina crucibles, by rising the temperature up to 300 °C in steps of 4 °C/min. Then, the respective polycrystalline nanoparticles were synthesized by annealing the as-prepared samples at the optimized temperature of 450 °C for 30 minutes. Details for this protocol were reported elsewhere [12]. Then, the coupled TiO_2/Ag/CuO photocatalysts were synthesized by taking the as prepared samples in three different weight percentages, viz. 80:15:05. 80:10:10 and 80:05:15, grinding them well for 2 hrs, and then annealing at 450 °C for 30 min.

X-ray diffraction studies were carried out on RICH SEIFERT, Germany (model 3000) diffractometer using Cu-$K_{\alpha 1}$ radiation ($\lambda = 1.54056$ Å), 30 kV voltage, and 10 mA current. Surface morphology and elemental composition were carried out using QUANTA 200 FEG high resolution scanning electron microscopy (HR-SEM) and energy-dispersive X-ray spectroscopy (EDX). The optical properties of the samples in UV and Visible ranges were investigated using CARY 5E UV-VIS-NIR spectrophotometer.

3. Results and discussions

3.1. Phase and structure confirmation

Figure 1 shows the powder XRD patterns of the TiO_2, Ag, and CuO, and that of coupled TiO_2/Ag/CuO samples prepared at weight percentages 80:05:15, 80:10:10 and 80:15:05, and annealed at 450 °C. The primary diffraction peaks of the TiO_2 were indexed to anatase phase Titania with tetragonal crystal structure, and the values well matched with the JCPDS card 84-1285. The calculated lattice parameter values are: $a = b = 3.784$ Å and $c = 9.561$ Å.

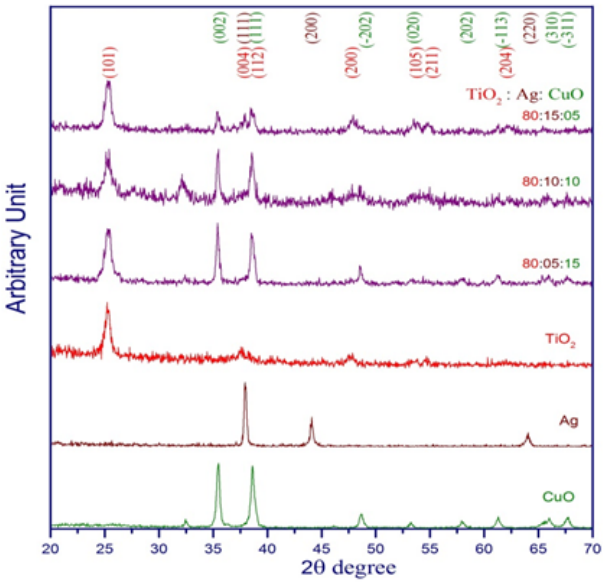

FIG. 1. XRD patterns of all the prepared samples, annealed at 450 °C for 30 min.

The characteristic peaks of the CuO were indexed to monoclinic structure and the values are in good agreement with the reported values in the JCPDS card 89-5896. The determined lattice parameters are: $a = 4.683$ Å, $b = 3.424$ Å and $c = 5.129$ Å.

The diffraction peaks of the prepared sample Ag were indexed to cubic structure and could be matched well with the JCPDS card number 03-0921. The calculated lattice parameters are: $a = b = c = 3.914$ Å.

The crystallite sizes were estimated using the Scherrer's formula, and the estimated average crystallite sizes ranged from 9 to 64 nm. No significant peak shifts were observed in the XRD patterns of the coupled systems.

The HRSEM images, as shown in Fig. 2, of the coupled photocatalysts reveal irregularly-shaped particles, which are agglomeration of the tiny spherically shaped particles. The average particle sizes of the isolated spheres were in the range from 25 to 80 nm. The EDX analysis confirmed the elemental composition in the respective coupled photocatalysts.

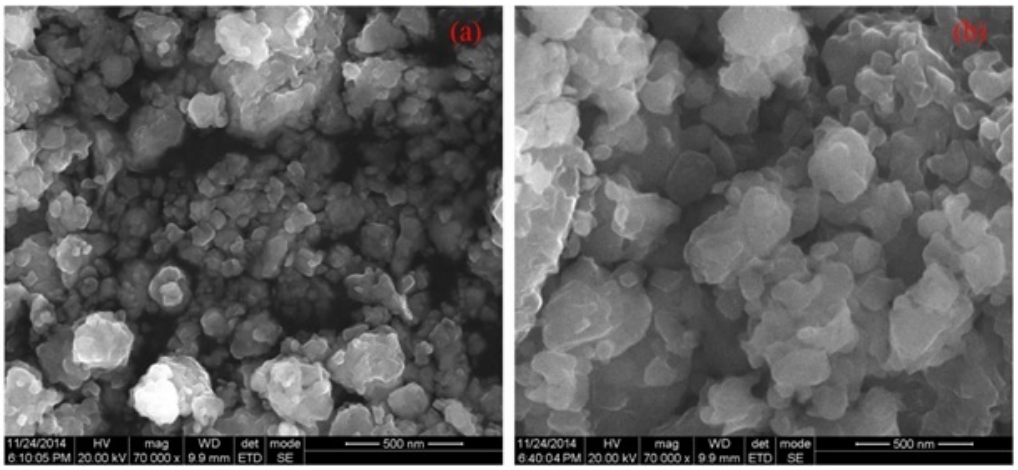

FIG. 2. HRSEM images TiO_2/Ag/CuO at wt%: (a) 80:10:10; (b) 80:15:05

3.2. Optical properties and bandgap energies

UV-Vis Diffuse Reflectance spectrum of the prepared photocatalytic samples TiO_2, TiO_2/Ag/CuO (80:15:05), TiO_2/Ag/CuO (80:10:10) and TiO_2/Ag/CuO (80:05:15) are shown in Fig. 3. The absorption edge of the pure TiO_2 was in the UV region. However, red shifts were observed for the coupled TiO_2/Ag/CuO photocatalysts prepared at three different weight percentages 80:15:05, 80:10:10 and 80:05:15 and their absorption edges have fallen in the visible region.

The estimated optical band gap energies of pure TiO_2 as well as those of the coupled TiO_2/Ag/CuO nanophotocatalysts prepared at three different weight percentages 80:15:05, 80:10:10 and 80:05:15 are shown in Table 1.

TABLE 1. Optical band gap energies of the prepared photocatalysts

Photocatalysts	**Band gap**
TiO_2	3.3 eV
TiO_2/Ag/CuO (80:05:15)	3.0 eV
TiO_2/Ag/CuO (80:10:10)	2.9 eV
TiO_2/Ag/CuO (80:15:05)	3.0 eV

3.3. Photocatalytic degradation test results

All the photocatalysts were tested for their decoloration efficiency on the methylene blue (MB) dye under visible irradiations and the results are shown in Fig. 4. The photocatalyst TiO_2/Ag/CuO synthesized at 80:10:10 wt % showed best efficiency with more than 75 % of decoloration in 120 minutes under visible light irradiation.

Then the best photocatalyst TiO_2/Ag/CuO (80:10:10) was employed in the degradation of the textile effluent and the results are shown in Fig. 5. More than 80 % decoloration of the textile effluent was achieved in 240 minutes under visible light irradiation.

4. Conclusions

TiO_2, Ag and CuO, and coupled TiO_2/Ag/CuO photocatalysts at three different weight percentages 80:05:15, 80:10:10 and 80:15:05 were synthesized. Their structural, morphological and optical properties were analyzed with various characterization techniques. Among the prepared photocatalysts, TiO_2/Ag/CuO (80:10:10) gave the best decoloration (about 79 %) of MB in 2 hours under visible light irradiation. This is in agreement with the results obtained from the optical property studies. The best photocatalyst effectively degraded the textile effluent with an efficiency of about 82 % of decoloration in 4 hours under visible light irradiation. Inclusion of optimal amount of CuO and Ag was found to modify the band gap significantly and make the photocatalyst active under visible light. The CuO acts as sink for photogenerated electrons, prevents recombination and thus enhances the redox reaction and hence the efficiency of the degradations.

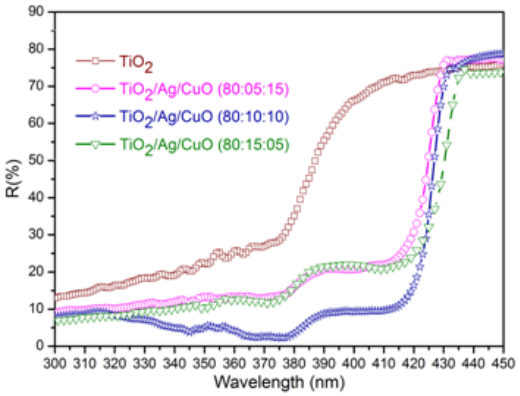

FIG. 3. Diffuse reflectance spectrum of the prepared photocatalysts

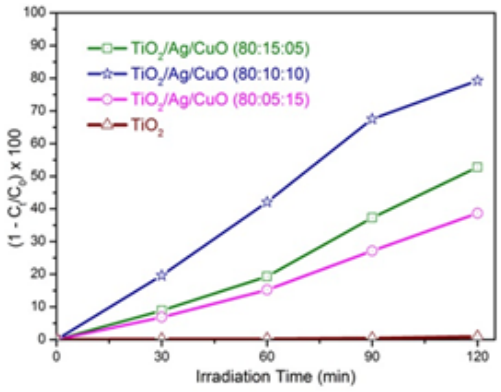

FIG. 4. Degradation profile – Methylene Blue

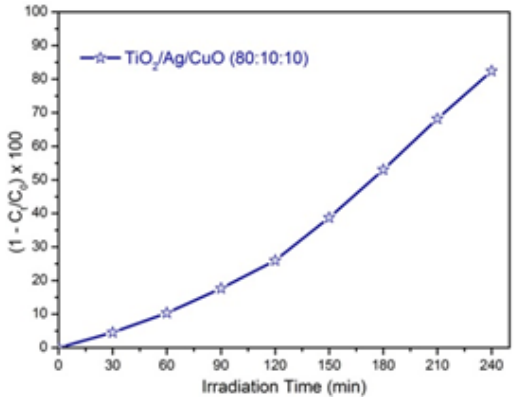

FIG. 5. Degradation profile – Textile Effluent

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