

Preparation and Characterization of SrO/Cu₂O for Photocatalytic Oxidation of Diphenylamine under UV Light

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Abstract: Generally cuprous oxide has higher photocatalytic activity in the visible region. It is widely applicable in the field of dye degradation. SrO/Cu₂O nanocomposites were synthesized by sol-gel method and characterized using SEM, EDAX, AFM and particle size analyzer. SEM, EDAX, AFM and particle size analysis studies indicate that SrO/Cu₂O composites are in nano-size range. The catalytic efficiency of nanocomposites was compared with commercial mixture of SrO/Cu₂O photocatalyzed oxidation of diphenylamine (DPA) using UV light of wavelength 365 nm on SrO/Cu₂O nanocomposites and SrO/Cu₂O semiconductor mixture surfaces in ethanol yield N-phenyl-p-benzoquinonimine. The photocatalysis was examined as a function of (DPA), airflow rate and intensity of illumination. The photocatalytic studies revealed the sustainable photocatalytic efficiencies. The product formation was high with illumination at 254 nm than at 365 nm. Electron donors like triphenylphosphene, hydroquinone and tetraethylamine do not enhance the photo-oxidation. Both anionic and cationic surfactants favor photocatalysis. Vinyl monomers neither slowdown the photo-oxidation nor undergo polymerization. Singlet oxygen quencher azide ion does not suppress the photo-oxidation. Singlet oxygen generator enhances the photocatalysis. The catalytic efficiencies of nanocomposites were nearly four times higher than that of commercial mixture of SrO/Cu₂O.

Keywords: Photo-catalysis, SrO/Cu₂O, diphenylamine, nanocomposite

1. INTRODUCTION

Cuprous oxide (Cu₂O) is a reddish p-type semiconductor, which has attracted current interest because of its direct band gap of 2–2.2 eV [1], which makes it a promising material for the conversion of solar energy into electrical and chemical energy [2–9]. Cu₂O has low toxicity and excellent environmental acceptability and that is inexpensive and readily available. The band gap of Cu₂O can be tuned to visible light by some factors such as preparation methods, doping etc. as photo-catalyst, but also can be used as sensitized semiconductor for a solar cell [10]. Moreover, Cu₂O has a high absorption coefficient in the visible region [11] and a powerful adsorption for molecular oxygen, which can forage photoelectrons to constrain the combination of electrons and holes. In particular,

Cu₂O has been widely exploited for use in the fields of photocatalysis and as a photo-electrode in electrochemical cells. However, nano-Cu₂O particles tend to aggregate in aqueous solutions, which diminish both surface area and photocatalytic efficiency [12]. Many attractive advantages have been pointed out for cuprous oxide for use as a photocatalyst [13]. The water splitting activity of Cu₂O, especially under visible light irradiation to produce hydrogen has been the focus of many debates [14–17]. Cu₂O nanoparticles have also been used as a photocatalyst in the photocatalytic degradation of methyl orange [18, 19]. Researchers have worked on stabilizing nano-Cu₂O particles on various carriers. Cu₂O exhibited good catalytic performance and stability. So, electrons at ground band are easily excited under visible light irradiation. However, the easy recombination of electron and hole results in low catalytic activity of Cu₂O. In order to control the rate of recombination, Li et al. [20] prepared the catalyst Cu₂O-TiO₂ and

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found that the $\text{Cu}_2\text{O-TiO}_2$ composite oxides using the mixture of Cu_2O with commercial P25 TiO_2 exhibited a superior activity.

Numerous composites have been prepared and reported so far. There is lack of similar reports on $\text{SrO/Cu}_2\text{O}$ nanocomposites. Hence, we decided to synthesize and characterize the photocatalytic application of $\text{SrO/Cu}_2\text{O}$ composite. Numerous works have been done on the photo-oxidation of diphenylamine in the presence of semiconductors and nanoparticles. There is lack of similar reports on photo-oxidation of diphenylamine (DPA) in the presence of $\text{SrO/Cu}_2\text{O}$ composites. Hence, we chose the photo-oxidation of DPA in the presence of $\text{SrO/Cu}_2\text{O}$ composites and compare the photo-oxidation results with commercial mixtures.

2. EXPERIMENTAL

2.1. Experimental Procedure

Nanocrystalline $\text{Cu}_2\text{O/SrO}$ was obtained by the sol-gel method. Required volume of millimolar CuCl_2 aqueous solution was added drop wise under vigorous stirring to 20 mL of distilled ethanol, acidified with 4 mL of 1:1 aqueous acetic acid. This was followed by drop wise addition of SrCl_2 (2.5 mL) under stirring. After the addition, the stirring was continued for an hour. The resulting clear colloid was dried at 100°C for 1.5 h and calcined at 500°C for 3 h in a muffle furnace fitted with a PID temperature controller and the heating rate was set at $10^\circ\text{C min}^{-1}$. A similar procedure was followed to obtain the undoped oxide.

2.2. Characterization Techniques

SEM analysis was carried out with a Model SUPRA 40 scanning electron microscope with accelerating voltage of 3-5 kV with a working distance of 5-9 mm. All the sample surfaces were finely coated with a gold sputtering unit, to make the surface to conduct and stored in desiccators before investigation under the SEM.

A small volume of sample was spread on a well-cleaned glass cover slip surface mounted on the AFM stub and dried with nitrogen flow at room temperature. Images were obtained in tapping mode using a silicon probe cantilever and resonance frequency of 209–286 kHz. The scan rate used was 1 kHz. A minimum of five images for each sample were obtained with AFM and analyzed to ensure reproducible results.

The UV photocatalyzed oxidations were made under UV light at 365 nm. The reactions were carried out in pyrex glass vessel case. Freshly prepared solutions of DPA were taken in a narrow reaction vessel. Air was bubbled using micro pumps. The airflow rate was measured by the soap bubble method. The volume of the reaction solution was kept as 25 ml and the loss of solvent due to evaporation was compensated periodically. The reaction solution was centrifuged and the absorbance measured at 350 nm using Shimadzu U-1601 UV-Visible spectrometer. The intensity of light was measured using ferrioxalate chemical actinometry. The UV-Vis spectra of the reaction solutions irradiated with UV light were identical with that of N-phenyl-*p*-benzoquinonimine, PBQ ($\lambda_{\text{max}} = 450 \text{ nm}$) [15]. The absorbance of the product formed conforms to the Beer-Lambert law and the product was estimated using the reported value of the molar extinction coefficient ($4.2658 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$) [16, 17, 18]. The raw experimental data are listed in the following pages.

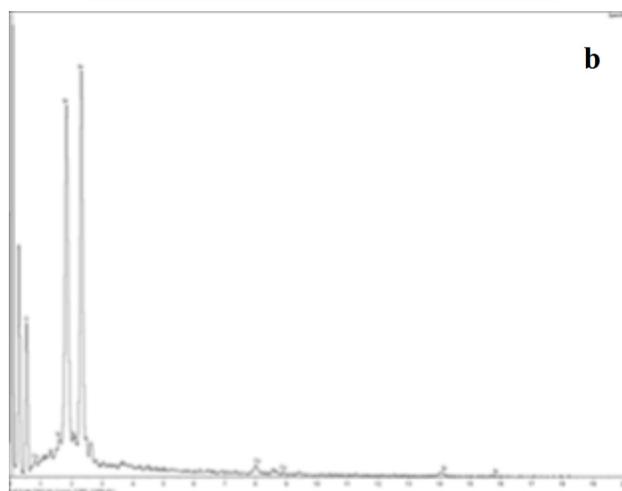
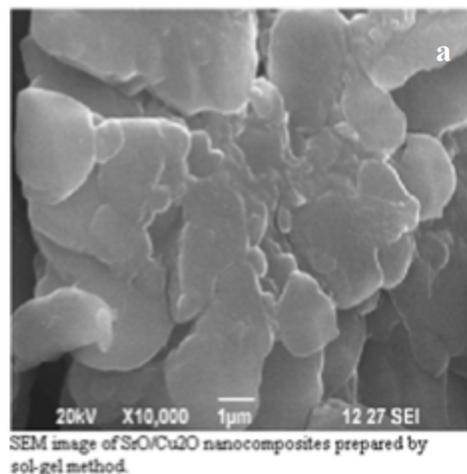


Figure 1. a. SEM image of $\text{SrO/Cu}_2\text{O}$ nano-composites
b. EDX pattern of $\text{SrO/Cu}_2\text{O}$ nano-composites

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization

The surface morphology of the strontium copper oxide composite was studied by scanning electron microscopy. Figure 1a & 1b represents the SEM and EDX of $\text{SrO/Cu}_2\text{O}$ nanocomposites. These figures suggest that aggregation of the particles and small grains were present at the surface. The particles look like nanoflakes which are self-assembled into a hierarchical microstructure. The nanoflakes exhibit fairly regular sheets that are of a few micrometers size. The energy dispersive X-ray (EDX) spectrum of the mixed oxide, also shown in figure, confirms the presence of Sr & Cu in the prepared oxide and the composition of this was found to be 1:1.

The size distribution of the synthesized $\text{SrO/Cu}_2\text{O}$ nanocomposites is also shown in the histogram, which ranges from 500 to 800 nm. In addition, the uniform spherical nature of our synthesized nanocomposites is also confirmed from the inset image observed from AFM. Thus, from the AFM observations, it was clearly confirmed that the synthesized nanocomposites were formed without

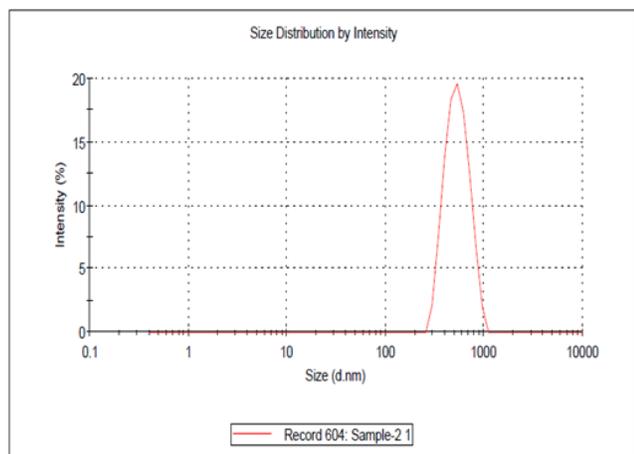


Figure 2. Particle size distribution

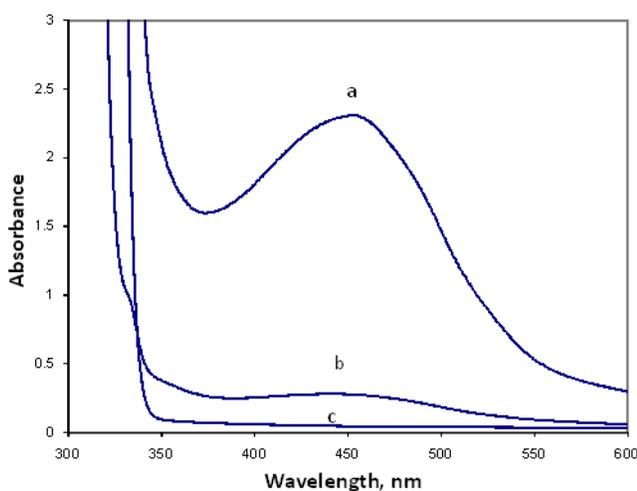
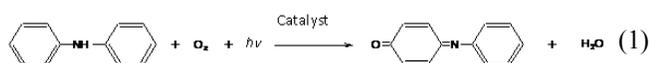


Figure 3. UV photo-oxidation of diphenylamine in ethanol in the presence of SrO/Cu₂O nano-composites. A) initial concentration, b) after 10 min irradiation, c) after 20 min irradiation

agglomeration and were flakes in nature. From figure 2, the average particle size of the SrO/Cu₂O nano composites prepared was obtained as 740nm.

3.2. UV Photooxidation of DPA in the Presence of Nanocomposites and Semiconductor mixtures

UV photo-oxidation of DPA in ethanol on SrO/Cu₂O nanocomposites and commercially available SrO and Cu₂O mixture yields PBQ as the product. The UV-Visible spectra of the irradiated solutions were identical with that of PBQ. Hence the reaction is represented as in equation (1), where the catalysts are SrO/Cu₂O nano-composite and commercial 1:1 mixture of SrO/Cu₂O.



The progress of the UV photo-oxidation of DPA in ethanol on SrO / Cu₂O nano composites and commercially available SrO and

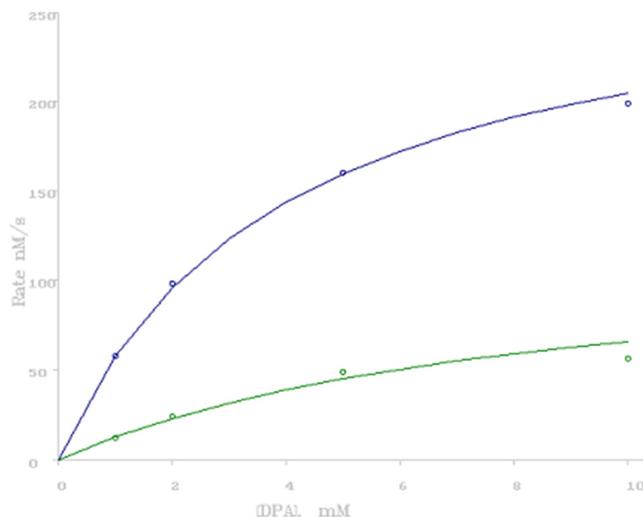


Figure 4. SrO/Cu₂O nano-composites and SrO/Cu₂O semiconductor mixture catalyzed UV photo-oxidation of diphenylamine at different [DPA].

CuO mixture was followed. The oxidations were carried out in narrow pyrex glass vessels. Air was bubbled through the reaction solution. The loss of solvent due to evaporation was compensated periodically by maintaining a fixed volume of the reaction solution. After completion of the photochemical reaction, the reaction solution was centrifuged. The supernatant solution was subjected to UV-Visible spectral analysis. The UV-Visible spectra observed using catalysts, at the beginning and after 60 min irradiation with UV light are shown in figure 3. The spectra observed at 60 min clearly shows a maximum absorbance (λ_{max}) at 450 nm, however there is no such absorbance is observed at 0 min. It reveals that the maximum absorbance at 450 nm is corresponding to PBQ. Similar report is available in the literature for PBQ [19]. The absorbance of the reaction solution confirms to the Beer-Lambert law; proportionate dilution affords linear variation of absorbance.

The various factors such as concentration of DPA, air flow rate and intensity effect influencing the photo-catalyzed reactions in ethanol was examined. The rate of formation of *p*-benzoquinonimine (PBQ) at different concentrations of DPA was carried out. Rate measurements for the formation of PBQ at semiconductor catalysts show that the oxidation rate of DPA increases with increase in the concentration and the variation conforms to Langmuir-Hinshelwood model (figure 4).

The effect of airflow rate on the rate of formation of PBQ was also carried out. Study of the photo-catalyzed oxidation of DPA as a function of airflow rate reveals the enhancement of photo-catalysis with oxygen concentration in the formation of PBQ. The variation of rate with airflow rate suggests Langmuir-Hinshelwood kinetic model in displayed in figure 5. The reaction was also studied without bubbling air but the solutions were not deaerated. The dissolved oxygen itself brings out the reaction but the photo-oxidation is weak. The reaction does not occur in dark. The photo-catalysts used do not lose their catalytic activities on irradiation. Study of the photo-catalyzed oxidation of DPA as a function of

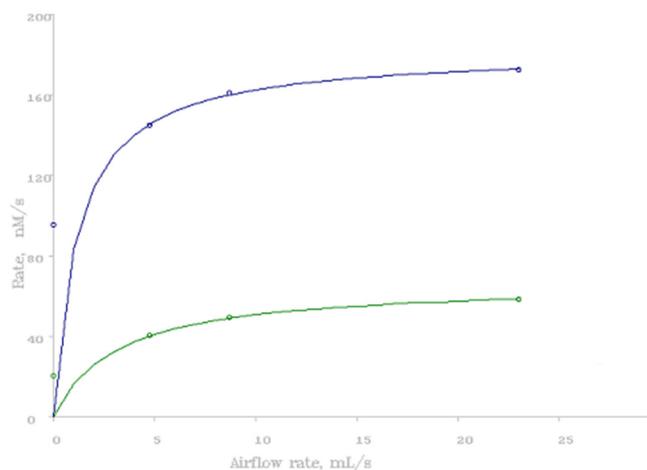


Figure 5. SrO/Cu₂O nano-composites and SrO/ Cu₂O semiconductor mixture catalyzed UV Photo-oxidation of diphenylamine at different air-flow rate.

Intensity effect on the rate of formation of PBQ was carried out. The reaction rate increases with the intensity of light in as shown in figure 6.

The rate of formation of PBQ in the presence of surfactant, vinyl monomer and azide ion was examined. It was found that the surfactants like triethylamine (TEA) and sodium lauryl sulfate (SLS), enhances the photocatalytic oxidation of DPA. Sacrificial electron donors like hydroquinone (HQ) and triphenyl phosphine (TPP) were also enhance the photo-oxidation of DPA. But, vinyl monomer acrylamide neither suppresses the photocatalytic oxidation in presence of catalysts nor polymerizes during the course of photocatalysis, which indicates absence of involvement of radical mechanism. Azide ion, a singlet oxygen quencher, fails to suppress the photocatalyzed oxidation indicating the absence of involvement of singlet oxygen in the surface photocatalysis. Table 1 shows the formation of PBQ at SrO/Cu₂O catalysts in the presence and absence of reagents. Rosebengal singlet oxygen generator enhances the photo-catalysis, which indicates that the system can uptake singlet oxygen from the generator. The study was also examined

Table 1. Photo-oxidation of DPA with UV radiation in the presence of SrO/Cu₂O nano-composites and SrO/Cu₂O semiconductor mixture; PBQ formation with reagents

Reagent	Rate of PBQ formation, nM s ⁻¹	
	SrO / Cu ₂ O Nanocomposite	1:1 commercial mixture of SrO / Cu ₂ O
-	160.62	49.09
NAN ₃	159.91	48.98
HQ	183.08	74.44
TEA	198.74	64.92
TPP	189.19	77.31
Acrylamide	160.31	50.08
SLS	179.81	86.85
RB	290.86	94.08

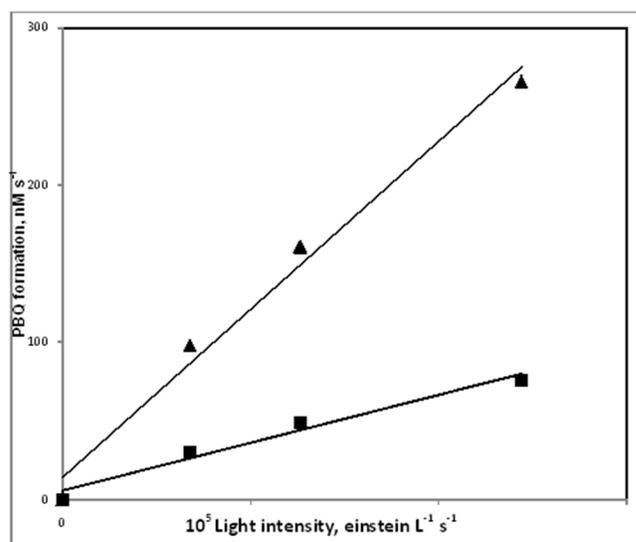


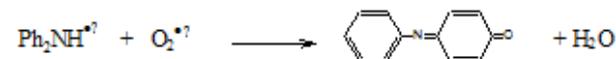
Figure 6. SrO/ Cu₂O nano-composites and SrO/ Cu₂O semiconductor mixture catalyzed UV photo-oxidation of diphenylamine at different light intensities.

with that different wavelength of light source, which indicates that the rate increases with decrease of wavelength due to the increase in energy gap.

3.3. Mechanism of the formation of PBQ

The bandgap excitation of semiconductors results in the creation of electron-hole pairs such as holes in the valence band and electrons in the conduction band. Illumination of the semiconductors with radiation of energy greater than the band-gap results in electron-hole pair generation [21].

Since the recombination of a photo-generated electron-hole pair in a semiconductor is so rapid (occurring in a picoseconds time scale), for effective photo-catalysis the reactants are to be adsorbed on the catalysts surface [15]. The hole reacts with the adsorbed DPA molecule to form DPA radical-cation (Ph₂NH^{•+}), while transfer to the adsorbed oxygen resulting in highly active superoxide radical-anion effectively removes the electron, O₂^{•-} [16]. The DPA radical-cation may react with superoxide radical-anion yielding PBQ and water molecules. And this mechanism is similar to the ZnO photo-catalyzed oxidation of aniline in ethanol [17].



The donor and acceptor adsorbed on the photo catalyst surface undergo photoexcitation followed by electron transfer. The donor excitation results in the transfer of excited electron whereas the acceptor excitation leads to an electron jump from the donor level to the vacant acceptor level [18].

3.4. Kinetic Law

The photo-catalysis on reactive as well as non-reactive surfaces requires adsorption of DPA and oxygen molecules on the catalyst surface. The rate of formation of PBQ is a function of : (i) the fraction of the surface adsorbed by the DPA molecule, (ii) the fraction of the surface on which oxygen molecule is adsorbed, (iii) the surface area of the catalyst, and (iv) the intensity of illumination. Hence,

$$\text{Rate} = \frac{kK_1K_2SI C[\text{Ph}_2\text{NH}]\gamma}{1 + K_1[\text{Ph}_2\text{NH}] + K_2\gamma + K_1K_2[\text{Ph}_2\text{NH}]\gamma}$$

Where, K_1 and K_2 are the adsorption coefficients of diphenylamine and oxygen molecules on the catalyst surface, k is the specific rate of oxidation of DPA, γ is the airflow rate, S the surface area of the catalyst bed and I is the intensity of light. The fitting of the experimental data to the Langmuir-Hinshelwood curve, drawn using a computer program based on saturation kinetics with respect to DPA and airflow rate, confirms the kinetic equation. The kinetic expression explains satisfactorily the product formation as a function of DPA concentration, the airflow rate and light intensity.

4. CONCLUSIONS

SrO/Cu₂O nanocomposites were synthesized by sol-gel method and characterized using SEM, EDAX, AFM and particle size analyzer. Photocatalytic activity of the prepared nanocomposites was evaluated towards the oxidation of DPA. The photocatalysis was examined as a function of concentration of DPA, airflow rate and intensity of illumination. The product formation is large with illumination at 254 nm than at 365 nm, which was analyzed using UV Visible spectrometer. The catalytic efficiencies of nanocomposites were nearly four times higher than that of commercial mixture of SrO/Cu₂O.

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