

Photodegradation Kinetics of Chloramphenicol in Silver nitroprusside suspension

Sibsankar Rahut¹, Jayanta Basu²*

¹Phd scholar, B-218, JCB hall, IIT campus, Kharagpur, India; ² Professor, A-173, IIT campus, Kharagpur, India *Corresponding author: jkb@che.iitkgp.ernet.in

- Silver nitroprusside was synthesized by simple ion exchange route.
- Morphology, crystallinity and optoelectronic property of the catalyst was studied.
- Chloramphenicol degradation was carried out in a cylindrical batch reactor.
- Rate equation was also established by non-linear regression.

1. Introduction

For the past few decades, semiconductor photocatalysis has attracted much attention towards removal of environmental contaminants from water as well as water splitting through direct solar irradiation. The utmost challenge in this area of research is to reduce the recombination of photogenerated hole and electron, so as to stabilize the steady state carrier concentration in photocatalyst. As a solution to this problem, photocatalyst principally requires two segments: a semiconductor for light absorption, and electro-catalyst (cocatalyst) to enhance carrier separation over the surface of semiconductor and participate in electrochemical reaction. In present study, silver nitroprusside (SINP) was found to be an excellent visible light photocatalyst. Linear sweep voltammetry also displays a very good electrocatalytic oxygen evolution reaction (OER) performance with a measured current density of 60 mA/cm² at an overpotential of 370 mV, which is beneficial for photocatalysis. Visible light photocatalytic test has been drawn by the degradation of an antibiotic drug, chloramphenicol (CAP). Photodegradation rate equation has also been established by non-linear regression.

2. Methods

Powder precipitation of silver nitroprusside (SINP) was obtained by ion-exchange route. All chemicals are analytical grade. Aqueous solutions (Ag/Na = 2:1) of sodium nitroprusside (Na₂[Fe(CN)₅NO], Merck, 99%) and silver nitrate (AgNO₃, Merck , 99%) were mixed and stirred under sonication for 1 h. A light pink color precipitate has been observed which was then centrifuged three times thoroughly with deionized water and then dried at 70° C under vacuum for 3 hours.

The photo catalytic degradation of CAP was studied in a 500 ml cylindrical glass reactor. A CFL lamp ($\lambda >$ 400 nm, Philips, India) with a cutoff filter was planted inside a quartz tube mounted centrally on the pivot of the reactor. All photodegradation experiments were carried out inside the annular space and the reaction blend was fomented by moderate air of 0.5 LPM at the base of the reactor by a peristaltic pump. Firstly, CAP was dissolved in 200 ml water in which 0.05 gm of SINP was dispersed by sonication. Initial concentration of CAP was kept at around 20 ppm for all experimental studies. The suspension was then mixed vigorously in absence of light for 2 hours to reach adsorption-desorption equilibrium. After irradiation, 3 ml of sample was collected at every 15 min and centrifuged at 10000 rpm for 10 minutes. Supernatant was transferred to a quartz Cuvette and analyzed by UV-vis spectrophotometer.

3. Results and discussion

PXRD pattern of silver nitroprusside was observed to determine the crystallinity and material identity. The surface morphology, accurate dispersion and particle sizes were examined by field electron scanning electron microscope (FESEM) and high resolution transmission electron microscopy (HRTEM). PL measurement was conducted to trace the photogenerated electron-hole recombination capability and defect density of the material.

A conventional three electrode cell was used for photo-electrochemical studies. First of all, 30 mg sample was sonicated with 9 ml ethanol, 1ml nafion. An ITO glass cell with an exposure of 1 cm^2 area was spin-



coated with SINP to fabricate a working electrode. A saturated calomel electrode (SCE) as reference electrode, and a Pt wire as counter electrode were connected to the CHI 643B electrochemical workstation using 1.0 M KOH solution as electrolyte. A 300 W Xe light covered with a cutoff channel ($\lambda > 400$ nm) was utilized as the illumination source. Cyclic voltammetry and linear sweep voltammetry were employed to observe the photoelectrochemical and electrochemical property of the material respectively. Based on tafel equation, A possible mechanism for electrochemical oxygen evolution is proposed.

 $\begin{array}{rcl} Ag_{2}[Fe(CN)_{5}NO] + OH & \leftrightarrows & Ag_{2}[Fe(CN)_{5}NO_{2}H] + e^{-} & \leftrightarrows & Ag_{2}[Fe(CN)_{5}NO_{2}]^{-} & + H_{2}O \\ & & 2 \ Ag_{2}[Fe(CN)_{5}NO_{2}]^{-} & - 2e^{-} & \leftrightarrows & 2 \ Ag_{2}[Fe(CN)_{5}NO] & + O_{2}\uparrow \end{array}$

81% degradation of chloramphenicol was achieved under visible light irradiation with a kinetic rate constant of 0.02 min⁻¹ presuming the photo-reaction as pseudo-first order kinetics, as shown in figure 1. CAP and O_2 molecules are adsorbed on the surface of the SINP particle. Then under visible light illumination, photoinduced electron-hole generation occurs. The holes in valence band sites directly oxidize water to form OH radical, which is the main active oxidation species for the degradation. Subsequently, O_2 molecules in the system directly get attacked by conduction band site to form another active species (O_2 ⁻), which then propagates the final product formation due to degradation of the CAP molecule. Rate equation was also generated by non-linear regression, as shown in Eq. 1.

$$\mathbf{r}_{A} = \mathbf{0.015C}_{A} \hat{\mathbf{C}}_{B}^{0.93}$$
 ------ (1)



Figure 1. (a) Photodegradation of chloramphenicol, (b) kinetics for Photodegradation

4. Conclusions

This work presents an opening ground for SINP towards semiconductor photocatalytic applications as well as electro-catalytic (oxygen evolution) applications. More generally, it recommends the methodology to fabricate novel photoelectrodes or photocatalysts. Since, all the results are reported for average particle sizes in the range 200-300 nm, further research can be initiated in the nanoscale (1-100 nm), so as to improve the photocatalytic and electrocatalytic activities of SINP. It can be predicted that photocatalytic activity of SINP can be more enhanced in nano scale with controlled morphology.

References

- A. Nurlaela, E.; Shinagawa, T.; Qureshi, M.; Dhawale, D.; Takanabe, K. Temperature Dependence of Electrocatalytic and Photocatalytic Oxygen Evolution Reaction Rates Using NiFe Oxide. ACS Catal 2016, 6, 1713-1722.
- [2] 2. Maeda, K.; Domen, K. Photocatalytic Water Splitting: Recent Progress and Future Challenges. J. Phys. Chem. Lett 2010, 1, 2655{2661.

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