

## Semiconductor catalysis of solar photooxidation

C. Karunakaran\* and S. Senthilvelan

Department of Chemistry, Annamalai University,  
Annamalainagar 608 002, India

**Cadmium oxide (CdO) photocatalyses the oxidation of aniline to azobenzene and shows sustainable catalytic activity. The reaction in ethanol was studied with natural sunlight and UV irradiation (365 nm) as a function of [aniline], catalyst loading, airflow rate, solvent composition, etc. The effects on the rate of solar oxidation are similar to those with UV light. The problem of fluctuation of sunlight intensity is overcome by carrying out a set of experiments simultaneously to compare the results. The yield of the product is higher with illumination at 254 rather than at 365 nm. Electron donors enhance photocatalysis and singlet oxygen quencher fails to inhibit catalysis. Photocatalysis occurs in protic as well as aprotic solvents. The mechanism of photocatalysis is discussed and the product formation analysed using a kinetic model.**

PHOTOCATALYTIC processes over semiconductor powders continue to receive considerable interest from the standpoint of solar energy utilization, but only a few studies involve natural sunlight, which are preliminary<sup>1</sup>. TiO<sub>2</sub> and ZnO are the most widely used photocatalysts, but they require UV light for activation<sup>2-4</sup>; solar UV light reaching the earth surface is relatively small (ca. 3–5%). Use of dye-sensitizers improves the performance of the photocatalyst and extends its light-absorption capacity to the visible portion of the solar spectrum<sup>5,6</sup>. However, the problem in chemical transformations is the cost and reuse; dye-sensitizers are only adsorbed over the photocatalyst. The bandgap energy<sup>7</sup> of cadmium oxide (CdO) is 2.1 eV and can be activated with visible light (<590 nm). Here we report the results of solar photocatalysis; the problem of fluctuation of sunlight intensity even under clear sky is overcome by conducting a set of experiments simultaneously to compare the results. Amines are used as sacrificial single-electron donors in many photoinduced redox studies<sup>2</sup> and hence the substrate for this study; air-equilibrated solution of aniline yields azobenzene on irradiation at 365 nm with benzophenone sensitizing the oxidation<sup>8,9</sup>. UV-irradiated ZnO catalyses the oxidation of aniline to azobenzene<sup>10,11</sup> and aniline undergoes photocatalytic degradation on TiO<sub>2</sub> immobilized on porous nickel<sup>12</sup>.

CdO (Chemco) was used as supplied and the BET surface area was determined as 14.45 m<sup>2</sup> g<sup>-1</sup>. The particle sizes were measured using Easy particle sizer M1.2, Malvern Instruments (focal length 100 mm, beam length 2.0 mm, wet (methanol) presentation) as 11.4, 9.8, 8.5, 4.1, 3.5,

3.0, 2.6  $\mu$ m at 3.0, 44.2, 8.6, 3.3, 10.4, 23.5, 6.4% respectively. Aniline, AR was distilled before use. Commercially available ethanol was distilled over calcium oxide; other organic solvents were of LR grade and distilled prior to use.

The solar photocatalysed oxidations were made from 10.30 a.m. to 12.30 p.m. during summer (March–July) under clear sky. The intensity of solar radiation was measured using Global pyranometer, MCPT, supplied by Industrial Meters, Mumbai. Fresh solutions of aniline of desired concentrations were taken in wide cylindrical glass vessels of uniform diameter and appropriate height; the catalyst powder covered the entire bottom of the vessel. Air was bubbled using a micro pump without disturbing the catalyst bed. The volume of the reaction solution was kept as 25 ml and the loss of solvent due to evaporation was compensated periodically. One millilitre of the reaction solution was withdrawn at regular intervals, diluted five times and the absorbance measured at 375 nm using Hitachi U-2001 UV–Vis spectrophotometer.

Photocatalytic studies with UV light were carried out in a multilamp photoreactor (HML MP88, supplied by Heber Scientific, Chennai) fitted with eight 8 W mercury UV lamps of wavelength 365 nm (Sankyo Denki, Japan) and highly polished anodized aluminum reflector; the sample was placed at the centre. Four cooling fans at the bottom of the reactor dissipate the generated heat. The reaction vessel was a borosilicate glass tube of 15 mm inner diameter. Photooxidation was also carried out in a micro photoreactor (HMI SL W6, supplied by Heber Scientific) fitted with a 6 W, 254 nm, low-pressure mercury lamp and a 6 W, 365 nm mercury lamp. Quartz and borosilicate glass tubes were used for 254 and 365 nm lamps respectively. The light intensity ( $I_0$ ) was determined by ferrioxalate actinometry.

The volume of the reaction solution was always maintained as 25 ml in the multilamp photoreactor and 10 ml in the micro reactor. Air was bubbled through the reaction solution that effectively stirs the solution and keeps the suspended catalyst under constant motion. Absorbance was measured at 375 nm after centrifuging the catalyst and diluting the solution five times to keep the absorbance within the limits of the Beer–Lambert law.

Solar photooxidation of aniline in ethanol on CdO yields azobenzene as the only product. The GC-mass, IR and UV–Vis spectra of the extracted solid product are identical with those of *trans*-azobenzene (Fluka).

In both solar and UV photocatalysis, the UV–Vis spectra of the reaction solution recorded during the progress of the reaction are similar (Figure 1;  $\lambda_{\text{max}}$  = 375 nm), but not identical with that of the extracted solid product ( $\lambda_{\text{max}}$  = 434 nm). This is because of the formation of both *cis* and *trans*-azobenzenes during the course of the reaction, and the unstable *cis* form (*Z*) transforms to the *trans* form (*E*) slowly on standing. The UV–Vis spectrum of the irradiated reaction solution allowed to stand for a few days in dark is identical with that of the authentic *trans*-azobenzene,

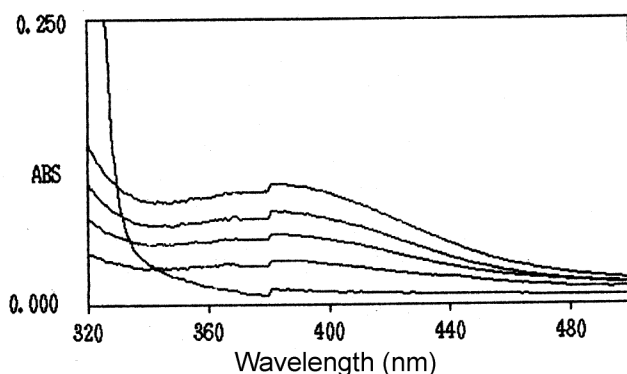
\*For correspondence. (e-mail: karunakaran@rediffmail.com)

confirming the slow transformation of the unstable *cis* form to *trans* form. For a solution of *cis* and *trans*-azo-benzenes,

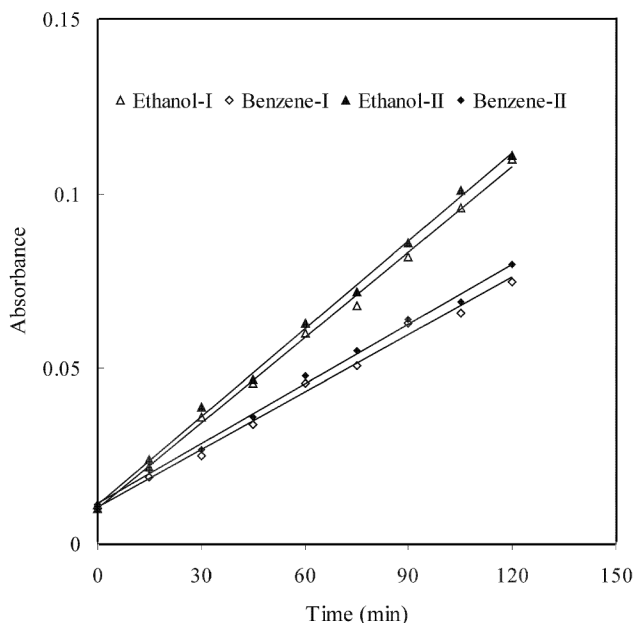
$$[E] = (\text{abs}_{281}\epsilon_{Z(433)} - \text{abs}_{433}\epsilon_{Z(281)})/(\epsilon_{E(281)}\epsilon_{Z(433)} - \epsilon_{Z(281)}\epsilon_{E(433)}) \text{ and}$$

$$[Z] = (\text{abs}_{281}\epsilon_{E(433)} - \text{abs}_{433}\epsilon_{E(281)})/(\epsilon_{Z(281)}\epsilon_{E(433)} - \epsilon_{Z(433)}\epsilon_{E(281)}),$$

where  $\epsilon$  is the corresponding molar extinction coefficient. Calculation of the ratio  $[E]/[Z]$  using the above equations,



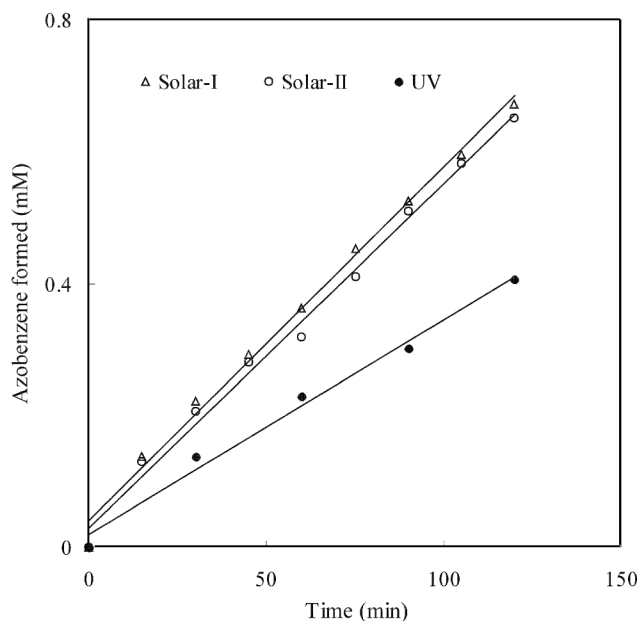
**Figure 1.** Solar photooxidation of aniline in ethanol on CdO. UV-Vis spectra of the reaction solution, diluted five times and recorded at 0, 30, 60, 90 and 120 min (); [aniline] = 0.113 M, CdO bed = 12.5 cm<sup>2</sup>, weight of CdO = 1.0 g, airflow rate = 4.75 ml s<sup>-1</sup>, volume of reaction solution = 25 ml.



**Figure 2.** Solar photooxidation of aniline in ethanol and benzene on CdO. Absorbance-time plots (experiments in each set were conducted simultaneously and sets I and II on different days; the reaction solution was diluted five times prior to absorbance measurements); [aniline] = 0.113 M, CdO bed = 12.5 cm<sup>2</sup>, weight of CdO = 1.0 g, airflow rate = 4.75 ml s<sup>-1</sup>, volume of reaction solution = 25 ml.

the experimentally determined  $\epsilon_{E(433)}$  and  $\epsilon_{E(281)}$ , the reported  $\epsilon_{Z(433)}$  and  $\epsilon_{Z(281)}$  and the measured absorbance of the reaction solution at 433 and 281 nm at different periods of the reaction shows that the ratio remains practically the same (1.86) during the course of photooxidation. The total concentration of azobenzene,  $([E] + [Z]) = \text{abs}_{375} \{1 + ([E]/[Z])\} / \{\epsilon_{Z(375)} + \epsilon_{E(375)}([E]/[Z])\}$ ;  $\epsilon_{E(375)}$  was determined experimentally and  $\epsilon_{Z(375)}$  calculated from the measured  $\text{abs}_{375}$ ;  $\text{abs}_{375} = \{\epsilon_{Z(375)} + \epsilon_{E(375)}([E]/[Z])\}[Z]$ .

The measurement of solar radiation shows fluctuation of sunlight intensity ( $530 \pm 40 \text{ W m}^{-2}$ ) during the course of photooxidation, even under clear sky. Now, identical sunlight intensity was maintained for a set of photooxidation experiments of different reaction conditions by performing the experiments simultaneously, thus making possible the comparison of the solar results. The solar photooxidation results are reproducible. For example, Figure 2 is the linear increase of absorbance of the reaction solution with reaction time; one set of experiments was conducted in ethanol and benzene side by side on one day and the other set similarly on another day. The ratio of the slopes of the absorbance-time profiles of the reactions in ethanol and benzene remains the same (1.5), although the experiments were conducted on different days, obviously under different sunlight intensities. This reproducibility is not surprising, as the fluctuation of sunlight intensity is identical in test and control (standard) experiments and the ratio turns out to be independent of fluctuation of intensity. Further, the results of a pair of experiments performed simultaneously confirm the reproducibility of the rates of solar photocatalysis. Figure 3 presents the solar photoformation of azobenzene



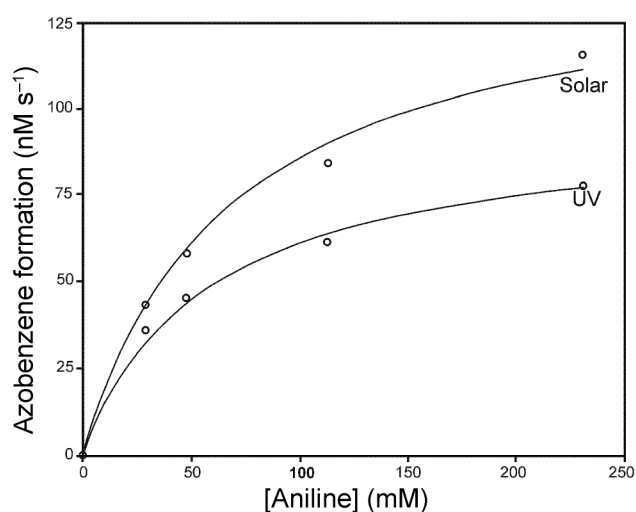
**Figure 3.** Photoformation of azobenzene in ethanol on CdO; [aniline] = 0.113 M, weight of CdO = 1.0 g, volume of reaction solution = 25 ml, airflow rate = 4.75 ml s<sup>-1</sup>; solar: CdO bed = 12.5 cm<sup>2</sup>; UV:  $\lambda = 365 \text{ nm}$ ,  $I_0 = 2.46 \times 10^{-5} \text{ einstein l}^{-1} \text{ s}^{-1}$ .

in ethanol under identical conditions and carried out simultaneously. The ratio of the rates obtained from the linear plots is unity (1.04).

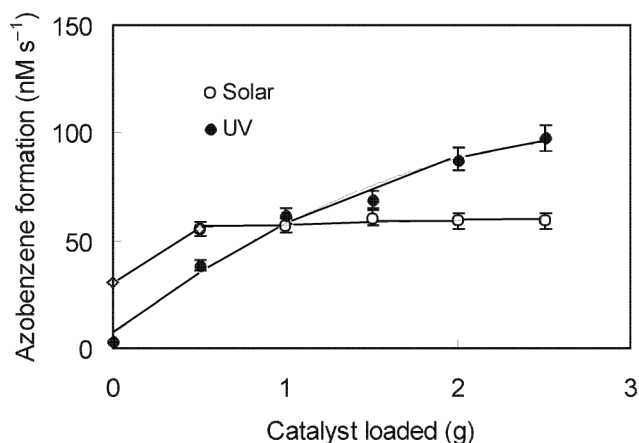
The influence of various factors on the solar photocatalysis in ethanol was examined by carrying out the given set of experiments simultaneously; data in each figure correspond to a set of photocatalytic experiments conducted simultaneously. The least squares slope of the linear plot of [azobenzene] versus time (e.g. Figure 3) yields the rate of formation of azobenzene. Experiments at different concentrations of aniline show that the reaction rate increases with [aniline] (Figure 4) and the variation conforms to the Langmuir–Hinshelwood model. The double reciprocal plot of rate versus [aniline] yields a straight line with a positive  $y$ -intercept. The variation in the amount of CdO spread at the bottom of the reaction vessel (catalytic bed) does not lead to any appreciable change in the photocatalysis rate (Figure 5); the bottom of the cylindrical reaction vessel was fully covered by the catalyst in all the cases and increase in the amount of CdO does not lead to increase in the area of the catalyst bed, but only results in increased thickness of the CdO bed. In the absence of the photocatalyst, the reaction is an uncatalysed one and hence the small rate. The photoformation of azobenzene increases linearly with the apparent area of the catalyst bed (Figure 6). Study of the photooxidation as a function of airflow rate reveals enhancement of photocatalysis by oxygen (Figure 7). The variation of reaction rate with airflow rate indicates Langmuir–Hinshelwood kinetics and the linear double reciprocal plot of reaction rate versus airflow rate confirms the same. The reaction was also studied without bubbling air, but the solution was not deaerated. The dissolved oxygen itself brings in the oxidation, but the photocatalysis is weak. The reaction does not occur in dark. The photocatalyst

does not lose its catalytic activity on repeated use. Reuse of the photocatalyst yields identical results. Addition of water to the reaction medium slows down the reaction (Figure 8).

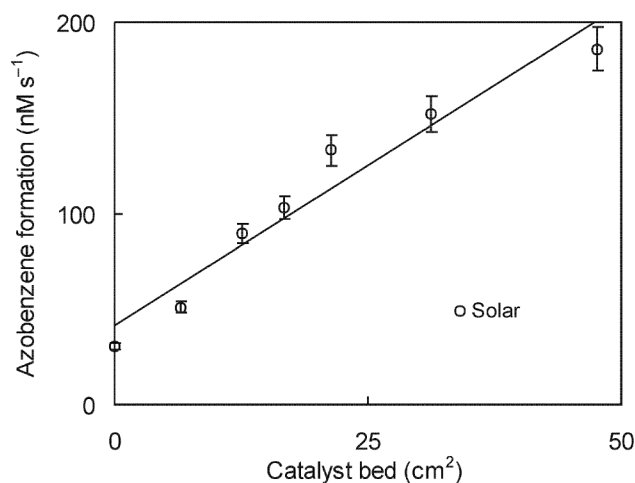
Electron donors like triphenylphosphine (TPP), hydroquinone (HQ), diphenylamine (DPA) and triethylamine (TEA), enhance the photoformation of azobenzene. Addition of 0.287 M TEA to the reaction solution increases the azobenzene formation rate by ca. 165% (the reaction conditions as in Figure 9). Variation of the enhanced photoformation rate with [TPP], [HQ] and [DPA] (Figure 9) reveals the Langmuir–Hinshelwood kinetics, and the linear double reciprocal plots of the enhanced rate versus [TPP], [HQ] and [DPA] confirm the same. Use of sacrificial electron donors leads to hole-trapping, resulting in enhanced photocatalysis<sup>2</sup>. Both anionic and cationic surfactants enhance the photocatalysis; addition of aerosol OT (sodium *bis*-2-ethylhexyl sulphosuccinate, 0.0225 M), sodium lauryl



**Figure 4.** Azobenzene formation in ethanol on CdO at different [aniline]; weight of CdO = 1.0 g, volume of reaction solution = 25 ml, airflow rate = 4.75 (solar), 7.8 (UV) ml s<sup>-1</sup>; solar: CdO bed = 12.5 cm<sup>2</sup>; UV:  $\lambda = 365$  nm,  $I_0 = 2.46 \times 10^{-5}$  einstein l<sup>-1</sup> s<sup>-1</sup>.



**Figure 5.** Azobenzene formation in ethanol at different amounts of CdO loading; [aniline] = 0.113 M, volume of reaction solution = 25 ml, airflow rate = 4.75 (solar), 7.8 (UV) ml s<sup>-1</sup>; solar: CdO bed = 12.5 cm<sup>2</sup>; UV:  $\lambda = 365$  nm,  $I_0 = 2.46 \times 10^{-5}$  einstein l<sup>-1</sup> s<sup>-1</sup>.



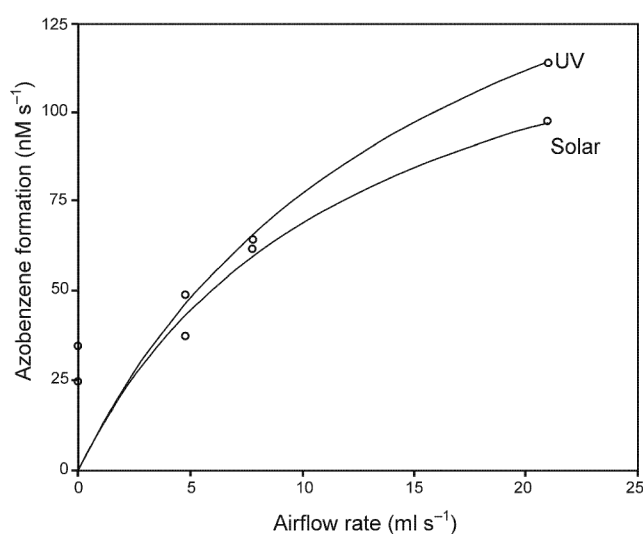
**Figure 6.** Azobenzene formation (solar) in ethanol at varying areas of CdO bed; [aniline] = 0.113 M, weight of CdO = 1.0 g, volume of reaction solution = 25 ml, airflow rate = 4.75 ml s<sup>-1</sup>.

sulphate (SLS, 0.0347 M) and cetyltrimethylammonium bromide (CTAB, 0.0274 M) to the reaction solution (conditions as in Figure 9) increases the photoformation rate by 21, 127 and 83% respectively. Vinyl monomers like acrylonitrile (0.608 M) and acrylamide (0.141 M) neither suppress the photocatalysis nor undergo polymerization, indicating the absence of free radicals in the reaction solution during the course of photocatalysis.

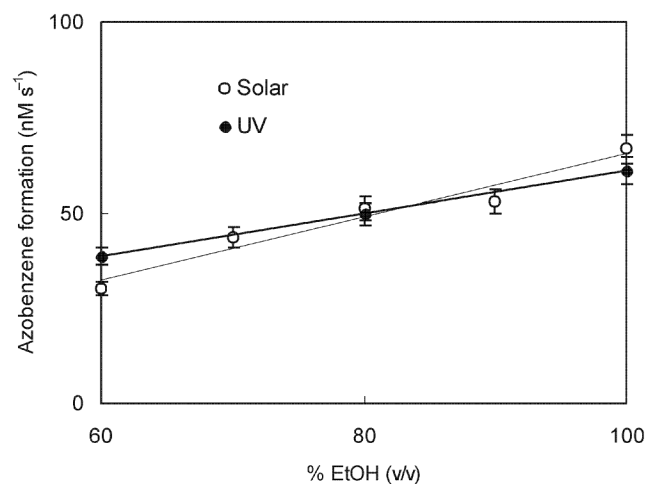
CdO photocatalyses the oxidation in *n*-butanol, *t*-butanol, propane-1,2-diol, 2-butoxyethanol, ethyl methyl ketone, acetic acid, dimethylformamide, acetonitrile, ethyl acetate, 1,4-dioxane, benzene, toluene, chlorobenzene, nitrobenzene, *n*-hexane, chloroform and carbon tetrachloride, besides

ethanol as seen from the UV-Vis spectra of the reaction solutions at different illumination times ( $[\text{PhNH}_2] = 0.113 \text{ M}$ , CdO suspended = 1.0 g, airflow rate =  $7.8 \text{ ml s}^{-1}$ ,  $\lambda = 365 \text{ nm}$ ,  $I_0 = 2.46 \times 10^{-5} \text{ einstein l}^{-1} \text{ s}^{-1}$ , volume of reaction solution = 25 ml).

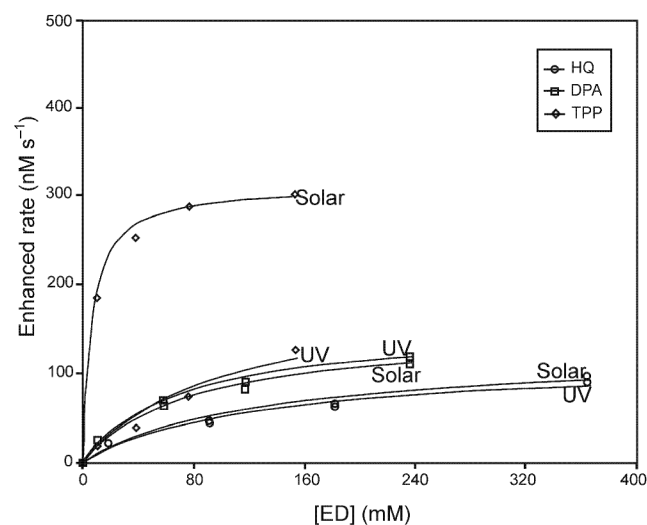
The photocatalysed oxidation of aniline in ethanol in the presence of air on CdO was studied using a multilamp photoreactor with mercury UV lamps of wavelength 365 nm. Linear increase of azobenzene concentration with illumination time yields the photochemical formation rate (e.g. Figure 3) and the rates are reproducible to  $\pm 6\%$ . Rate measurements at different [aniline] show increase in the oxidation rate with [aniline] (Figure 4) and the increase is



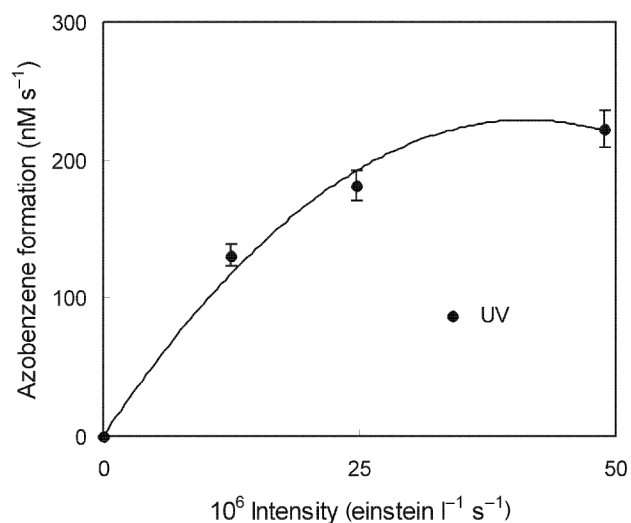
**Figure 7.** Azobenzene formation in ethanol on CdO at different airflow rates; [aniline] = 0.113 M, weight of CdO = 1.0 g, volume of reaction solution = 25 ml; solar: CdO bed =  $12.5 \text{ cm}^2$ ; UV:  $\lambda = 365 \text{ nm}$ ,  $I_0 = 2.46 \times 10^{-5} \text{ einstein l}^{-1} \text{ s}^{-1}$ .



**Figure 8.** Azobenzene formation on CdO in aq. EtOH; [aniline] = 0.113 M, weight of CdO = 1.0 g, volume of reaction solution = 25 ml, airflow rate = 4.75 (solar), 7.8 (UV)  $\text{ml s}^{-1}$ ; solar: CdO bed =  $12.5 \text{ cm}^2$ ; UV:  $\lambda = 365 \text{ nm}$ ,  $I_0 = 2.46 \times 10^{-5} \text{ einstein l}^{-1} \text{ s}^{-1}$ .



**Figure 9.** Azobenzene formation in ethanol on CdO in the presence of electron donors (ED); [aniline] = 0.113 M, weight of CdO = 1.0 g, volume of reaction solution = 25 ml, airflow rate = 4.75 (solar), 7.8 (UV)  $\text{ml s}^{-1}$ ; solar: CdO bed =  $12.5 \text{ cm}^2$ ; UV:  $\lambda = 365 \text{ nm}$ ,  $I_0 = 2.46 \times 10^{-5} \text{ einstein l}^{-1} \text{ s}^{-1}$ .



**Figure 10.** Azobenzene formation in ethanol on CdO at different light intensities; [aniline] = 0.113 M, CdO suspended = 1.0 g, airflow rate =  $7.8 \text{ ml s}^{-1}$ ,  $\lambda = 365 \text{ nm}$ , volume of reaction solution = 25 ml.

according to the Langmuir–Hinshelwood kinetics. Increase in the amount of CdO suspended in the reaction medium leads to increased azobenzene formation, but the rate reaches a limit at high catalyst loading (Figure 5). Study of the photooxidation as a function of airflow rate reveals enhancement of photocatalysis by oxygen and the variation of the reaction rate with flow rate conforms to the Langmuir–Hinshelwood kinetics (Figure 7). The reaction was also studied without bubbling air, but the solution was not deoxygenated. The dissolved oxygen itself brings in the oxidation, but the photocatalysis is slow.

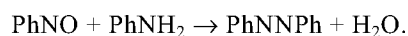
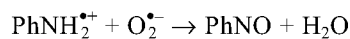
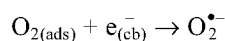
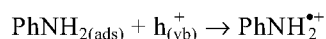
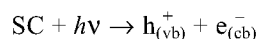
The photooxidation was examined as function of light intensity. Oxidation was carried out with two, four and eight lamps; the angles sustained by the adjacent lamps at the sample are 180, 90 and 45° respectively. Figure 10 presents the variation of rate with light intensity. The reaction does not occur in dark. Investigation of photocatalysis using a 6 W, 365 nm mercury lamp ( $I_0 = 1.81 \times 10^{-5}$  einstein  $\text{l}^{-1} \text{s}^{-1}$ ) and a 6 W, 254 nm, low-pressure mercury lamp ( $I_0 = 5.22 \times 10^{-6}$  einstein  $\text{l}^{-1} \text{s}^{-1}$ ) separately in the micro reactor under identical conditions reveals that high-energy radiation is more effective in bringing out the photocatalysis. Azobenzene formed in 10 min on illumination at 365 and 254 nm is 95 and 363  $\mu\text{M}$  respectively, ( $[\text{aniline}] = 0.113 \text{ M}$ , CdO suspended = 0.2 g, airflow rate = 7.8  $\text{ml s}^{-1}$ , volume of reaction solution = 10 ml). The metal oxide does not lose its photocatalytic activity on illumination. Reuse of the catalyst reveals sustainable photocatalytic efficiency. Addition of water to the reaction solution suppresses the photocatalysis (Figure 8).

Electron donors like TPP, HQ, DPA and TEA enhance azobenzene formation. Variation in the enhanced photocatalysis rate with [TPP], [HQ] and [DPA] suggests Langmuir–Hinshelwood kinetics (Figure 9). Addition of TEA (0.287 M) to the reaction mixture doubles the rate of azobenzene formation. Aerosol OT (0.0225 M), SLS (0.0347 M) and CTAB (0.0274 M) enhance photocatalysis with UV light by 82, 67 and 16% respectively. Also, vinyl monomers like acrylonitrile (0.608 M) and acrylamide (0.141 M) fail to inhibit the photocatalysis, nor do they polymerize. Azide ion (0.154 M), a singlet oxygen quencher, fails to suppress the formation of azobenzene, indicating the absence of involvement of singlet oxygen in photocatalysis (conditions as in Figure 9).

Photooxidation on CdO surfaces with UV light also occurs in *n*-butanol, *t*-butanol, propane-1,2-diol, 2-butoxyethanol, ethyl methyl ketone, acetic acid, dimethylformamide, acetonitrile, ethyl acetate, 1,4-dioxane, benzene, toluene, chlorobenzene, nitrobenzene, *n*-hexane, chloroform and carbon tetrachloride, as shown by the UV–Vis spectra of the reaction solutions at different illumination times.

The bandgap energy<sup>7</sup> of CdO is 2.1 eV. Illumination of the semiconductor with light of energy greater than the bandgap leads to bandgap excitation of the semiconductor, resulting in the creation of electron–hole pairs; holes in the valence band and electrons in the conductance band.

Since the recombination of photogenerated electron–hole pairs in semiconductors is so rapid (occurring in a pico-second timescale), for an effective photocatalysis the reactants are to be adsorbed on the photocatalyst<sup>13</sup>. The hole reacts with adsorbed aniline molecule to form aniline radical-cation ( $\text{PhNH}_2^{\bullet+}$ ). In the presence of oxygen, transfer to the adsorbed oxygen molecule resulting in highly active superoxide radical-anion,  $\text{O}_2^{\bullet-}$ , effectively removes the electron<sup>2</sup>. The reaction of aniline radical-cation with superoxide radical-anion results in nitrosobenzene. Condensation of nitrosobenzene with aniline, present in large excess, yields azobenzene.



Ethanol may undergo oxidation in the presence of an illuminated semiconductor and generation of radicals is possible<sup>14,15</sup>. If the photooxidation of aniline were due to the radicals generated from solvent ethanol, contrary to the experimental observations, azobenzene formation should not depend on [aniline]. The photogenerated radicals are short-lived and react almost instantaneously, demanding non-dependence of the reaction rate on [aniline]. Also, the oxidation occurs in a number of organic solvents.

The kinetic law that governs heterogeneous photocatalysed reaction in a continuously stirred tank reactor<sup>16</sup> is,

$$\text{Rate} = kK_1K_2SI_0C[\text{PhNH}_2]\gamma/(1 + K_1[\text{PhNH}_2])(1 + K_2\gamma),$$

where  $K_1$  and  $K_2$  are the adsorption coefficients of aniline and oxygen on CdO,  $k$  is the specific rate of oxidation of aniline,  $\gamma$  is the airflow rate,  $S$  is the specific surface area of CdO,  $C$  is the amount of CdO suspended per litre and  $I_0$  is the light intensity in einstein  $\text{l}^{-1} \text{s}^{-1}$ . The linear double reciprocal plots of rate of azobenzene formation versus (i)  $[\text{PhNH}_2]$  and (ii) airflow rate are in agreement with the kinetic law and afford the adsorption coefficients as  $K_1 = 23 \text{ l mol}^{-1}$ ,  $K_2 = 0.08 \text{ ml}^{-1} \text{ s}$ ;  $k = 20 \mu\text{mol l m}^{-2} \text{ einstein}^{-1}$ . The data-fit to the curves (Figures 4 and 7), drawn according to the above kinetic law using a computer program, supports the rate equation. However, the rate of photocatalysis fails to vary linearly with the amount of CdO suspended. This is because of the high catalyst loading. At high catalyst loading, the surface area of the catalyst exposed to illumination does not commensurate with the weight of the catalyst. The amount of CdO employed is beyond the critical amount corresponding to the volume of the reaction solution and reaction vessel; the whole amount of CdO is

not exposed to illumination. Photocatalysis lacks linear dependence on illumination intensity; less than first power dependence of surface-photocatalysis rate on light intensity at high intensity is well known<sup>17</sup>.

1. Karapire, C., Kolancilar, H., Oyman, U. and Icli, S., Fluorescence emission and photooxidation studies with 5,6- and 6,7-benzocoumarins and a 5,6-benzochromone under direct and concentrated sunlight. *J. Photochem. Photobiol. A*, 2002, **153**, 173–184.
2. Srinivasan, C., Oxygenation and deoxygenation of organic compounds on irradiated semiconductor catalyst, TiO<sub>2</sub>. *Curr. Sci.*, 1999, **76**, 534–539.
3. Nageswara Rao, N. and Natarajan, P., Particulate models in heterogeneous photocatalysis. *Curr. Sci.*, 1994, **66**, 742–752.
4. Fox, M. A. and Dulay, M. T., Heterogeneous photocatalysis. *Chem. Rev.*, 1993, **93**, 341.
5. Zakeeruddin, S. M. *et al.*, Design, synthesis, and application of amphiphilic ruthenium polypyridyl photosensitizers in solar cells based on nanocrystalline TiO<sub>2</sub> films. *Langmuir*, 2002, **18**, 952–954.
6. Iliev, V., Tomova, D., Bilyarska, L., Pirahov, L. and Petrov, L., Phthalocyanine modified TiO<sub>2</sub> or WO<sub>3</sub>-catalysts for photooxidation of sulfide and thiosulfate ions upon irradiation with visible light. *J. Photochem. Photobiol. A*, 2003, **159**, 281–287.
7. Kamat, P. V., Photochemistry on nonreactive and reactive (semiconductor) surfaces. *Chem. Rev.*, 1993, **93**, 267–300.
8. Santhanam, K. and Ramakrishnan, V., Photosensitized oxidation of aniline. *Indian J. Chem.*, 1968, **6**, 88–90; A mechanistic study of the photosensitized oxidation of aniline. *Indian J. Chem.*, 1972, **10**, 927–928.
9. Davidson, R. S., Lambeth, P. F. and Santhanam, M., The photoreactions of aromatic carbonyl compounds with amines. Part II. The reactions of triplet benzophenone and other ketones with primary and secondary aromatic amines. *J. Chem. Soc. Perkin Trans. 2*, 1972, 2351–2355.
10. Hema, M. A., Ramakrishnan, V. and Kuriacose, J. C., Photocatalysed oxidation of aniline by zinc oxide. *Indian J. Chem. B*, 1977, **15**, 947–949.
11. Hema Kasturirangan, Ramakrishnan, V. and Kuriacose, J. C., Photosensitized reactions of toluidines on zinc oxide. *J. Catal.*, 1981, **69**, 216–217; Oxidation of toluidines on illuminated zinc oxide surfaces. *Indian J. Technol.*, 1981, **19**, 327–329.
12. Wenhua, L., Hong, L., Sao'an, C., Jianqing, Z. and Chunan, C., Kinetics of photocatalytic degradation of aniline in water over TiO<sub>2</sub> supported on porous nickel. *J. Photochem. Photobiol. A*, 2000, **131**, 125–132.
13. Linsebigler, A. L., Lu, G. and Yates, Jr. J. T., Photocatalysis on TiO<sub>2</sub> surfaces: Principles, mechanism, and selected results. *Chem. Rev.*, 1995, **95**, 735–758.
14. Müller, B. R., Majoni, S., Memming, R. and Meissner, D., Particle size and surface chemistry in photoelectrochemical reactions at semiconductor particles. *J. Phys. Chem. B*, 1997, **101**, 2501–2507.
15. Iseda, K., Towata, A., Watanabe, E., Fukaya, M. and Taova, H., Relationship between the yields of products from ethanol over titanium dioxide and the quantity of light. *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1249–1253.
16. Karunakaran, C., Senthilvelan, S., Karuthapandian, S. and Balaraman, K., Photooxidation of iodide ion on some semiconductor and non-semiconductor surfaces. *Catal. Commun.*, 2004, **5**, 283–290.
17. Vincze, L. and Kemp, T. J., Light flux and light flux density dependence of the photomineralization rate of 2,4-dichlorophenol and chloroacetic acid in the presence of TiO<sub>2</sub>. *J. Photochem. Photobiol. A*, 1995, **87**, 257–260.

## Angiotensin-converting enzyme insertion/deletion genotype is associated with premature coronary artery disease in Indian population

C. Emmanuel<sup>1</sup>, S. Kanthimathi<sup>2</sup>, R. Saibabu<sup>1</sup>, K. M. Cherian<sup>1</sup> and A. Ramesh<sup>2,\*</sup>

<sup>1</sup>International Centre for CardioThoracic and Vascular Diseases, Frontier Life Line, R-30-C, Ambattur Industrial Estate Road, Chennai 600 101, India

<sup>2</sup>Department of Genetics, Post Graduate Institute of Basic Medical Sciences, University of Madras, Taramani Campus, Chennai 600 113, India

**The insertion/deletion polymorphism of angiotensin-converting enzyme (ACE) gene has been implicated in the pathogenesis of cardiovascular diseases. However, the precise association between them remains unclear. The objective of the present study was to find the influence of angiotensin-converting enzyme (insertion/deletion) polymorphism on cardiovascular diseases. We genotyped the *Alu* insertion/deletion of the ACE gene in 434 patients and 500 control subjects. Information on severity of vessel disease, clinical status, age, smoking and alcohol status, lipid profile and body mass index was also collected. The present study indicated a significant association of coronary artery diseases (CADs) with *Alu* ACE insertion/deletion polymorphism, located in the intron 16 region of the ACE gene. Thus, we identified a clinical subgroup of CAD patients, characterized with triple vessel defect and most often associated with diabetes.**

ANGIOTENSIN-converting enzyme (EC 3.4.15.1; dipeptidyl carboxypeptidase) is a zinc metallopeptidase which cleaves the C-terminal dipeptide (His–Leu) from angiotensin 1 and generates a vasoconstrictor<sup>1</sup>, angiotensin II. Through protease activity it also inactivates bradykinin, which is a potent vasodilator. Due to its role in the renin-angiotensin-aldosterone system, human vascular tone and blood salt/water balance have been maintained. The gene for angiotensin converting enzyme (ACE) has been mapped to chromosome 17q23 and comprises 26 exons and 25 introns<sup>2,3</sup>. The activity of ACE was strongly influenced by a quantitative trait locus which is in linkage disequilibrium with the *Alu* insertion/deletion (I/D) marker<sup>4–7</sup> in intron 16. A relationship between D-allele dose and enzymatic levels was established for both circulating and cellular ACE<sup>8–13</sup>. Numerous studies reported association of D-allele with cardiovascular diseases<sup>14–17</sup>, in addition to the diseases like non-insulin-dependent diabetes mellitus, nephropathy<sup>18–20</sup>, knee osteoarthritis<sup>21</sup> and breast cancer<sup>22,23</sup>. However, this association was not observed in all the studies<sup>24–29</sup>. Thus, there has been a considerable controversy over the association of ACE (I/D) polymorphism and disease status. Also, the influence of the

Received 2 August 2004; revised accepted 16 November 2004

\*For correspondence. (e-mail: arabandir@yahoo.co.in)