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Solar-driven electrochemically assisted semiconductor-catalyzed iodide ion oxidation. Enhanced efficiency by oxide mixtures

Research Article

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Abstract: Oxidation of iodide ion from an air-saturated solution under natural sunlight (900±50 W m^{-2}) on the surfaces of TiO_2, ZnO, Fe_2O_3, MoO_3 and CeO_2 enhances by 6 to 12-fold on application of a cathodic bias of -0.2 to -0.3 V (*vs* NHE) to the semiconductors; light, the semiconductor and dissolved oxygen are essential for iodine generation. The semiconductors under an anodic bias of +0.2 to +0.3 V (*vs* NHE) fail to oxidize iodide ion from air-saturated solution under sunlight. Under cathodic bias, semiconductor mixtures like TiO_2-ZnO, TiO_2-Fe_2O_3 and ZnO-Fe_2O_3 show enhanced photocatalytic activity, indicating improved charge separation in oxide mixtures. The mechanism of photocatalysis under cathodic bias is discussed.

Keywords: *Semiconductor • Photocatalysis • Potential bias • Sunlight*

1. Introduction

Semiconductor-photocatalysis is of interest due to its potential to tap solar radiation. Band gap-illumination of semiconductor generates electron-hole pairs, electrons in the conduction band and holes in the valence band [1]. A portion of these electron-hole pairs diffuses out to the surface of the crystal and participates in chemical reactions with electron donors and acceptors, resulting in photocatalysis. Application of a small potential bias to an illuminated semiconductor suppresses the recombination of the electron-hole pairs and thus enhances the photocatalytic efficiency [2-4]. We report for the first time, enhanced photocatalysis with semiconductor under cathodic bias using natural sunlight. Reports on photocatalysis using natural sunlight are rare, probably due to the fluctuation of sunlight intensity even under clear sky on sunny days during the period of the experiment. We have overcome the same by carrying out a set of experiments under the required experimental conditions simultaneously, side by side, thereby making the sunlight irradiances in the set of experiments identical. In our experiments with natural sunlight we observe that semiconductor mixtures, due to enhanced charge separation, show better photocatalysis under potential bias. Production of energy bearing chemicals through thermodynamically uphill reactions is the objective of solar energy conversion and storage and iodide ion-oxidation is one such reaction (ΔG° = +51.6 kJ mol^{-1}). Photooxidation of iodide ion on TiO_2 [5-8], Pt-loaded TiO_2 [9], TiO_2 sensitized by phthalocyanines [10] and flower pigment cyanidine [11], MoO_3, Fe_2O_3 and ZnO [5-7] have been reported but they are in absence of any potential bias.

2. Experimental Procedures

2.1. Materials

TiO_2 (Merck), ZnO (Merck), MoO_3 (Sd fine), Fe_2O_3 (Fischer) and CeO_2 (Sd fine) were of analytical grade and used as received.

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2.2. Methods

The solar photooxidation of iodide ion using semiconductors under potential bias was made with AM 1 sunlight under clear sky in summer (March – July). The intensity of sunlight was measured using a Daystar Solar Meter (USA). For each experiment, fresh air-saturated KI solution (50 mL) was taken in wide cylindrical glass vessels of uniform diameter, fitted with a copper bottom, which was fully covered by the catalyst [12,13]. The concentration of the dissolved oxygen was determined using an Elico dissolved oxygen analyzer PE 135 (India). A potential bias was applied to the semiconductor bed using a DC power supply and was measured against SCE employing a potentiostat with copper wire as the counter-electrode. The iodine formed was determined from the absorbance of the 30-min illuminated KI solution, measured at 350 nm using a Shimadzu 1650 PC spectrophotometer, as previously reported [5-7].

3. Results and Discussion

3.1. Catalysts characterization

Powder XRD studies were made with a Bruker D8 system using Cu K_α radiation of 1.5406 Å in a 2θ range of 5-60° at a scan speed of 0.050° s^{-1} or with a PANalytical X'Pert PRO diffractometer using Cu K_α rays at 1.5406 Å in a 2θ range of 15-75° with a scan rate of 0.020° s^{-1}. The XRD pattern of the TiO_2 used is identical with the standard pattern of anatase (JCPDS 01-078-2486 C) and the rutile lines (01-089-0553 C) are absent. This clearly reveals that the TiO_2 used in this study is of anatase phase. The XRD of ZnO is that of the JCPDS pattern of zincite (00-005-0664 D). The diffraction pattern of CeO_2 reveals its crystal structure as face centered cubic system with a = 5.411 Å and α = 90.0° and matches with the standard JCPDS pattern (898436). The particle sizes, measured using particle sizer Horiba LA-910 or Malvern 3600E (focal length 100 mm, beam length 2.0 mm, wet (methanol) presentation) are as follows: TiO_2: 27.6, 23.8, 20.5, 17.7, 9.8, 8.5, 7.3, 4.1, 3.5, 3.0, 2.6 μm at 9.1, 18.0, 15.0, 1.4, 12.1, 17.7, 10.5, 1.2, 4.6, 6.5, 2.0%; ZnO; 27.6, 23.8, 20.5, 17.7, 11.4, 9.8, 8.5, 4.1, 3.5 μm at 12.0, 18.9, 12.3, 1.1, 2.1, 30.7, 6.6, 5.2, 10.3%; Fe_2O_3: 27.6, 23.8, 20.5, 17.7, 11.4, 9.8, 8.5, 7.3, 4.1, 3.5, 3.0, 2.6 μm at 4.8, 7.3, 17.6, 2.2, 1.7, 22.2, 15.0, 10.6, 1.7, 5.8, 7.1, 2.1%; MoO_3: 26.20, 22.49, 19.31, 16.57, 14.22, 12.21, 10.48, 9.00, 7.72, 6.63, 5.69, 4.88, 4.19, 3.60, 3.09, 2.65, 2.28 μm at 1.25, 2.83, 4.28, 5.57, 6.93, 8.22, 9.29, 9.53, 9.44, 8.92, 8.03, 6.86, 5.57, 4.31, 3.16, 2.24, 1.48%; CeO_2: 16.57, 14.22, 12.21, 10.48, 9.00, 7.72, 6.63, 5.69, 4.88, 4.19, 3.60, 3.09, 2.65, 2.28, 1.95, 1.68, 0.58, 0.49, 0.42, 0.36, 0.31, 0.27, 0.23, 0.20, 0.17, 0.15, 0.13 μm at 1.43, 2.12, 2.9, 3.74, 4.52, 5.17, 5.54, 5.71, 5.66, 5.39, 4.90, 4.26, 3.52, 2.74, 1.98, 1.30, 1.05, 2.04, 3.05, 4.01, 4.81, 5.11, 4.70, 3.80, 2.80, 1.91, 1.22%. The specific surface areas, determined by the BET method, are as below: TiO_2 14.68, Fe_2O_3 17.84, ZnO 12.16, CeO_2 11.0 $m^2\ g^{-1}$; the corresponding value for MoO_3 is too small to be determined by the BET method. Fig. 1, the diffuse reflectance spectra recorded using a Shimadzu UV-2450 UV-visible spectrometer with $BaSO_4$ as the reference, reveals that Fe_2O_3 is activated by visible light itself whereas the others require UV-A light for the band gap excitation.

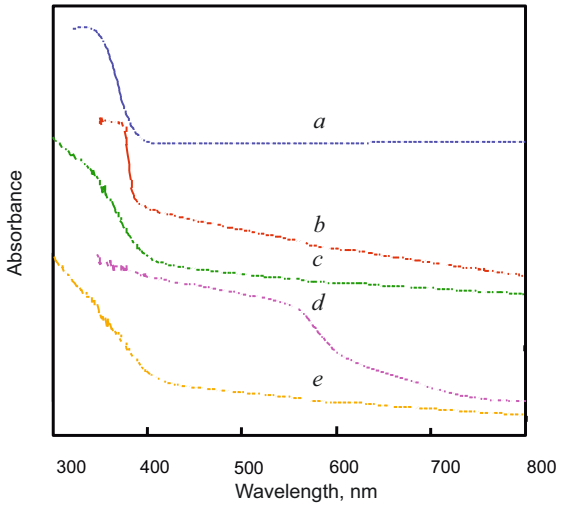


Figure 1. Absorbance edges of semiconductors: (a) TiO_2, (b) ZnO, (c) CeO_2, (d) Fe_2O_3 and (e) MoO_3.

3.2. Obtaining solar results

The sunlight intensity during the course of the experiment, even under clear sky on sunny days, fluctuates (900±50 W m^{-2}). Also, the intensity of solar radiation differs from day to day. Now, the solar irradiance for a set of experiments of the required reaction conditions has been kept identical by carrying out the experiments simultaneously, side by side, thereby making possible to compare the solar results. The results of the solar oxidation of iodide ion with each of the catalysts TiO_2, MoO_3, Fe_2O_3, ZnO and CeO_2 are consistent. For each semiconductor, a pair of solar experiments of identical reaction conditions carried out simultaneously, side by side, yields results within ±5% and this is so on different days (data not given). This consistency is not surprising as the irradiance of sunlight is the same in both the experiments, conducted side by side. As all the solar photooxidation experiments with the stated five catalysts under varied conditions could not be

made simultaneously, side by side, an experiment for each catalyst under the standard (specified) reaction conditions, called control experiment, has been carried out with each set of experiments. The relative rate, the ratio of iodine generated at the required experimental condition to that at the standard condition has been obtained and this relative rate is independent of the solar irradiance in the range 850 – 950 W m^{-2}.

3.3. Solar photocatalysis under potential bias

Application of a cathodic bias to the semiconductor bed under sunlight enhances the photooxidation of iodide ion. Out of the four experiments that have been conducted simultaneously in a set under identical solar irradiance for each catalyst, cost effective copper bottom has been used for three, over which the catalyst particles have been spread [12,13]. A positive potential bias has been applied to one, a negative potential to another and none to the third. While an anodic bias and no bias fail to bring in significant photocatalysis, a cathodic bias enhances the photooxidation by 6 to 12 times compared to the control experiment, where the catalyst has been spread on a glass bottom without any bias; the relative rate of a given catalysis is the ratio of iodine formed under the given experimental condition to that with the same catalyst on glass bottom without any bias but under identical sunlight irradiance (Table 1). The solar-driven electrochemically assisted semiconductor-photocatalysis has been confirmed by carrying out the experiments under identical conditions but in dark. Identical cathodic bias in the dark fails to effect significant iodide ion-oxidation. Also, the solar iodine generation with semiconductors under potential bias requires dissolved oxygen; the oxidation of iodide ion on each semiconductor in nitrogen-purged KI solution (4.2 mg L^{-1} dissolved O_2) under cathodic bias is only one-tenth of the air-saturated KI solution (31.2 mg L^{-1} dissolved O_2); the data are not listed. Further, in the absence of semiconductor the oxidation is insignificant under all the experimental conditions. These results unequivocally prove the solar-driven electrochemically assisted semiconductor-catalyzed oxidation of iodide ion.

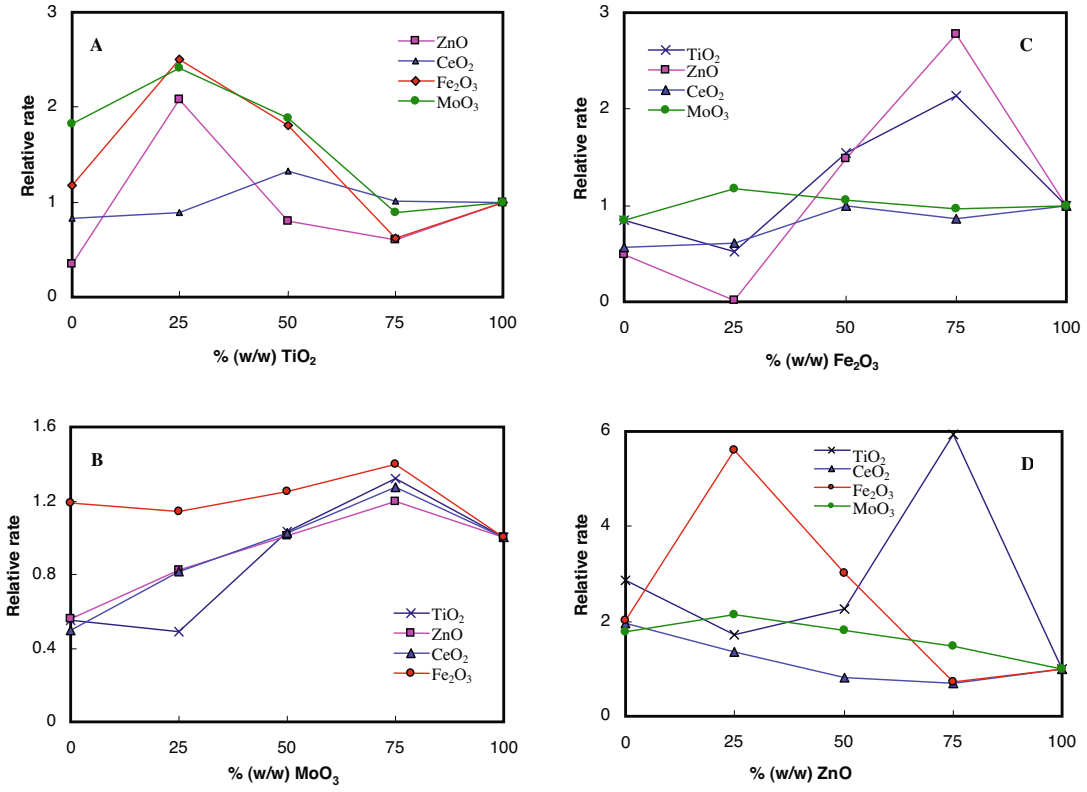
3.4. Enhanced photocatalysis by oxide mixtures under potential bias

Mixed semiconductors enable a vectorial transfer of electrons and holes from one semiconductor to another [14]. On illumination, both semiconductors are excited and electrons accumulate at the lower-lying conduction band of one semiconductor while holes move to the less anodic valence band. These processes of charge separation are very fast, decrease the electron-hole pair recombination and thus enhance the photocatalytic efficiency. Although enhanced photocatalysis by mixed semiconductors is known [14], this is the first report of the enhancement of photocatalysis with natural sunlight by application of a cathodic bias on semiconductor mixtures. Under cathodic bias, TiO_2-ZnO, TiO_2-Fe_2O_3 and ZnO-Fe_2O_3 mixtures show enhanced efficiency; the oxides were mixed in requisite weight ratios, ground well and used. Figs. 2A-D present the improved photooxidation of iodide ion under a cathodic bias with natural sunlight. The solar iodine generation by individual semiconductor under cathodic bias has been taken as the standard and the relative rates are presented; each line corresponds to identical sunlight irradiance. Further, the relative rates by semiconductor mixtures presented in Figs. 2A, 2B, 2C and 2D are with respect to 100% TiO_2, 100% MoO_3, 100% Fe_2O_3 and 100% ZnO. The relative rates should not be compared across the figures as for each figure the standard is different.

Table 1. Solar-driven electrochemically assisted iodide ion oxidation with semiconductors[†#]

Catalyst	Relative rate*				
	Control[a]	No bias	Anodic bias[b]	Cathodic bias[c]	Cathodic bias in dark[c]
TiO_2	1.0	0.1	0.1	6.5	0.4
MoO_3	1.0	0.2	0.2	9.2	0.3
Fe_2O_3	1.0	0.1	0.1	6.3	0.2
ZnO	1.0	0.3	0.6	12.3	1.4
CeO_2	1.0	0.2	0.1	11.2	0.8
Nil	~0	~0	0.1	0.1	0.1

[†]50 mL 0.05 M KI, 31.2 mg L^{-1} dissolved O_2, 15.1 cm^2-catalyst bed, 1.0 g-catalyst covered on copper bottom, 30 min-sunshine at 900±50 W m^{-2};
[#]Values in a row (not in a column) are to be compared as they correspond to identical sunlight irradiances;
** The relative rate of a given catalysis is the ratio of iodine formed under the given experimental condition to that with the same catalyst on glass bottom without any bias under identical sunlight irradiance (control);*
[a]Catalyst on glass bottom without bias;
[b]+0.2 to +0.3 V vs SCE;
[c]-0.2 to -0.3 V vs SCE.



Figures 2. Enhanced solar-driven iodine generation by mixed semiconductors under cathodic bias (-0.2 to -0.3 V vs SCE).† 50 mL 0.05 M KI, 31.2 mg L^{-1} dissolved O_2, 15.1 cm^2 catalyst bed, 1.0 g-catalyst spread on copper bottom, 30 min-sunshine at 900±50 W m^{-2}.
† Each line in a figure corresponds to identical sunlight irradiance and the relative rates are with respect to (A) 100% TiO_2; (B) 100% MoO_3; (C) 100% Fe_2O_3; (D) 100% ZnO; the relative rates should not be compared across the figures as for each figure the standard is different.

3.5. Mechanism

Fe_2O_3 absorbs in the visible region and is effectively excited by sunlight (Fig. 1). However, TiO_2, ZnO, CeO_2 and MoO_3 require UV-A light for the band gap excitation and the observed photocatalysis is due to the UV light of the solar radiation, which is about 4% at the ground level. In absence of any bias, band gap-illumination of semiconductors that are spread on the glass bottom (Table 1: control) creates electron-hole pairs, which react with the adsorbed iodide ion and an oxygen molecule to generate iodine. In absence of any potential bias, both the oxidation and reduction occur on the illuminated surface of the semiconductor. However, the photocatalysis becomes insignificant with semiconductors spread on the copper bottom (Table 1: no bias). This may be due to a short-circuit of the photogenerated charges by copper. Anodic bias on an illuminated semiconductor may lead to oxidation at the semiconductor surface and reduction at the counter electrode. The reverse should be the case with a cathodic bias, impressed upon an illuminated semiconductor. Here, anodic bias fails to effect iodide ion oxidation whereas a cathodic bias does. That is, molecular oxygen adsorbed on the illuminated semiconductor is reduced to superoxide radical ion and the iodide ion is also oxidized at the counter electrode (Fig. 3). The possible reason is as follows. The reduction of molecular oxygen by the illuminated semiconductor is slow and rate determining and application of a cathodic bias eases the same. It has been shown that in the photooxidation of methanol (1.6 M), electrons on TiO_2 particles persist for at least ~1 min even in O_2-saturated solutions [15]. Also, the iodide ion-oxidation at the copper electrode with oxygen-reduction on the illuminated semiconductor is kinetically and thermodynamically more favorable than the reduction of oxygen at the copper electrode and iodide ion-oxidation on the semiconductor. The reduction potentials of the conduction band electron (TiO_2) and superoxide radical ion are -0.50 and -0.33 V, respectively. The enhanced photocatalysis exhibited by oxide mixtures under a potential bias is in tune with the improved charge separation by semiconductor mixtures.

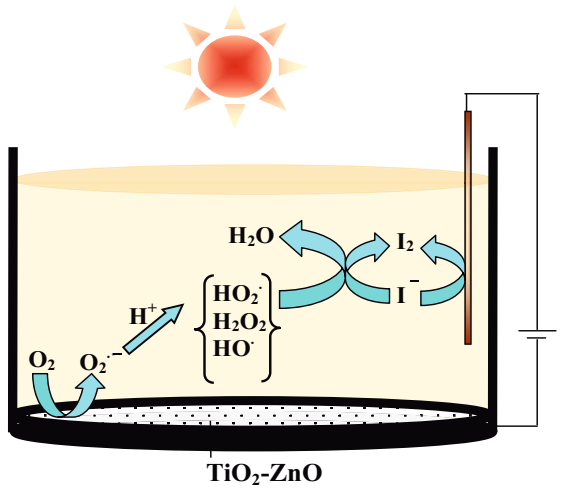


Figure 3. Photocatalytic mechanism under cathodic bias

4. Conclusions

Under a cathodic bias of -0.2 to -0.3 V (*vs* SCE), TiO_2, MoO_3, Fe_2O_3, ZnO and CeO_2 show enhanced oxidation of iodide ion with natural sunlight (900±50 W m^{-2}). Further, with natural sunlight the TiO_2-ZnO, TiO_2-Fe_2O_3 and ZnO-Fe_2O_3 mixtures exhibit larger generation of iodine under a cathodic bias due to improved charge separation.

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