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Uses of TiO_2 as Photocatalysts in Green Chemistry

Dr. Meghna Dubey
Head of the Department,
Department of Engg. Chemistry,
Jai Narain College of Technology,
Bhopal (M.P.) [India]
E-mail : dr_meghnadubey@rediffmail.com

ABSTRACT:

Environmental pollution and destruction on a global scale have drawn attention to the vital need for totally new environmentally friendly, clean chemical technologies and processes, the most important challenge facing chemical scientists in the field of green chemistry. Strong contenders as environmentally harmonious catalysts are photocatalysts that operate at room temperature and in a clean manner, while applications of such safe photocatalytic systems are urgently desired for the purification of polluted water, the decomposition of offensive atmospheric odors as well as toxins, the fixation of CO and the decomposition of NOx and chlorofluorocarbons on a huge global scale. To address such enormous tasks, photocatalytic systems that are able to operate effectively and efficiently not only under UV light but also under the most environmentally ideal energy source, sunlight, must be established. To this end, we are moving in a positive direction with various practical applications already at hand, as is described.

I. INTRODUCTION

The present report involves 1) new approaches in the design and development of second generation titanium oxide photocatalysts which can operate effectively under visible light and/ or solar beam irradiation, 2) practical industrial applications of titanium oxide photocatalysts in India, and 3) recent advances in green chemistry in India.

New Approaches in the Design and Development of Second-Generation Titanium Oxide Photocatalysts Operating Undervisible Light Irradiation.

As shown in Figures I a and I b, when titanum oxides are irradiated with UV light that is greater than the band gap energy of the catalyst ($\lambda < 380$ nm), electrons and holes are produced in the conduction and valence bands, respectively. The electrons have a highly reactive reduction potential while the holes have a highly reactive oxidation potential, which together induce catalytic reactions on the catalyst surfaces—namely, photocatalytic reactions. Because of its similarity to the mechanism observed with the photosynthesis in plants, photocatalysis may also be referred to as artificial photosynthesis. As will be introduced in the Section "Practical Industrial Applications of Titanium Oxide Photocatalysts in India", there are no limits to the possibilities and applications of titanium oxide photocatalysts and photocatalytic reactions as "environmentally harmonious catalysts".

However, as can be seen in Figure 2a and unlike photosynthesis in green plants, the titanium oxide photocatalyst in itself does not allow the use of visible light and can make use of only 3—4% of solar beams that reach the earth. Therefore, lo establish clean and safe photocatalytic reaction systems using the solar beam and/or visible light, it is vital to develop titanium oxide photocatalysts that can absorb visible light and operate with high efficiency under solar beam and/or visible light irradiation.

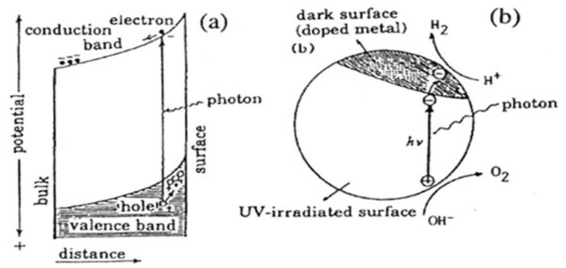

Figure 1. Schematic representation of the photoexcitation of the titanium oxid photocatalyst (a), photo-formation of electrons (e) and holes(h) and their charge separation, and the reduction of H* to produce H_2 and the oxidation of OH to product O_2 via the formation of OH redicals in an aqueous system (b).*

We have applied the metal ion-implantation method to modify the electronic properties of titanium oxide photocatalysts by bombarding them with high-energy metal ions and have found that this advanced physical method is the most suitable and promising for the dramatic modification of the Electronic state of the pholocalalysts.

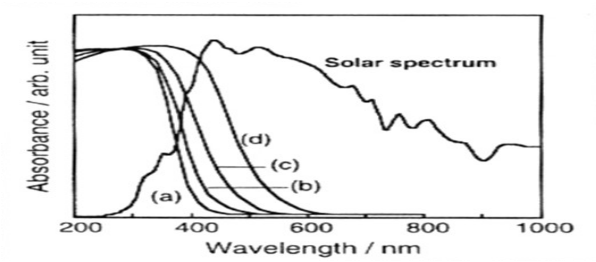

Figure 2 UV-Vis absorption specira (difluse reflectance) orihe original un-implanled titanium oxide catalyst (a) and The Cr ion-implanled titanium oxide catalysis (b-d), the action spectrum (open circle points) of the pholocalalytic reaction on the Cr ion-implanted photocatalyst corresponding to the spectrum (d), and the solar spectrum which reaches the earth, (amounts of Cr ions-implanted [in 10 ' mol/g], b: 2.2, c: 6.6, d: 13, e: 26).

As can be seen in Figures. 2b-2d, the absorption band of the rental ion-implanled titanium oxide was found to shift smoothly to visible light regions, the extent of the red shift depending on the amount and type of metal ions implanted with the absorbance maximum and minimum values always remaining constant. Such a shift allows the metai ion-implanted titanium oxide to use solar beams more effectively and efficiently. at up to 20—30%.

As mentioned above, with titanium oxide photocatalysts, the photocalalytic reaction does not proceed under visible light irradiation ($\lambda >$ 450 nm). However, we have found that visible light irradiation of these metal ion-implanted titanium oxide photocatalysts led to various significant photocatalytic reactions.

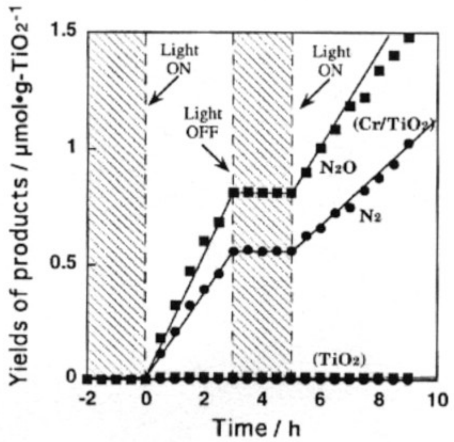

Figure 3 Pholocalalytic tIecomposUion of NO into N_2O as well as N_2 and O_2 on the Cr ion-implanted titanium oxide photocatalyst under visible light irradiation ($\lambda >$ 450 nm) at 295 K. Original un-implanted photocatalyst did not show any pholocalalytic reactivity under the same conditions.

As shown in Figure 3, visible light irradiation ($\lambda >$ 450 nm) of the metal ion-implanted titanium oxide in the presence of NO at 275 K leads to the direct decomposition of NO into N_2, O_2 and N_2O with a good linearity against the irradiation time. Under the same conditions of visible light irradiation, the original non ion-implanted titanium oxide did not exhibit any photocatalytic reactivity. As also seen in Figure 2, the action spectrum for the reaction on the metal ion-implanted titanium oxide was in good agreement with the absorption spectrum of the catalyst, indicating that only metal ion-implanted catalystsis were effective for the pholocatalytic decomposition of NO. Thus, the metal ion-implanted catalysts enabled the absorption of visible light up to a wavelength of 400-600 nm and were able to operate effectively as photocatalysts under visible light irradiation, hence their name, "second-generation titanium oxide photocatalysts".

Uses of TiO_2 Photocatalysts in green chemistry, in fact, as can be seen in Figure 4, under outdoor solar light irradiation at ordinary temperatures, the metal ion-implanted catalyst exhibited photocatalytic reactivity several times higher than the original non ion-implanted catalyst, showing the great possibility of the use of solar energy in an effective and efficient manner by the application of second-generation titanium dioxide photocatalysts.

Photocatalysts implanted with Cr or V ions were found to exhibit the largest shift to visible light regions up lo a wavelength of 550-600 nm. However, the implantation of Mg^+ Ti or Ar^+ ions scarcely changed the absorption band of the photocatalyst. We have found that metal ions implanted within the bulk of the catalyst modified the electronic properties of the titanium oxide photocatalyst in which the d-electrons of the implanted metal ions may be associated with this phenomenon, showing that photocatalylic reactions can take place under visible light.

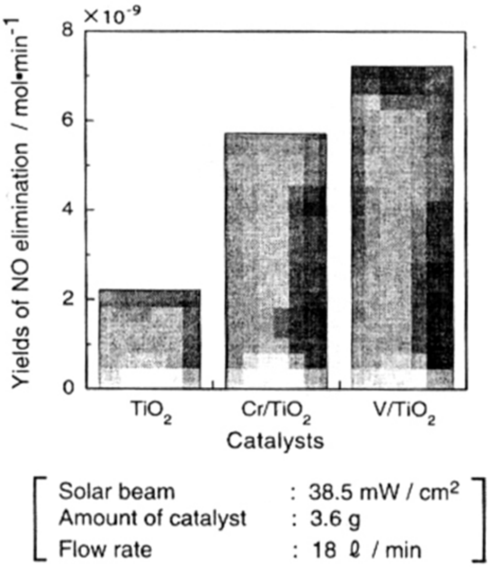

Figure 4: Effect of the metal ion-implantation on the photocatalytic reactivity of titanium oxide photocatalysts under the solar beam irradiation at 295K.

On the other hand, the photocatalytic decomposition of NO into N_2O as well as N_2 and O_2 proceeded both on the original non ion-implanted titanium oxide and on the metal ion-implanted titanium oxide photocatalysts under UV light irradiation ($\lambda > 380$ nm). Under UV light irradiation, the photocatalytic reactivity for the decomposition of NO on the metal ion-implanted photocatalyst was almost the same as for the non ion-implanted photocatalyst, suggesting that the implanted metal ions that are highly dispersed inside the deep bulk of the photocatalyst do not work as the electron-hole recombination center but only work to modify the electronic property of the catalyst, enabling the absorption of visible light.

The principles of titanium oxide photocatalysts and photocatalytic reactions have been briefly introduced as compared to the photosynthesis in green plants. Photocatalysis can be considered the most important and new, environmentally friendly, clean chemical technology for green chemistry. In fact, various applications of titanium oxide photocatalysis have already been developed to better our environment. Especially, these include successful developments in the purification of the polluted atmosphere as well as toxic water using ultraviolet light having a wavelength shorter than 380 nm (i.e., a larger energy than the bandgap of the titanium oxide photocatalysts). Furthermore, this advanced metal ion-implantation method has been successfully applied to modify the electronic properties of the photocatiilysts enabling the absorption of visible light even longer than 550 nm so that they are able to operate more efficiently under visible or solar light irradiation. The design and development of such unique titanium oxide photocatalysts can be considered a breakthrough in the efficient and large-scale utilization of solar energy.

In the next section, several practical industrial uses of photocatalysts to green chemistry which have already been adapted for industrial applications in India have been described.

II. Practical Industrial Applications Oftitanium Oxide Photocatalysts in India

The photocatalytic reactivity of titanium oxides under UV irradiation using a special black lamp or UV light from solar beams (3-4% of solar beams are made up of UV light) can be applied for the reduction or elimination of polluted compounds in air such as NOx (Figure 5), cigarette smoke, as well as volatile compounds arising from various construction materials. Also such high photocatalytic reactivity can be applied to protect lamp-houses and walls in tunneling, as well as to prevent white tents from becoming sooty and dark. The reactivity is high enough to decompose or kill bacteria so that new cement and tiles mixed with titanium oxides can be commercialized and may even be used in operating rooms in hospitals to keep them sterile and bacteria-free.

Furthermore, titanium oxide thin films have been found to exhibit a unique and useful function (i.e., a super-hydrophilic property). Usually, metal oxide surfaces such as titanium oxides become cloudy when water is dropped on them because the contact angle of the water droplet and the surface is 50-80 degrees. However, under UV light irradition this contact angle becomes smaller, its extent depending on the irradiation time. Thus under UV light irradiation, titanium oxide surfaces never become cloudy, even in the rain. This remarkable function can also be applied for the production of new mirrors that can be used in bath areas and the side mirrors of cars.

Some practical applications are as follows:

1. Air cleaner containing TiO_2, photocalalysts: Sharp Co., Ltd.;
2. White paper containing TiO_2 photocatalysts: Mitsubishi Paper Mills.
3. Antibacterial textile fibers containing TiO_2 photocatalysts.
4. Systems for the purification of polluted air. e.g., the elimination of NOx. (Figure 5).
5. Super-hydrophilic, self-cleaning systems, and coating materials for cars. Toto Ltd.
6. Soundproof walls using TiO_2 photocatalysts:
7. Glass tableware: Kalo Machinery, Ltd.

III. Recent Advances in Green Chemistry in India

In India several organizations such as the Chemical Society of India and the Chemical Engineering Society of India are involved in the development and promotion of green chemistry. Although there has been some collaborative work between academia and industries, still there is ample opportunity for increased collaboration. There is immediate need for technology transfer from academic labs to industrial plants for meaningful application of green research. The best examples are the applications of enzymes in various industries ranging from drugs to leather. The textile industry is one of the highly revenue generating industries in India. And they are now switching over to microbial decolorization and degradation. There is an increasing need of exploring biodiversity for natural dyes and developing eco-friendly methodology for synthetic dyes.

Government can do a lot of good for the cause of green chemistry by increasing public awareness and by bringing and enforcing strict environmental legislations. One of the recent and controversial examples of government initiative is the conversion of diesel vehicles to compressed natural gas (CNG) in order to reduce pollution in the capital city Delhi.

Relocation of industries into industrial areas away from residential parks in another bold step taken by the Delhi government. Further, the government is also concentrating on new projects such as fuel pellets from municipal waste, aspirated H-cylinder engines for light commercial vehicles (LCVs). Meeting India 2000 emission norms, battery powered cars for pollution free driving hydrogen energy and energy towers for new environment friendly fuel development of traditional herbal drugs as adaptogens and immune modulators. The government should also increase funding to encourage research in green chemistry. By introducing green chemistry education at all levels, the government can build a solid foundation toward green chemistry in India.

The recently constituted green chemistry chapter of India has already started working to popularize green chemistry in India. As a part of environmental movement, a national symposium on green chemistry was organized by the department of Chemistry. University of Delhi in January 1999 to bring together all who are practicing green chemistry in India for the first time for green chemistry education a refresher course was organized for college teachers by the centre for professional development in higher education in University of Delhi. Inspired by the overwhelming response of participants in these events, recently an IUPAC international symposium on green Chemistry was organized by the department of chemistry. University of Delhi, which proved to be an excellent event for scientists world over to interact on the one common platform.

III. CONCLUSIONS

In conclusion uses of TiO_2 as a photocatalys in India in necessity rather than an option, as this is now a high time to protect our caring environment from further damage. The future of TiO_2 as catalyst in the hands of young researchers and students as TiO_2 is strong photocatalyst and very useful in purification of polluted water. Industries should understand the uses of TiO_2 as a photocatalys in green chemistry.

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