**Enhanced photocatalytic Fe$^{3+}$ reduction with H$_2$O$_2$ generation by TiO$_2$ anatase/rutile blend**

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TiO$_2$ P25 Degussa, TiO$_2$ Hombikat, anatase TiO$_2$ and WO$_3$ nanocrystals photocatalyze the reduction of iron(III) ion in aqueous acidic solution with generation of hydrogen peroxide. The photocatalytic activities of TiO$_2$ P25 and TiO$_2$ Hombikat are much higher than those of anatase TiO$_2$ and WO$_3$. The nanomaterials have been characterized by powder X-ray diffraction and solid state impedance, UV-visible diffuse reflectance and photoluminescence spectroscopies. The photoreduction decreases with increase of iron(III) ion concentration because of inner filter effect. While the photoreaction is slow at high acidity the reaction rate increases with increase in photon flux. Molecular oxygen does not play any role in the photoreduction. The Fe(III)-reduction is more effective with UV-C light than with UV-A light. The nanooxides show sustainable photocatalytic activity. Charge separation between anatase and rutile phases is the likely reason for the observed large photocatalytic activities of TiO$_2$ P25 and TiO$_2$ Hombikat.

**Keywords:** Photooxidation, Photoreduction, Photocatalysis, Interparticle charge transfer, Iron, Titania

Increased exploitation of oil and coal reserves leads to not only unsustainable energy management but also results in uncontrolled carbon emission. Attempts are now being made to find renewable energy sources with harnessing solar energy gaining importance, not only because of its unlimited potential but also on public acceptance based on safety considerations. Tapping solar energy gains further relevance in tropical countries where sunshine is in abundance almost throughout the year. Thermal reactions demand decrease of free energy for spontaneity but photocatalysed processes have no such restrictions. Semiconductor photocatalysis is an emerging technology because of wide applications like solar energy conversion and storage, synthesis of high energy chemicals, mineralization of pollutants at ambient conditions, etc.

The photocatalytic production of H$_2$O$_2$ from water is a subject of great interest from both scientific and technological point of view due to its possible application for converting and storing the abundant sunlight energy as chemical energy. Kormann et al. have observed formation of H$_2$O$_2$ in illuminated aqueous suspension of ZnO, TiO$_2$, and desert sand in the presence of O$_2$ and organic electron donors. Hoffman et al. have reported evolution of H$_2$O$_2$ from oxygenated carboxylic acids using Q-sized ZnO colloids as photocatalyst illuminated at 320–370 nm; the efficiency of the photocatalytic process depends on the hole scavenger employed and is of the order: formate > oxalate > acetate > citrate. Tsukamoto et al. have employed bimetallic alloy Au/Ag loaded TiO$_2$ nanoparticles as photocatalyst for H$_2$O$_2$ production from oxygenated ethanol. Cai et al. have observed enhancement of H$_2$O$_2$ formation on addition of Cu$^{2+}$ ion to UV light illuminated aqueous suspension of TiO$_2$. H$_2$O$_2$ is also produced photocatalytically by TiO$_2$ from humidity-controlled air. Photocatalytic production of H$_2$O$_2$ by CuO powder in aqueous suspension is also known. Fe$^{3+}$ ion could be employed as electron acceptor for photocatalytic oxidation of water with rutile TiO$_2$. Fe$^{3+}$ ion has been found to be a better electron capture agent than Ag$^+$ ion in the UV laser induced α-Fe$_2$O$_3$-catalyzed splitting of water. In addition, the advantage of using Fe$^{3+}$ ion as electron acceptor is that the reduced product (Fe$^{2+}$ ion) could be oxidized to Fe$^{3+}$ and the combined process serves to convert light energy into chemical energy. Furthermore, the preferential adsorption of Fe$^{3+}$ ion on TiO$_2$ over Fe$^{2+}$ ion enables efficient oxidation of water. Bamwenda et al. reported splitting of water with WO$_3$ powder employing Fe$^{3+}$/Fe$^{2+}$ redox couple. Fe$^{3+}$ is reduced to Fe$^{2+}$ and prolonged irradiation is required for H$_2$ and O$_2$ generation; the illumination time needed to reach the stationary state are 6 and 30 h for the inner- and
Materials and Methods

TiO$_2$ P25 Degussa, TiO$_2$ Hombikat (Fluka), TiO$_2$ anatase nanopowder (Sigma-Aldrich), WO$_3$ nanopowder (Sigma-Aldrich) and ZnO nanoparticles (Sigma-Aldrich) were used as received. The other chemicals used were of analytical grade. Deionized distilled water was employed throughout the study.

The X-ray diffraction (XRD) patterns were recorded with a Bruker D8 system using CuK$_\alpha$ radiation at 1.5406 Å in the 2\(^\theta\) range of 5-70° at a scan rate of 0.05° s\(^{-1}\) with a tube current of 30 mA at 40 kV and with a Rich. Siefert (model 3000) X-ray diffractometer in the 2\(^\theta\) range of 15-70°. The solid state electrochemical impedance spectra (EIS) at room temperature were obtained with a CH Instrument electrochemical analyzer 604C in the frequency range of 0.1 MHz–1 Hz. The disk area was 0.5024 cm\(^2\) and the thicknesses of the pellets of TiO$_2$ P25 Degussa, TiO$_2$ Hombikat (TiO$_2$ (H)), TiO$_2$ anatase (TiO$_2$ (A)) and WO$_3$ were 1.22, 0.92, 1.90 and 1.11 mm, respectively. A Shimadzu UV-2600 spectrophotometer with ISR-2600 integrating sphere attachment was employed to record the UV-visible diffuse reflectance spectra (DRS). A Perkin-Elmer LS 55 fluorescence spectrometer was used to obtain the solid state photoluminescence (PL) spectra at room temperature.

Photocatalytic study

The photocatalytic experiments were conducted systematically with a photoreactor fixed with 8 W medium pressure mercury vapor lamps (Sankyo Denki, Japan) emitting mainly at 365 nm. A highly polished anodized aluminum reflector fixed in the reactor preserved the light intensity. A borosilicate glass tube of 15 mm inner diameter was the reaction vessel used and was placed at the center of the photoreactor. The fans fixed at the bottom of the reactor dissipate the heat generated. The photon flux (25.2 \text{meinstein L}^{-1} \text{s}^{-1}) was determined by ferrioxalate actinometry. The photocatalytic experiments were also carried out with a microphotoreactor fixed with a 6 W 254 nm low pressure mercury lamp or a 6 W 365 nm medium pressure mercury lamp. Quartz and borosilicate tubes were used for the low pressure and medium pressure lamps, respectively. Aqueous solution of ferric ion (1.0 mmol L\(^{-1}\) unless otherwise stated) was prepared afresh before use. The reaction was studied in acidic solution ([H\(^+\)] = 5.0 mmol L\(^{-1}\) unless stated otherwise). The volume of the solution kept as 25 mL in multilamp photoreactor and 10 mL in microreactor, while the catalyst loadings in the multilamp and micro photoreactors were 0.8 and 1.0 g L\(^{-1}\), respectively. Air (7.8 mL s\(^{-1}\)) was bubbled through the reaction solution using a micropump which effectively stirred the solution and kept the suspended particles under constant motion. Iron(III) was estimated spectrophotometrically (Hitachi U-2001 or Shimadzu UV-1650C) after centrifuging the nanoparticles and acidifying with concentrated hydrochloric acid, complexing with thiocyanate and diluting the solution to double its volume. Calibration curve was constructed using standard iron(III) solution.

Results and Discussion

Crystalline structure

The XRD pattern of anatase TiO$_2$ (TiO$_2$ (A), (shown in Supplementary Data, Fig. S1(a)), confirms the anatase phase of the sample. The obtained diffractogram matches with that of anatase TiO$_2$ (JCPDS 89-4921) and no rutile line is observed indicating its absence. The XRD of TiO$_2$ P25 Degussa (TiO$_2$ (P25)) (Supplementary Data, Fig. S1(b)), shows the existence of anatase and rutile phases in the sample. The JCPDS patterns of anatase TiO$_2$ (00-021-1272 (*)) and rutile TiO$_2$ (01-089-0553 (c)) are observed in the XRD of TiO$_2$ P25. The phase percentages for the anatase and rutile phases are 81 and 19 respectively (as deduced from the integrated intensities of the peaks at 2\(^\theta\) values of 25.3° (101-plane) for anatase and 27.4° (110-plane) for rutile. A (\%) = 100/[1+1.265(I_R/I_A)], where I_A and I_R are the intensities of anatase and rutile peaks, respectively). This is in agreement with the literature values. The XRD of TiO$_2$ Hombikat (TiO$_2$ (H)), exhibits the presence of anatase and rutile in the sample (Supplementary Data, Fig. S1(c)). The XRD peak-fitting conforms to the combined diffraction patterns of anatase TiO$_2$ (JCPDS 89-4921) and rutile TiO$_2$ (JCPDS 89-4202). The percentages of anatase and rutile, obtained from the XRD results, are 69 and 31, respectively. The XRD of WO$_3$ shows the primitive monoclinic crystal structure of WO$_3$. 

outer-irradiation systems, respectively. TiO$_2$-coated WO$_3$ particles are found to be a better photocatalyst for the oxidation of water with Fe$^{3+}$ ion as the electron acceptor$^{12}$. The present work shows that TiO$_2$ P25 Degussa and TiO$_2$ Hombikat, which are blends of anatase and rutile phases of TiO$_2$, are more efficient than anatase TiO$_2$ in photocatalytic generation of H$_2$O$_2$ from water with Fe$^{3+}$ ion as electron acceptor.
The mean crystallite sizes \((L)\) of the nanocrystals have been obtained from the full width at half maxima (FWHM) of the most intense peaks of the samples using the Scherrer formula \(L = \frac{0.9\lambda}{\beta\cos\theta}\), where \(\lambda\) is the wavelength of the X-ray used, \(\theta\) is the Bragg angle and \(\beta\) is the corrected line broadening. The mean crystallite sizes of anatase TiO\(_2\), TiO\(_2\) P25, TiO\(_2\) Hombikat and WO\(_3\) are 9, 23, 18 and 23 nm, respectively. The specific area \((S)\) of the nanoparticles have been deduced using the relationship \(S = \frac{6}{L\rho}\), where \(L\) is the mean crystallite size and \(\rho\) is the material density. The obtained surface area of anatase TiO\(_2\), TiO\(_2\) P25, TiO\(_2\) Hombikat and WO\(_3\) are 165, 68, 87 and 39 m\(^2\) g\(^{-1}\), respectively.

**Charge transfer resistance**

Solid state impedance spectroscopy is a potent tool to probe the electrical properties of nanocrystalline semiconductors. It may be employed to study the dynamics of the mobile and bound charges in the bulk or interfacial region of the semiconductor. In polycrystalline materials, the overall crystal resistance is a combination of bulk or intragranular resistance and grain boundary or intergranular resistance. Figure 1 displays the complex solid state impedance spectra of anatase TiO\(_2\), TiO\(_2\) P25, TiO\(_2\) Hombikat and WO\(_3\). The ohmic \((R_o)\) or uncompensated resistance corresponds to the intergranular or grain boundary resistance and the charge-transfer or polarization resistance \((R_{CT}\) or \(R_p\)) refers to the intragranular or bulk crystal resistance. \(R_{CT}\) is related to the Warburg resistance, the resistance to mass transfer and is controlled by specific conductance. The constant phase element is associated with a non-uniform distribution of current because of material heterogeneity and is equivalent to double layer capacitance. The Nyquist plots show that the \(R_{CT}\) of WO\(_3\) nanocrystals is the largest. This is probably due to the inherent nature of WO\(_3\) nanocrystals. The \(R_{CT}\) of anatase TiO\(_2\) is less than that of TiO\(_2\) P25 and TiO\(_2\) Hombikat, probably due the heterogeneity of TiO\(_2\) P25 and TiO\(_2\) Hombikat; TiO\(_2\) P25 and TiO\(_2\) Hombikat are mixtures of anatase and rutile phases of TiO\(_2\).

**Band gap energy and photoluminescence**

The UV visible diffuse reflectance spectra of anatase TiO\(_2\), TiO\(_2\) P25, TiO\(_2\) Hombikat and WO\(_3\) nanocrystals are displayed in Fig. 2. The DRS are given in terms of \(F(R)\); the \(F(R)\) was deduced from the measured reflectance \((R)\) by the application of Kubelka-Munk \((K-M)\) algorithm, \(F(R) = (1 - R)^2/2R\). Figure 2 shows that TiO\(_2\) in all the three forms requires UV-A light for photoactivation, whereas WO\(_3\) is photoexcited by visible light itself. The normalized photoluminescence spectra of TiO\(_2\) P25, TiO\(_2\) Hombikat, anatase TiO\(_2\) and WO\(_3\) are displayed in Fig. 3. The emission spectra of the three different TiO\(_2\) are similar. They show near
band gap emission (NBE) and deep level emission (DLE). The DLE occurs because of various intrinsic structural defects in the nanocrystals, while the NBE stems from the radiative recombination of free photoformed electron-hole pairs. All the three TiO$_2$ samples display strong violet emission at 420 nm, blue emission at 457 nm and blue-green emission at 482 nm and weak green emission at 530 nm. The violet emission is attributed to the self-trapped excitons localized on TiO$_6$ octahedra$^{13,14}$. Two electrons trapped on an oxygen vacancy create the $F$ center which is 0.51 eV below the CB and is believed to provide the blue emission$^{14,15}$. The bound-exciton emission at 482 nm has been assigned to trapping of free excitons near defects$^{16,15}$. Liu et al.$^{17}$ have assigned the blue-green emission to charge-transfer transition from Ti$^{3+}$ to oxygen anion in a TiO$_6$ octahedron associated with oxygen vacancies at the surface. $F^+$ center is attributed to oxygen vacancy 0.82 eV below the CB which is responsible for the green emission$^{13-16,18}$. The observed weak blue emission at 465 nm is also associated with an oxygen vacancy$^{13,15,16}$. Thus, the PL spectra reveal the presence of different defects due to several types of oxygen vacancies in all the examined TiO$_2$ nanocrystals. The PL spectrum of WO$_3$ nanocrystals exhibits strong bluish green emission at 487 nm, moderate blue emission at 457 nm and weak green (529 nm) and greenish yellow (569 nm) emissions. The determined band gap of WO$_3$ nanocrystals is 2.88 eV (lit. value: 2.8 eV$^{19}$) and hence none of the displayed emissions could be attributed to band to band transition. The observed DLE are associated with defects such as oxygen vacancies and surface states$^{20-23}$. Thus, the observed strong DLE indicates the presence crystal defects in the WO$_3$ nanoparticles.

**Photoreduction of iron(III) ion**

The reduction of iron(III) ion, catalyzed by TiO$_2$ P25 Degussa, TiO$_2$ Hombikat, anatase TiO$_2$ and WO$_3$ nanocrystals under UV-A light was studied in aqueous acidic solution. Iron(III) ion was estimated spectrophotometrically at 480 nm after complexing it with thiocyanate in acidic medium. The ZnO nanocrystals dissolved under the experimental (5 mmol L$^{-1}$) acidity and could not be used as photocatalyst. Photoreduction of iron(III) ion to iron(II) ion is well known and the counter reaction in presence of organics is its oxidation. In the present study, ferric ammonium sulfate is the source of iron(III) ion and the reaction medium is aqueous HCl. The species present in the reaction solution are Fe$^{3+}$, NH$_4^+$, H$^+$, SO$_4^{2-}$ and Cl$^-$. Hence, the possible counter reaction could be oxidation of NH$_4^+$ and or Cl$^-$. However, the photoreduction of iron(III) with ferric sulfate as a source of Fe$^{3+}$ under identical conditions proceeds smoothly and affords similar results (Fig. 4). The efficiency of photoreduction...
was obtained from the initial concentration of iron(III) ($q_0$), its concentration at equilibrium after adsorption on the nanocrystals ($q_1$) and its residual concentration after illumination ($q_2$).\(^{(24)}\)

Photoreduction efficiency (%): \[ \frac{100(q_0 - q_1 - q_2)}{(q_0 - q_1)} \] \(\ldots (1)\)

Also, the reaction solution after the photoreduction of iron(III) using ferric ammonium sulfate as source of Fe\(^{3+}\) ion tests for the presence of NH\(_4^+\). Moreover, addition of ammonium sulfate to the reaction solution does not enhance the photoreduction of iron(III) (Fig. 4). The observed decrease of the photoreduction efficiency is probably because of the decrease in acidity of the reaction solution (below the threshold limit) due to the addition of ammonium sulfate. At pH > 3.5, Fe\(^{3+}\) ion is hydrolyzed to Fe(OH)\(_3\) \((pK_a = 37.4)^{(11)}\). The photocatalytic reduction of iron(III) ion in aqueous sulfuric acid proceeds smoothly and under identical acidity provides similar results (Fig. 4). The results obtained with nitric and perchloric acids are similar. These results clearly show that neither the oxidation of NH\(_4^+\) nor that of Cl\(^-\) is the counter reaction. The reaction solution on illumination with semiconductor nanocrystals tests for the presence of hydrogen peroxide; H\(_2\)O\(_2\) was tested with Ti\(_4^+\) solution\(^{(25)}\). Figure 5 is the spectral evidence for the formation of H\(_2\)O\(_2\) on photoreduction of iron(III) (inset in Fig. 5 is the UV-visible spectrum of Ti\(^{4+}\)-H\(_2\)O\(_2\) complex).

Hence the photocatalyzed reactions are:

\[ \text{TiO}_2 \text{ or } \text{WO}_3 + h\nu \rightarrow h^+_{VB} + e^-_{CB} \] \(\ldots (2)\)

\[ \text{Fe}^{3+} + e^-_{CB} \rightarrow \text{Fe}^{2+} \] \(\ldots (3)\)

\[ h^+_{VB} + \text{H}_2\text{O} \rightarrow \text{HO}^- + \text{H}^+ \] \(\ldots (4)\)

\[ 2\text{HO}^- \rightarrow \text{H}_2\text{O}_2 \] \(\ldots (5)\)

The photoreduction of iron(III) ion to iron(II) ion with the formation of hydrogen peroxide indicates the overall reaction as below:

\[ \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} E^0 = 0.77 \text{ V} \] \(\ldots (6)\)

\[ 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- E^0 = -1.77 \text{ V} \] \(\ldots (7)\)

\[ 2\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + \text{H}_2\text{O}_2 + 2\text{H}^+ E^0 = -1.00 \text{ V} \quad (\Delta G^0 = 96.5 \text{ kJ mol}^{-1}) \] \(\ldots (8)\)

The process is endergonic.

**Fe\(^{3+}\) ion photoreduction**

Figure 6 presents the Fe\(^{3+}\) ion-concentration-illumination time profiles with TiO\(_2\) P25 Degussa, TiO\(_2\) Hombikat, anatase TiO\(_2\) and WO\(_3\) nanocrystals as photocatalyst. The corresponding profile in the absence of photocatalyst is also displayed for comparison. Sufficient time was provided prior to illumination for the adsorption of iron(III) ion on the nanocrystals and the displayed profiles present the photocatalytic process; TiO\(_2\) P25 and TiO\(_2\) Hombikat are the most active photocatalysts. Figure 6 also shows the adsorption of iron(III) ion on the nanocrystals prior to illumination. This is in agreement with the earlier reports\(^{(9,12)}\). Photoreduction

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**Fig. 5**—UV-vis spectrum of the illuminated solution on addition of Ti\(^{4+}\) ion. [Inset: the spectrum of H\(_2\)O\(_2\) with Ti\(^{4+}\) ion].

**Fig. 6**—Time profiles of photocatalytic reduction of Fe\(^{3+}\) ion [React. cond.: as given under Materials and Methods].
of iron(III) ion at different initial concentrations of Fe$^{3+}$ reveals inhibition of the same by Fe$^{3+}$ ion. The concentrations of the photoreduced iron at initial concentrations of 1.0, 2.0, 3.0 and 5.0 mmol L$^{-1}$ are 0.8, 0.8, 0.2 and 0.1 (TiO$_2$ P25) and 0.8, 0.5, 0.3 and 0.3 mmol L$^{-1}$ (TiO$_2$ Hombikat), respectively. These results are unique and the reason for the observed inhibition is the inner filter effect of Fe$^{3+}$ ion. Fe$^{3+}$ ion absorbs strongly at the wavelength of illumination and thereby decreases the photogeneration of charge carriers on the catalyst surface. This is confirmed by the UV visible spectra of Fe$^{3+}$ ion at different concentrations displayed in Fig. 7. The photocatalytic reduction of Fe$^{3+}$ ion is inhibited by H$^+$ ion in the reaction solution (Fig. 8). The inhibition of photocatalysis by H$^+$ is likely due to the adsorption of H$^+$ ion on the surface of the semiconductor nanocrystals at high acidity, thus making the particles

Fig. 7—UV-vis spectra of Fe$^{3+}$ ions. [curves 1–4 refer respectively to 1, 2, 3 and 5 mmol L$^{-1}$ in 5 mmol L$^{-1}$ HCl].

Fig. 8—Efficiency of photocatalytic reduction of Fe$^{3+}$ ion (a) at different acidities (illumination time = 60 min), (b) at different photon flux (illumination time: A: 20 min, B: 10 min), (c) at different wavelengths of illumination (illumination time = 20 min) and (d) with nitrogen or air purging (illumination time: C: 60 min, B: 10 min). [React. cond.: as given under Materials and Methods].
positively charged. Due to electrostatic repulsion the adsorption of Fe$^{3+}$ ion on the positively charged semiconductor surface is likely to be less and hence the photocatalysis. The photoreduction of Fe$^{3+}$ ion was carried out with two, four and eight lamps; the angles sustained by the adjacent lamps at the reaction vessel were 180°, 90° and 45°, respectively. The photocatalyzed reduction increases with increase of photon flux. Band gap-illumination generates electron-hole pairs on the surface of semiconductors and increase in light intensity increases the production of charge carriers, thus resulting in enhancement of photocatalysis (Fig. 8). UV-C light is more efficient than UV-A light in bringing about the photocatalyzed reduction of Fe$^{3+}$ ion. The results obtained using 6 W, 254 nm low pressure mercury lamp ($I_0 = 6.2 \, \text{µeinstein L}^{-1} \, \text{s}^{-1}$) and 6 W, 365 nm mercury lamp ($I_0 = 18.4 \, \text{µeinstein L}^{-1} \, \text{s}^{-1}$) in a microreactor, under similar experimental conditions are presented in Fig. 8. A possible reason could be the inner filter effect; Fe$^{3+}$ ion absorbs UV-A light thereby reducing the intensity of illumination responsible for semiconductor photoexcitation. In the present study, the semiconductor nanocrystals were kept in suspension and under constant motion by purging air through the reaction solution. Oxygen is an electron acceptor and it is believed that on band gap excitation of the photocatalyst, the conduction band electron is picked up by the molecular oxygen adsorbed on the semiconductor surface to form a superoxide radical ion, which through a series of reactions affords reactive oxygen species (ROS)\textsuperscript{26}. The ROS are responsible for the photocatalytic processes under moist conditions. Hence, to elucidate the role of oxygen in the photocatalytic Fe$^{3+}$ ion reduction the reaction was studied by purging nitrogen instead of air under identical experimental conditions. The photoreduction is smooth and is not suppressed by the absence of oxygen (Fig. 8). Hence, it may be concluded that Fe$^{3+}$ ion is directly reduced by the conduction band electron. The nanocrystals do not lose their photocatalytic efficiency on usage. Reuse of the catalysts without any treatment shows almost the same photocatalytic efficiency, revealing sustainable photocatalytic activity.

Enhanced photocatalysis by TiO$_2$ P25 and TiO$_2$ Hombikat

The photocatalytic results clearly show that TiO$_2$ P25 Degussa and TiO$_2$ Hombikat are more efficient photocatalysts than anatase TiO$_2$ and WO$_3$ nanocrystals. The surface area of WO$_3$ is the least and may be a reason for its observed low photocatalytic activity. However, the surface area is unlikely to be the sole reason for the observed photocatalytic efficiencies. The surface area of anatase TiO$_2$ is much larger than that of the rest but the photocatalytic activity of anatase TiO$_2$ is far less than that of the other forms of TiO$_2$. Crystal size influences the photocatalytic activity; smaller the crystal size, larger is the photocatalytic activity\textsuperscript{27}. The small crystal size yields large surface area and the large surface area results in high photocatalytic activity. Furthermore, the recombination of photoformed electron-hole pairs is less in small crystals. The average time ($\tau$) taken by the randomly generated charge carrier to diffuse from the bulk to the surface is given by $\tau = r^2 / 2D$, where $r$ is the crystal radius and $D$ is the diffusion coefficient of the charge carrier\textsuperscript{28}. Hence, crystal size and surface area are not the cause for the observed high photocatalytic activities of TiO$_2$ P25 and TiO$_2$ Hombikat. Charge transfer from semiconductor to the adsorbed molecules/ions also influences the photocatalytic activity. The charge transfer resistance of WO$_3$ is the largest and is in accordance with the observed low photocatalytic activity. However, the charge transfer resistance of TiO$_2$ P25 and TiO$_2$ Hombikat is less than that of TiO$_2$ P25 and TiO$_2$ Hombikat. Hence, the charge transfer resistance is not the reason for the observed high photocatalytic activities of TiO$_2$ P25 and TiO$_2$ Hombikat. Figure 2 shows that the band gap energies of the semiconductors employed are not the reason for the observed order of photocatalytic activity; while the absorption edges of anatase TiO$_2$ and rutile TiO$_2$ in the ratio 81:19 and 69:31, respectively. The widely reported band gap energies of anatase and rutile TiO$_2$ are 3.2 and 3.0 eV, respectively\textsuperscript{29} and the conductance band (CB) of anatase TiO$_2$ is more cathodic (-4.2 eV) than that of rutile TiO$_2$ (-4.4 eV)\textsuperscript{30}. This enables electron-transfer from the CB of TiO$_2$ anatase to CB of TiO$_2$ rutile (Fig. 9). This charge separation is likely to enhance the photocatalytic activity\textsuperscript{31,32}. Hence, it is concluded that the enhanced photocatalytic generation of H$_2$O$_2$ with reduction of iron(III) ion by TiO$_2$ P25 and TiO$_2$ Hombikat is
because of charge separation through electron transfer from anatase to rutile phases. Interparticle charge transfer in semiconductor-photocatalysis is known to increase the photocatalytic activity\textsuperscript{33,34}. 

Conclusions

TiO\textsubscript{2} and WO\textsubscript{3} photocatalyze reduction of Fe\textsuperscript{3+} ion in aqueous acidic solution with formation of H\textsubscript{2}O\textsubscript{2}. Due to the inner filter effect, the photocatalytic reduction decreases with increase of iron(III) concentration. The reaction is slow at high acidity and enhances with illumination intensity. Molecular oxygen is not required for the photocatalytic process. The reduction is higher with UV-C light than with UV-A light. The photocatalytic activities of TiO\textsubscript{2} P25 and TiO\textsubscript{2} Hombikat are higher than that of anatase TiO\textsubscript{2} and WO\textsubscript{3}. The separation of photoformed charges between anatase and rutile phases is probably the reason for the enhanced photocatalytic activities of TiO\textsubscript{2} P25 and TiO\textsubscript{2} Hombikat.

Supplementary Data

Supplementary Data associated with this article, viz., Fig. S1, is available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_54A(09)1066-1076_SupplData.pdf.

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