Study of dimension dependent diffusion coefficient of titanium dioxide nanoparticles

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ABSTRACT

In the present paper, we have studied size and dimension effect on diffusion coefficient of nitrogen and platinum doped TiO_2 nanoparticle using Arrhenius relation and Lindeman's criteria under their dynamic limit. The activation energy and melting point decreases with decrease in size. The TiO_2 diffused with metal and nonmetal gives rise to (meta-) stable structure and mid-gap state helps to increase surface to volume ratio and quantum confinement effects, and results in the increase of diffusion coefficient. The calculated diffusion coefficient of undiffused TiO_2 with size is in good agreement with available experimental data.

1. Introduction

Recently, there has been great interest in the nanocrystals due to both fundamental scientific interest and technological applications. Among the various shape and size dependent properties arising due to quantum confinement and large surface to volume ratio, the thermal properties such as surface energy, diffusion coefficient, melting temperatures represent an important class of properties which raises expectation for many novel applications in devices [1–5]. The melting temperature of nanoparticles is lower than the bulk and varies with size and shape. Further, it depends on the matrix/particle interface, which corresponds to superheating if matrix/particle interface is coherent or semicoherent and to supercooling if matrix/particle interface is non-coherent. For technological point of view, the knowledge of thermodynamical properties at nanoscale is necessary for the reliability of the device [6–10].

Titanium dioxide (TiO_2) is a popular material with many applications due to its high permittivity, refractive index, efficiency, low cost, chemical inertness, photocatalytic, photostability and capability of decomposing a wide variety of organics [11–17]. The very important use of TiO_2 as a photocatalyst has been hampered by its wide band gap (3.2 eV for anatase TiO_2) and it requires an ultraviolet radiation (UV) for its photocatalytic activation. Diffusion is an efficient process which shifts the optical response of TiO_2 from the UV to the visible spectral range, i.e. to longer wavelength and gives maximum utilization of the solar induced photocatalytic properties of this material. Further, the diffusion for any TiO_2 photocatalytic system helps in controlling electron–hole transport which may be hindered by any material interfaces, and hence it may lead to great interest in TiO_2 based electronics [14–16].

The shortcoming of TiO_2 can be overcome by diffusing certain element like metal or nonmetals in TiO_2 which shows different properties like ferromagnetism in metal doped TiO_2 [18], capacity to absorb visible light, decrease in working temperature, increase in field emission, etc. This may be due to the formation of new d-bands as a consequence of the interaction of interstitial metal ions in the TiO_2 lattice with host material. The metal dopant, which acts as an electron–hole recombination centers, photocatalyst tends to decrease [18]. Further, it is well known that the diffusion activation energy decreases which results an increase in the diffusion coefficient of atoms in nanocrystals than its bulk counterpart [19–22]. The band gap of TiO_2 can be narrowed by doping it with nonmetals like O [23], C [24–26] and N [27,28], which can replace the lattice oxygen atoms.

The size and shape dependent diffusion coefficient function is an important parameter for any phase transition process, and is related to the thermodynamical properties of material. The under-

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standing of this kind of scientific problem is a challenge particularly in the field of nanotechnology. Until now, to the best of our knowledge there is no study with consideration of shape and size on diffusion coefficient in the case of TiO$_2$ nanocrystals particularly to see the effect of diffusion of any metal/nonmetal nanoparticles in the TiO$_2$ nanocrystal. In the present work we propose to study, theoretically the effect of size and shape on diffusion process using a simple-empirical method within thermodynamical limit. In order to understand the effect of diffusion of metal/nonmetal in TiO$_2$, diffusion activation energy, diffusion time and diffusion coefficient are also calculated at the nanoscale in undiffused and diffused TiO$_2$. The size effect on the diffusion activation energy is analyzed through the size effect on the melting temperature. In the present study, we have considered the doping of nitrogen and platinum nanoparticles in the TiO$_2$ nanoparticle.

2. Methodology and computation

The size-dependent properties of the kinetic parameters are so useful, a unique attempt to establish a quantitative model for describing the size and shape dependent thermal properties using surface/volume ratio is necessary. To model quantitatively the size and temperature dependence of the diffusion coefficient $D(r, T)$ with r being the radius of nanoparticles or grains and T being the temperature, the diffusion coefficient $D(r, T)$ can be written as [29]:

$$D(r, T) = D_0 \exp\left[\frac{-E(\infty)}{RT}\right] \qquad (1)$$

where D_0 is a pre-exponential factor, $E(\infty)$ is thermal activation energy without considering size and shape effect (i.e. for bulk crystal), R is the ideal gas constant and T is temperature. The diffusion coefficient in Eq. (1) does not need any adjusting parameters. Thermal activation energy $E(\infty)$ which is different for different diffusion process is related to the melting temperature $T(\infty)$ via a coefficient C [30,31].

$$E(\infty) = CT_m(\infty) \qquad (2)$$

The coefficient C depends on a class of materials and type of diffusion process [30]. To obtain the diffusion coefficient at nanoscale, Eq. (1) can be modified by considering the two main responsible properties: (1) high surface to volume ratio and (2) quantum confinement effect. Considering no size effect on C, we can write the thermal activation energy at the nanoscale as [31],

$$E(r) = CT_m(r) \qquad (3)$$

Dividing Eq. (3) by Eq. (2), we get

$$\frac{E(r)}{E(\infty)} = \frac{T_m(r)}{T_m(\infty)} \qquad (4)$$

At the nanoscale, the activation energy decreases when the size decreases [31], which implies that diffusion is more activated at the nanoscale, hence we can write Eq. (1) as [32]

$$D(r, T) = D_0 \exp\left[-E(r)\left[\frac{T_m(r)}{T_m(\infty)}\right]/RT\right] \qquad (5)$$

To find a convenient means for correlating $T_m(r)/T_m(\infty)$ in Eq. (4), we can find $T_m(r)/T_m(\infty)$ function by considering the average mean square displacement (msd) of atoms in a nanocrystal $\sigma^2(r)$ using Lindemann's criterion as [32]

$$\frac{T_m(r)}{T(\infty)} = \exp\left\{\frac{-2S_{vib}(\infty)}{[3R(r/r_0 - 1)]}\right\} \qquad (6)$$

where $S_{vib}(\infty)$ is the bulk melting entropy and essential contribution on the overall bulk melting entropy, $r_0 = c_1(3 - d)h$, where d is extended for different dimension with $d = 0$ for nanosphere, $d = 1$ for nanowires and $d = 2$ for thin films, c_1 is added as an additional
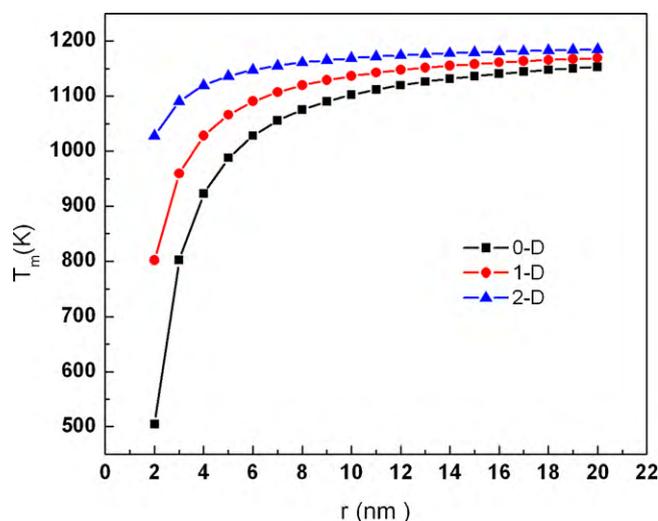

Fig. 1. $T_m(r)/T_m(\infty)$ functions of TiO$_2$ denoted as a solid lines in terms of Eq. (6). The related parameter in Eq. (6) are $h = 0.3768$ nm [38], $T_m(\infty) = 1200$ K and $S_m(\infty) = 126.60$ J mol^{-1} K^{-1} [39].

condition for different surface states which in the case of nanocrystals is equal to unity [32]. Using Eqs. (6) and (5) we can find the expression for diffusion coefficient as,

$$D(r, T) = D_0 \exp\left[\frac{-E(\infty)}{RT} \exp\left[\frac{-2S_{vib}(\infty)}{3R}\frac{1}{r/r_0 - 1}\right]\right] \qquad (7)$$

The diffusion time, τ_{diff} is the quantity which determines the rate of diffusion, critical temperature and critical stress and we can express it as [30],

$$\tau_{diff} = \frac{L^2}{\zeta D}, \qquad (8)$$

where ζ is a numerical constant equal to 2, 4, 6 for one, two, or three dimensions respectively. L is diffusion length, i.e. displacement of one atom by diffusion during a time τ_{diff}. To obtain a statistical limit, we have considered the relative temperature fluctuation inside a cube and the size limit nearly equal to 2 nm for the application of thermodynamics. Therefore any shape effect due to thermal fluctuation above 3% are not addressed in this work and other methods such as molecular dynamics simulation and density functional calculation can be considered for such small nanostructures [30].

3. Results and discussion

The present paper reports the calculated results on the size and shape dependant thermal properties such as melting temperature, diffusion coefficient, and diffusion time of TiO$_2$ nanoparticles. We present the variation of melting temperature with size for the TiO$_2$ nanoparticles of different dimension (shapes) in Fig. 1 and observe that the melting temperature of TiO$_2$ nanoparticles decreases as the size of the particle decreases similar to earlier results on some metal nanoparticles [33–35]. We observe a considerable difference in the behavior of melting temperature of nanoparticle of different dimensions in the case of particles of smaller size. As the particle size increases, melting temperature increases and approaches to bulk melting temperature point, of 1160 K irrespective of the shape. We find a rapid drop of the melting temperature below the size nearly 5 nm which is consistent with earlier findings [33–35]. We further observe that the melting temperature which decreases with size is minimum for 0D structure and maximum for 2D structure, for the same size. This is due to the fact that the size of nanoparticles decreases, surface to volume ratio increases, so there are more number of surface atoms which are loosely bound and are
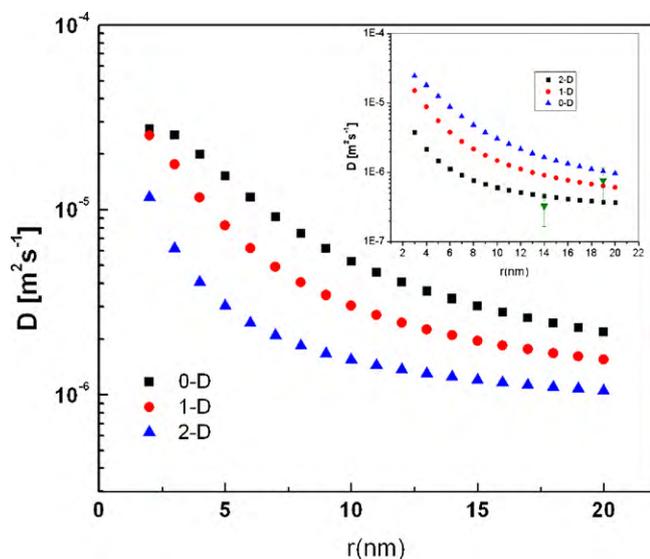
Fig. 2. $D(r,T)$ function of TiO$_2$ as a function of size. The related parameter in Eq. (7) are $h = 0.3768$ nm [37], $T_m(\infty) = 600$ K and $S_m(\infty) = 78.22$ J mol^{-1} K^{-1} [40], $D_0 = 2.75 \times 10^{-5}$ m^2 s^{-1} [41], and $E(\infty) = 18.33$ kJ mol^{-1} [41]. Inset figure is the plot of diffusion coefficient of TiO$_2$ as a function of size for 2D. The parameter are $h = 0.3768$ nm [38], $T_m(\infty) = 453$ K, $S_m(\infty) = 78.22$ J mol^{-1} K^{-1} [40], $D_0 = 2.75 \times 10^{-5}$ m^2 s^{-1} [41], and $E(\infty) = 18.33$ kJ mol^{-1} [41]. Inset diffusion coefficient of TiO$_2$ at 453 K is also shown.

responsible for the melting of nanoparticles. As far as the dimension dependent melting temperature is concerned, the melting for 0D structure is faster than other structured (dimension) material.

We present size and dimension dependent coefficient of TiO$_2$ nanoparticles in Fig. 2 and find that the diffusion coefficient in the case of TiO$_2$ nanoparticles (spherical) is more than the nanostructure of other dimensions such as wire and films due to the fact that the activation energy as well as melting point temperature for spherical particle is lesser than the corresponding cylindrical wire (1D) and thin film (2D) structures. This suggests that the reaction or diffusion can be made faster in the case of spherical nanoparticles. The size and shape dependent activation energy shows the same behavior as of melting temperature. We observe a remarkable feature that the diffusion coefficient is nearly equal in the case of spherical and cylindrical structures for smaller size resulting from the shape instability effect due to the thermal fluctuation [30]. We could not compare the present result on the size and shape dependent diffusion coefficient with any experimental data due to their unavailability. However, to check the accuracy of approach we include the effect of temperature in the calculation of size dependent diffusion coefficient for the comparison with available experimental data at temperature 453 K (inset of Fig. 2). We observe a reasonably good agreement between calculated and only available experimental size dependent diffusion coefficient in the case 2D nanostructure for the size of 14 and 19 nm [36].

We present the diffusion coefficient of nitrogen-diffused TiO$_2$ for different dimensions and sizes in Fig. 3. Nitrogen doping seems to be more attractive among all anionic elements because of its comparable atomic size with oxygen, small ionization energy, metastable center formation and stability [37–40]. We observe from Fig. 3 that the diffusion coefficient depends on both dimension and size of the TiO$_2$ nanoparticles. We find that the diffusion coefficient increases with decrease in the size of the TiO$_2$ nanoparticles. Furthermore, we observe a remarkable increase in the case of doped TiO$_2$ nanoparticles. This increase in diffusion coefficient of nitrogen-diffused TiO$_2$ is the consequence of the decrease in melting temperature and activation energy resulting from the decrease in band gap of TiO$_2$. The nitrogen octet rule is satisfied without
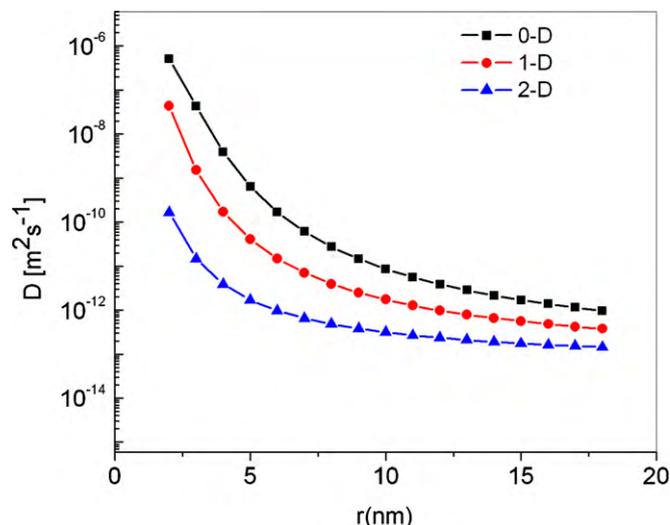

Fig. 3. $D(r,T)$ function of N diffusing into anatase TiO$_2$ shown as the solid lines in terms of Eq. (7) where r is the radius of the grain size of TiO$_2$. The parameter in Eq. (7) is as follows: $h = 0.3768$ nm, for nitrogen sublimation entropy Sc for N is used to substitute $Sm(\infty)$ with $Sc = 36.106$ J mol^{-1} K^{-1} [39], $D_0 = 7.46 \times 10^{-7}$ m^2 s^{-1}, and $E(\infty) = 78.3$ kJ g atom^{-1}, and $T = 573$ K [31].

inducing any significant structural change as the nitrogen occupies the oxygen sites.

In Fig. 4, we present the diffusion coefficient of TiO$_2$ nanoparticles diffused with platinum (Pt) nanoparticles of different shapes. We have calculated the diffusion coefficient in the present case by considering the entropy and pre-exponential factor for different shape of Pt nanoparticles from the experimental work of Narayana et al. [37] which already considers the dimension effect $d = 0$. We observe from Fig. 4 that the diffusion coefficient rapidly increases in the case of diffused cubic Pt nanoparticles below the size of 4 nm. However, we do not find any variation for the diffusion coefficient in the case of tetrahedral shaped Pt nanoparticles. This may be due to the fact that the tetrahedral particle has sharp edges and corners corresponding to either very high value of activation energy or very low value of activation energy [37]. We know that in the case
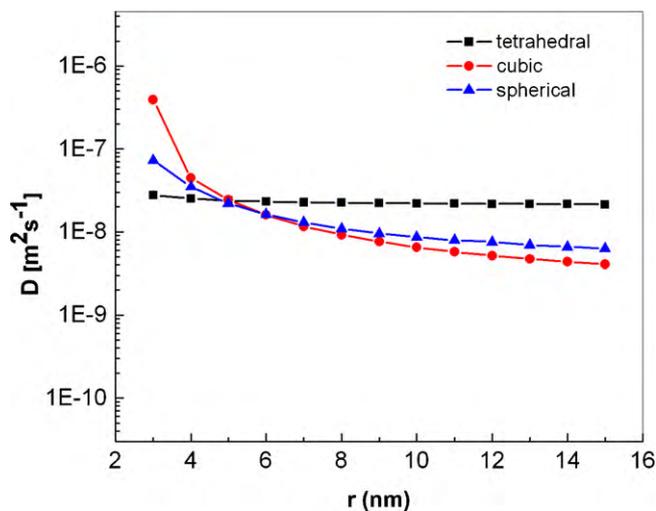

Fig. 4. $D(r,T)$ function of Pt diffusing into anatase TiO$_2$ shown as the solid lines in terms of Eq. (7) where r is the radius of the grain size of TiO$_2$. The parameter in Eq. (7) is as follows: $h = 0.3768$ nm, For Pt. having tetrahedral shape $Sm(\infty) = 2.18$ J mol^{-1} K^{-1} [37], $D_0 = 3.9 \times 10^{-7}$ m^2 s^{-1} [42] and $E(\infty) = 14$ kJ g atom^{-1} [37], and for Pt having cubic shape $Sm(\infty) = 29.60$ J mole^{-1} K^{-1} [37], $D_0 = 3.9 \times 10^{-7}$ m^2 s^{-1} [42] and $E(\infty) = 26.4$ kJ g atom^{-1} [37]. Similarly for Pt having tetrahedral shape $Sm(\infty) = 21.37$ J mol^{-1} K^{-1} [37], $D_0 = 3.9 \times 10^{-7}$ m^2 s^{-1} [42] and $E(\infty) = 22.6$ kJ g atom^{-1} [37].
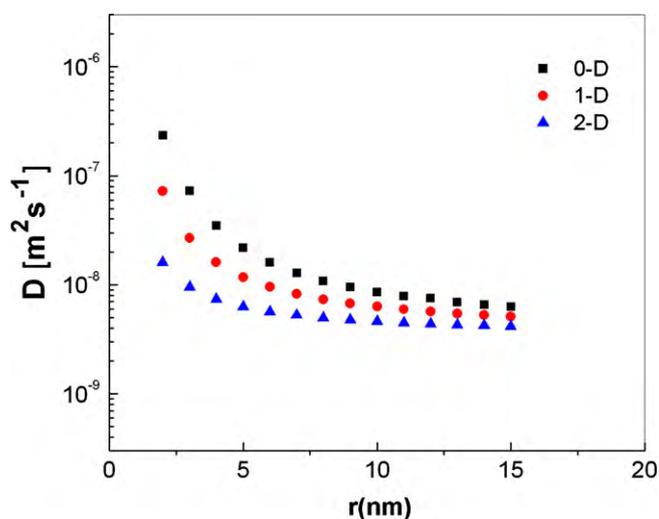
Fig. 5. $D(r,T)$ function of Pt diffusing into anatase TiO_2 shown as the solid lines in terms of Eq. (7) where r is the radius of the grain size of TiO_2. The parameter in Eq. (7) is as follows: $h = 0.3768\,nm$, for $Sm(\infty) = 21.37\,J\,mol^{-1}\,K^{-1}$ [37], $D_0 = 3.9 \times 10^{-7}\,m^2\,s^{-1}$ [42] and $E(\infty) = 22.6\,kJ\,g\,atom^{-1}$, and $T = 573\,K$ [37].

of cubic nanoparticle most of its atoms are located on (1 0 0) facet and are not tightly bound results in to a high value of activation energy and entropy of activation. Similarly in the case of spherical nanoparticles most of the atoms are located on (1 1 1) and (1 0 0) facets with edges at the interface of these facets [37]. We observe a remarkable feature in Fig. 4 that the diffusion coefficient is between cylindrical and tetrahedral shape is due to the fact the activation energy of spherical nanoparticles is between cylindrical and tetrahedral shape which in our view is due to the fact of having similar trend in the activation energy. We present the calculated diffusion coefficient of platinum diffused TiO_2 for 0D, 1D and 2D in Fig. 5 and observe a similar behavior as in the case of nitrogen-diffused TiO_2 nanoparticle. However, we note that the diffusion coefficient in the case of platinum diffused TiO_2 is more than the nitrogen-diffused TiO_2 in agreement with the experiment [37]. This is due to the fact that the activation energy of platinum is lower than the nitrogen which results to higher value of diffusion coefficient in the case of platinum diffused TiO_2 as compare to the nitrogen-diffused TiO_2.

We present the diffusion time for 1D, 2D and 3D nanostructures in Fig. 6 obtained using Eq. (8) and observed that the diffusion time and dimension of nanostruc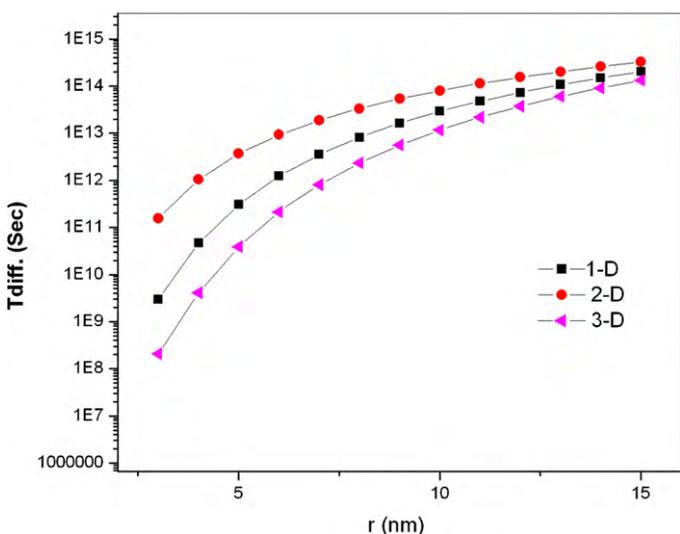tures are inversely proportional to each other, i.e. diffusion time increases as size and dimension of TiO_2 nanoparticle decreases.

4. Conclusion

In summary, we have systematically investigated the size and dimension dependent diffusion coefficient of undoped and doped TiO_2 nanoparticles. We find that there is suppression in diffusion coefficient of TiO_2 nanoparticles as its size or dimension decreases. The diffusion coefficient starts increasing near about 10 nm, however, the change is significant only for smaller size and dimension especially in the case of diffused TiO_2 nanoparticles. The inverse relation between diffusion time and diffusion coefficient is also observed. Diffusion coefficient of TiO_2 nanoparticles is in well agreement with the available experimental data.

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Fig. 6. Diffusion time of TiO_2 as a function of size and dimension.