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Effects of Ni-doping on the photo-catalytic activity of TiO_2 anatase and rutile: Simulation and experiment

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ABSTRACT

The Ni impurity has an inconsistent impact on the photo-catalytic activity of TiO_2 in different regions of electromagnetic radiation. In this work, the effect of different concentrations of Ni doping into anatase and rutile TiO_2 structures is investigated theoretically and experimentally. Doubling the concentration of doped Ni does not change the photo-catalytic activity of TiO_2 significantly according to photo-degradation of Acid Blue 92 (AB 92) under ultra violate and visible (UV–Vis) lights. However, increment of the dopant concentration enhances the thermodynamic yield of TiO_2 crystalline structure (i.e. rutile) at low temperature calcination of TiO_2. Density functional theory (DFT) calculations also confirm the impact of Ni impurity on the higher stability of rutile phase. Computational geometry optimization favors a heterogeneous distribution of Ni atoms in 12.5 at% Ni-TiO_2, that is verified by a broad impurity peak inside the band gap of TiO_2 in UV–Vis diffuse reflectance spectrum (UV–Vis DRS). The DRS and DFT results denote a negligible change in the band gap energy of TiO_2 compared to Ni-TiO_2. Based on DFT results, generation of defect states gives rise to photo-catalytic activities of Ni-TiO_2 in the invisible region. However, adding Ni to anatase TiO_2 changes the type of the band gap from indirect to direct and reduces its photo-efficiency in the degradation of AB 92 under UV irradiation. In addition, a positive shift of the valance and conduction band edges of TiO_2 occurs after Ni doping, which reduces the photo-oxidation activity of TiO_2.

1. Introduction

TiO_2 has drawn a wide interest owing to its low cost, high photo-catalytic activity, stability, and friendly environmental features [1–5]. The photo-catalytic activity of TiO_2 in the UV region, with a band-gap of 3.0–3.2 eV, could be extended to other regions via band-gap engineering [6–9]. For instance, metal doping can shift the absorption edge of TiO_2 from UV-region to lower energies giving rise to photo-catalytic efficiency in the visible region [10–15]. However, the efficiency of metal doping on the photo-catalytic activity of TiO_2 in the UV region is disputable yet [16–18]. Formation of defect states in the band-gap domain of TiO_2 by metal ions, facilitates the photo-excitation of TiO_2 in the visible region [19–21]. Several experimental and theoretical studies have been done on the impacts of nickel-doping on the photo-catalytic efficiency of TiO_2 [22–32]. Energetically favorable replacement of Ti with Ni (with similar ionic radii) in TiO_2 lattice and stability in photo-catalytic activity of Ni-TiO_2 make Ni an appealing dopant among other transition metals [33].

Efficient degradation of Azo-dyes, main pollutants (50–70%) of dyestuffs industrial sewages, is very critical for natural environments. Different concentrations of Ni dopant in TiO_2 lattice result in different photo-catalytic activity in degradation of Azo-dyes under the solar light. [18,23,27,34,35]. Ni-generated defect states in the middle of the band-gap domain would reduce the required energy for electronic transitions correlated with the catalytic activity. Nevertheless, recombination of electron-hole (e-h) pairs in higher concentrations of metal dopants might lower the photo-efficiency of the catalyst. Optimal impurity values (0.5–10%) exhibit more efficient photo-catalytic activities in the experiment, among which 6.25% and 12.5 at% Ni-TiO_2 are subject to many theoretical studies as well [33,35–39]. Among different possible structures for TiO_2, anatase and rutile phase have shown the highest photo-catalytic efficiency and stability, respectively [40–42]. Woll et al. [43] have demonstrated that the type of the band-gap plays predominant role in the photo-catalytic activity of different TiO_2 phases. The longer lifetime for photo-generated e-h pairs and thus the higher photo-catalytic activity in anatase phase in comparison with rutile is due to indirect band-gap in anatase phase vs. direct one in rutile

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In this work, theoretical and experimental investigations are combined to reveal the net impact of Ni impurity on photo-catalytic activity of TiO_2 in different regions of electromagnetic radiation. This impact is investigated in subcategories of geometry, concentration, phase, and electromagnetic domain, individually and combined. In both anatase and rutile phases, 6.25% and 12.5 at% concentrations of Ni dopant are taken into account in both theoretical and experimental study. The photo-catalytic efficiency of Ni-TiO_2 is evaluated in UV–Vis region by photo-degradation extent of AB 92 as a criterion. In order to interpret the experimental results, variations in the calculated geometries, band-gap energies, band-gap types, and band-edge positions of Ni-TiO_2 composites are tracked with respect to changes in phase and concentration.

2. Material and methods

2.1. Synthesis of pure and Ni-doped TiO_2 powders

TiO_2 with 6.25% and 12.5 at% concentration of Ni dopants were synthesized by co-precipitation method [44]. 5 g titanium isopropyl orthotitanate (Tittp) and 5.3 g ethylamine were added to 10.72 g ethanol. The result solution was stirred for 2 h (solution 1). The requisite amount of nickel nitrate (1 and 0.5 g for 12.5% and 6.25%, respectively), separately dissolved in 10.72 g ethanol, was added to the solution 1. After stirring for 2 h, two drops of distilled water were used to hydrolyze the final solution. It was experimentally observed that anatase and rutile phases are dominant at 450 and 700 °C, respectively [45]. The Ni-doped anatase and rutile crystals were filtered, dried (at 80 °C), and finally calcinated at 450 and 700 °C for 3 h, respectively. Hydrolysis of solution 1, by 2 drops of distilled water, followed by drying and calcination at 450 (anatase) and 700 °C (rutile) resulted in the pure powders of TiO_2.

2.2. Apparatus

For detecting the mineral phases, X-ray diffraction (XRD) patterns of the synthesized samples were obtained by Philips X′pert instrument operating with Cu Kα ($\lambda = 0.15406$ nm) irradiation as the X-ray source with 40 kV and 40 mA over a 2θ range from 20° to 60° with a step width of $0.02^\circ\,s^{-1}$. The BET specific surface area was measured in the nitrogen isotherm at 77 K, via Belsorp apparatus. All composites were degassed with N_2 for 4 h at 100 °C prior to the measurement. The absorbance percentage of the dye solution and powders were measured by a UV–Vis spectrophotometer (Varian, Australia, equipped with a DRS instrument) in the wavelength range of 200–800 nm.

2.3. Photo-catalytic activity evaluation

To evaluate the photo-catalytic activity of the synthesized catalysts, 100 mL of 100 $mg\,L^{-1}$ solution of AB 92 (695.58 $g\,mol^{-1}$, C.I.13396. textile dye from Ciba with ~ 40% purity) was mixed with 0.1 $g\,L^{-1}$ of the catalysts and the mixture was stirred vigorously (solution 2) for 1 h. Then, 3 mL aliquot of the solution 2 was separated from the catalyst by centrifuging at 30,000 rpm for 3 min and AB 92 de-colorization was monitored by UV spectroscopy (at $\lambda = 571.14$ nm). As a light source for both UV and visible (attached to UV cutoff) regions, 125 W mercury lamp was fixed in 15 cm above the dye solution [44,45]. The average intensity of incoming light was 0.52 and 13.7 mW/cm^2 in UV and visible regions, respectively. A reference sample containing the dye and catalyst was used in the absence of light to elucidate the adsorption effect in the target solution. Another reference sample containing pure dye in the presence of light was used to investigate the photolysis effect. After stirring the samples for 1 h, the adsorption of each was measured and the concentration of AB 92 was determined in pH = 7.

2.4. Computational details

In order to do first principle electronic structure calculations, the super cell approach was used. In this work, DFT results were obtained using the projector-augmented-wave (PAW) method implemented in the Abinit code [46]. The PBE functional and the generalized gradient approximation (GGA) were utilized to rectify exchange-correlation in DFT calculations. The Fritz-Haber-Institute (FHI) pseudo-potential code [47] was adopted for all atoms in calculations. The energy cut-off and convergence threshold of self-consistent energy were set to 32 Hartrees and 10^{-6} Hartrees, respectively. Also, the force on each atom in geometry optimization was set to 5×10^{-5} Hartree/Bohr, allowing a combined volume and geometry optimization. $Ti_{15}NiO_{32}$ and $Ti_{14}Ni_2O_{32}$ units were used as primitive cells in order to simulate 6.25% and 12.5 at% concentration of dopant in both rutile and anatase phases. A 48-atoms super cell was made using repetition unit values of $2 \times 2 \times 1$ and $2 \times 2 \times 2$ for anatase and rutile, respectively.

In order to investigate the effect of Ni-doping on the electronic structure of TiO_2, the band structure of anatase and rutile was calculated with and without nickel (6.25% and 12.5%) along the high symmetry direction of the first Brillouin zone. Eventually, band structure calculations were carried out at the L (0.5 0.0 0.0) -Γ (0.0 0.00.0) -X (0.0 0.5 0.5) -Γ (1.0 1.01.0) directions with 10, 12, and 17 k-points divisions, respectively.

3. Results

3.1. Experimental results

The X-ray diffraction (XRD) patterns of Ni-doped anatse and rutile powders are showcased in Fig. 1 having a major contribution of diffractional peaks of anatase and rutile. The XRD patterns of pure TiO_2 (rutile and anatase) are the same as the one of Ni-doped TiO_2. The absence of XRD patterns corresponding to metallic nickel and nickel oxide reassures the doping of nickel in TiO_2 structure. The signal associated with rutile is also present in the 12.5% Ni-doped anatse pattern that refers to the effect of higher Ni concentration on rutile stabilization even at lower temperature (450 °C).

The content ratio of anatase (A%) is estimated to be 90% from Eq. (1) [33],

$$A\% = 100/(1 + 1.265 I_R/I_A) \tag{1}$$

where, I_R is the intensity of the rutile (110) peak at 2θ = 27.41 and I_A is the intensity of the anatase (101) peak at 2θ = 25.31 (where θ is the incident angle). Within the detection limit of the XRD (5% wt) the associated peaks of Ni, NiO, and $NiTiO_3$ are not detectable indicating the major contribution of Ni in Ni-doped TiO_2 structure.

Band-gap energy can be calculated via Eq. (2):

$$\alpha h v = A(hv - Eg)^n \tag{2}$$

where, α, $h\nu$, A, and Eg are the absorption coefficient, photon energy, proportionality constant and band-gap energy, respectively. The value of exponent, n, determines the nature of electronic transition: for indirect transition, n = 2 and for direct transition, n = 1/2. The indirect and direct band-gaps were obtained from the intercept of the graphs drawn for $(\alpha)^{1/2}$ and $(\alpha.hv)^2$ versus hv, respectively [48]. Herein, absorption value is directly used as a replacement for α. The results in Table 1 indicate an indirect band-gap for anatase and a direct one for rutile. The respective values of direct and indirect gaps for anatase are 3.4 and 3.35 eV and for rutile are 3.2 and 3.3 eV. However, in both Ni-doped rutile and anatase phases, the direct band-gap energies (3.3 for anatase and 3.2 for rutile) are lower than indirect ones (3.35 for both anatase and rutile). Therefore, in spite of insignificant change in the band-gap energy in both rutile and anatase, Ni-doping changes the band-gap type of anatase from indirect to direct. The UV–Vis DRS results showcase the position of band-gaps of pure and Ni-doped rutile and anatase (see Fig. 2).