Increased photocatalytic activity of TiO₂ mesoporous microspheres from codoping with transition metals and nitrogen

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Abstract

The composition of anatase TiO₂ was modified by codoping using combinations of a transition metal and nitrogen in order to increase its photocatalytic activity and extend its performance in the visible region of the electromagnetic spectrum. The transition metals (Mn, Co, Ni, Cu) were added during the hydrothermal preparation of mesoporous TiO₂ particles, and the nitrogen was introduced by post-annealing in flowing ammonia gas at high temperature. The samples were analyzed by SEM, XRD, BET, inductively-coupled plasma spectroscopy, and diffuse reflectance UV-vis spectroscopy. The photocatalytic activity was assessed by observing the change in methylene blue concentrations under both UV-vis and visible-only light irradiation. The photocatalytic activity of the (Mn,N), (Co,N), (Cu,N), and Ni,N) codoped TiO₂ was significantly enhanced relative to (N) TiO₂.

Keywords: A: codoped, C: diffuse reflectance, D: TiO₂, E: photocatalysis,

1. Introduction

Titanium (IV) oxide, TiO_2 , has many characteristics that make it an attractive candidate for photocatalytic (PC) applications. It is earth abundant, corrosion resistant, and non-toxic. The anatase form, which has a more open structure than the rutile form, is shown in Figure 1. However, the relatively large band gaps of $\sim 3.0\text{-}3.4$ eV for phase pure TiO_2 polymorphs (~ 3.2 eV for anatase), limits their photocatalytic activity to the ultraviolet region of the spectrum. The band gap can be reduced by adding various anionic or cationic dopants [1-6]. A survey by Feng *et al.* [7] of the many transition metals used as dopants found that manganese had superior PC activity compared to cerium, copper, iron, silver and zirconium. Anions such as nitrogen [8] or boron [9] doping also act to reduce the band gap of TiO_2 .

The hydrothermal method affords a straightforward way for producing mesoporous, crystalline TiO_2 nano- and micro-particles with a narrow size distribution. Unlike many other crystal-forming processes that require high temperatures, the hydrothermal method uses relatively low temperatures, $\sim 200^\circ\text{C}$. This is important because the anatase phase, to be used in this study, transforms to the rutile phase at high temperatures.

Recent studies suggest that using a combination of transition metals and nitrogen as dopants is more effective at introducing intermediate states within the band gap, effectively narrowing it [10]. Using a combination of transition metals and nitrogen as dopants produces *n-p* codoping of TiO_2 [10]. A theoretical model by Zhang, *et al.* [11] indicates that the transition metals alter the density of electronic states immediately below the conduction band edge, while the *p*-orbitals of nitrogen populate the gap just below the valence band

edge. Further, the study predicts that manganese will have the highest absorbance in the visible, followed by copper, then cobalt. The Zhu, *et al.* study [10] posited that *n-p* codoping stabilizes the dopants because the electrostatic attraction between them suppresses thermodynamic instability, thus improving the kinetic solubility of the dopants. If the charges of the cation and anion dopants are not balanced, the codoping occurs in conjunction with oxygen vacancy formation or reduction of the metal, is considered to be “non-compensated,” and provides even greater stability [11].

Experimental studies confirm a narrowing of the band gap caused by codoping. An experimental study by Li, *et al.*, found that the non-compensated chromium-, nitrogen-codoped TiO₂ (denoted as (Cr, N)TiO₂) exhibited promising photocatalytic properties for the degradation of methylene blue in aqueous solutions [12]. Here, we report our systematic studies of synthesis and photocatalytic properties of codoped anatase TiO₂ with the following transition metals (Mn, Co, Ni, Cu) and nitrogen. We have successfully demonstrated that the photocatalytic activity of the (Mn,N), (Co,N), (Cu,N), and (Ni,N)-doped TiO₂ was significantly enhanced relative to (N)TiO₂.

2. Material and methods

2.1. Synthesis of TiO₂ codoped with metal ions and nitrogen ((M,N) TiO₂)

Mesoporous titania microparticles were doped with a transition metal using a hydrothermal method as outlined in earlier studies [13, 14]. All of the starting metals used were divalent in their water soluble compounds. A typical hydrothermal precursor solution consisted of 20% TiCl₃ in 3% HCl, an acetate of the transition metal, 3.0 g urea, and 3.0 mL de-ionized water dissolved in 8.5 mL ethanol. The amount of Ti was either 0.0975 mmol

or 0.0950 mmol, corresponding to 2.5 mol % or 5.0 mol % of the transition metal cations present, respectively. After the solution was stirred overnight, it was transferred to a Teflon-lined autoclave, which was then heated at 180°C for ten hours. The samples were then filtered, rinsed with de-ionized water, and dried. Nitrogen doping was accomplished by annealing pure and metal-doped TiO₂ samples at 550°C for five hours in a tube furnace under an ammonia gas flow.

2.2. Characterization and measurements

The microstructures of the samples were analyzed using scanning electron microscopy. X-ray diffraction data were used to identify the crystalline phases present in the samples, and data were collected using a Bruker D5005 diffractometer employing Cu K_α radiation. Determination of mesoporosity, surface area, and average pore size was accomplished using Brunauer, Emmett, Teller (BET) analysis. The samples' absorbance of light in the ultraviolet-visible (UV-vis) region was measured using a Varian Cary 5000 diffuse-reflectance spectrometer.

Photocatalytic activity was measured by monitoring the color change in a solution consisting of 1.0 g/L of the doped TiO₂ and 12 mg/L of methylene blue dissolved in isopropanol. The solution was stirred in the dark overnight to attain adsorption/desorption equilibrium and then constantly stirred during the photocatalysis experiment. A Schoeffel 125 watt Xenon arc lamp provided illumination of the 50 mL Pyrex reaction vessel. The illuminance at the sample was 9.5×10^4 lux. The temperature of the solution was monitored with a type K thermocouple and was found to remain within 0.5 °C over the course of three hours under full illumination. Aliquots were taken at 15 minute intervals, then filtered

using 0.2 μm disc filters. A Varian Cary 5000 spectrometer was used to measure the absorbance of the solution in the range of 550 nm to 700 nm. The wide range was used to monitor for any shifts due to the oxidation of isopropanol. Blank solution samples consisting of just methylene blue and isopropanol were tested for changes in methylene blue concentration by exposing them to the light. No decay in concentration was observed. For the visible activity measurements, a 420 nm cutoff filter was placed in the light path. Inductively-coupled plasma spectroscopy (ICP) was used to measure the concentrations of dopant metal in the cobalt sample to confirm that the synthesis process introduced the proper quantity of dopant into the TiO_2 . Calibration of the Thermo ICP IRIS Intrepid II spectrometer used 5 point calibration line of standards that bracketed the unknown.

3. Results and discussion

3.1. Scanning electron microscopy

Micron-sized, spherical particles synthesized using a hydrothermal process is shown in the SEM image in Figure 2. The particles typically ranged in size from 1 μm to approximately 2 μm . The surfaces have numerous spiny outgrowths in the nanometer size range. A similar microstructure was observed for all the metal-doped TiO_2 samples, as well as for samples codoped with nitrogen.

3.2. X-ray diffraction and BET analysis

X-ray diffraction (Figure 3) of the powders showed mainly the anatase phase for the 2.5 percent (M,N) TiO_2 and the 5 percent samples. The anatase phase is preferable for energy applications, owing to its more open architecture. BET gas adsorption profile measurements performed on four of the samples reveal the mesoporous nature of the

microspheres, as shown in Figure 3. The analyses gave an average surface area of 86 m²/g and an average pore diameter of 8 nm.

3.3. Elemental analysis

The results of the ICP analysis of the 2.5% (Co,N) indicate that the doping level is similar to the expected level, with measured cobalt content of 2.2 ± 0.3 mol %. It is therefore expected that the differences in absorbance among the samples are not due to deviation in metal content from the nominal stoichiometry; due to the apparent lower solubility of the cation as suggested from the X-ray diffraction results.

3.4. UV-Vis diffuse reflectance spectroscopy

Significant differences exist in the UV-vis diffuse reflectance spectra as a function of doping as shown in Figure 4. Before the introduction of nitrogen, the manganese-doped TiO₂ had the highest level of absorbance in the region from 500 nm to 700 nm, followed by the cobalt-doped and copper-doped, with the nickel-doped having the lowest. After the metal-doped samples were doped with nitrogen, their absorbance increased, and the shape of the shift after N doping for Co and Ni appears similar. Moreover, there is a prominent red shift to the visible region upon doping for all the samples. The largest absorbance change occurred with (Co,N) doping, and this sample had the highest absorbance value. (Mn, N), and (Cu,N) had the lowest values, but still had significant absorption in the visible with average absorbance of about 0.6 and 0.5, respectively. When the metal doping level was increased to 5 percent, the absorbance in the visible region fell for cobalt and manganese, but increased slightly for nickel.

These results may be compared with the predictions from the theoretical study of transition metal/nitrogen codoping by the Zhang group [10], which predicted that manganese would have the largest absorption coefficient in the visible region of the spectrum, followed by copper. The zinc/nitrogen combination was predicted to have the least orbital overlap and therefore the lowest absorbance coefficient. The overall order of strongest absorbance within the 500 nm to 800 nm range was predicted to be led by Mn, followed by Cu, Co, Zn, Fe, Ni and Cr.

3.5. Photocatalytic activity measurements

The photocatalytic (PC) activity of the codoped TiO₂ samples when exposed to the UV-vis portion of the spectrum followed somewhat the theoretical results of Zhang *et al.* [10]. TiO₂ codoped, mesoporous powders doped with the transition metals manganese, nickel, cobalt, and copper, and codoped with nitrogen, were examined. As shown in Figure 5, the TiO₂, codoped at the 2.5 percent level with these metals and nitrogen, exhibited the largest decreases in methylene blue concentrations, which is correlated with higher PC activity. In addition, in all cases, their PC activities were better than the activity of the TiO₂ doped with just nitrogen. The result for (Mn,N) is in accord with those by Hu, *et al.* [15] and Xue, *et al.* [10] who found PC activity greater than TiO₂ doped only with nitrogen. Other (M,N)TiO₂ studies that have shown increased photocatalytic activity include those for M = Fe³⁺ [16] and M = La³⁺ [17]. The three best performers in the present study also have the largest calculated dipole moments [10], which have been shown to be correlated with photocatalytic activity [18]. Increasing the metal-doping level to five percent caused a decrease PC activity, relative to N-TiO₂ and the co-doped samples, with the (Mn,N) co-

doped sample showing the largest decrease. Only the (Co,N) co-doped sample at this level had a PC activities comparable to nitrogen-doped TiO₂.

Filtering out the UV portion of the spectrum reduced the PC activity of all the samples when compared to full-spectrum PC activity. Part of this reduction can be attributed to the 18 percent reduction in overall light intensity as the light passed through the 420 nm cutoff filter. As shown in Figure 6, the 2.5 % (Ni,N) sample topped the list with a 9.5 percent reduction in methylene blue concentration, followed by (Co,N) at 4 percent. For comparison, the N-TiO₂ reduced the concentration by just 1.8 percent.

Table 1. Comparison of the decrease in methylene blue concentration at different levels of metal doping for (M,N) TiO₂ when exposed to UV-visible light.

Metal doping level	Percent decrease in methylene blue concentration after 1 hour				
	N TiO ₂	(Mn/N)TiO ₂	(Co,N)TiO ₂	(Ni,N)TiO ₂	(Cu,N)TiO ₂
2.5%	15.2	19.3	21.2	20.6	19.5
5%		2.2	15.7	9.8	13.8

3.6 Theoretical understanding of the electronic structure of codoped TiO₂

A further refinement of the theory was undertaken to improve the estimation of the reduction in the band gap due to codoping. In order to theoretically model the process of codoping in TiO₂, density functional theory (DFT) was employed to investigate the electronic structure of the various doped compounds. However, as is well known, standard approximations such as the local density approximation (LDA) or generalized gradient approximation (GGA) for the exchange correlation functional, of DFT, typically results in underestimation of the band gap of semiconductors. Hence, in order to achieve a greater accuracy for band-gap estimation, one needs to go beyond local or semi-local functionals.

In this work, therefore, the Hybrid Scuzeria Ernzerhof (HSE) functional [19] [20] [21] was used, which, compared to LDA or GGA, greatly improves on the prediction of band gaps for a wide range of semiconductors [22]. Within the HSE formalism, the exchange correlation functional is constructed from a fraction of Hartree-Fock exchange (E_x) and the generalized gradient approximation due to Perdew, Burke and Ernzerhof (PBE) [23, 24]. The method has an advantage over the PBEh hybrid functional [25, 26] due to its faster convergence. This is because in HSE, as proposed by Heyd. *et al.* [19], the exact nonlocal exchange is further decomposed into a long range and a short range part in real space. The range separation is determined by a parameter, μ , which is typically chosen as a distance at which the non-local long range interaction becomes negligible. The HSE exchange correlation functional is written as:

$$E_{xc}^{HSE} = \alpha E_x^{sr,\mu} + (1 - \alpha) E_x^{PBE,sr,\mu} + E_x^{PBE,lr,\mu} + E_c^{PBE}$$

where α is called the ‘mixing parameter’; which accounts for the amount of Hartree-Fock like exchange in the exchange correlation functional. The superscript *sr* and *lr* denote the short range and long range part, respectively and μ refers to the screening parameter as mentioned earlier.

The calculations have been performed using the Vienna Ab-initio Simulations Package (VASP) code [27-29]. As far as the pseudopotentials are concerned, the Projector Augmented Wave pseudopotentials (PAW) [30] and a plane-wave cut-off energy of 600 eV was used.

All the calculations have been performed on a 2x2x2 super-cell of anatase TiO₂ as shown in Figure 1 where a single Ti atom is substituted by a transition metal, M, and an O

atom is substituted by N. The transition metal ions that have been considered here, are V, Cr, Mn, Co, Ni, Cu and Zn.

First, the electronic structure of bulk anatase TiO_2 within HSE and the total density of states were computed and are presented in Figure 7. The valence band edge of bulk TiO_2 is mainly composed of O p states while the conduction band edge is composed mainly of the Ti d states. Our computed band gap within HSE is 3.5 eV which is in agreement to previously reported results for bulk TiO_2 computed with the same functional [31]. This is a slight overestimation compared to the experimentally obtained band gap of 3.2 eV [32] .

In Table 2, the variation of band gaps obtained as a result of the above doping procedure is presented. Previous studies [33] had examined effects of similar substitutional defects using different functionals such as GGA [11] (which is known to severely underestimate band gaps) or GGA+ U (where U is an empirical parameter) [10]. Given that with HSE we obtain the band gap of bulk TiO_2 within a 10% of the experimental value (10%) this is a useful approach to compare the modified band gaps, obtained after doping, to those already existing in literature. Incidentally an HSE calculation for Cr-N codoping in anatase TiO_2 has been reported in the literature for a much smaller concentration [34].

Tauc plots of the experimental data were used to estimate the band gaps. As can be seen from Table 2, the HSE calculations for Ni-N and Cu-N agreed quite well with the experimental estimates, but recall that the experimental work had metallic doping at the a lower level, which is lower than the 6 percent level used in this theoretical model.

Table 2. Comparison of band gaps, in eV, of various codoped TiO₂ samples derived from theoretical and experimental methods.

	Bulk TiO ₂	V-N TiO ₂	Cr-N TiO ₂	Mn-N TiO ₂	Co-N TiO ₂	Ni-N TiO ₂	Cu-N TiO ₂	Zn-N TiO ₂
HSE	3.5	2.05	1.7	1.6	1.3	1.2	0.92	0.7
GGA+U		2.2	1.63					
GGA	2.18		0.6					
Experimental	3.2		0.68 [35]	1.9	2.1	2.1	2.0	1.5 [35]

4. Conclusions

This study demonstrated the capability to markedly alter the UV-vis absorbance of TiO₂ through codoping, while retaining the spherical mesoporous morphology of undoped, mesoporous TiO₂. Codoping with nitrogen anions increases the absorbance in every case. The effect of codoping carried over to photocatalytic activity. When the doping level was 2.5 percent, all of the codoped samples had higher PC activity than N-doped TiO₂. Metal doping at the five percent level led to a decreased PC activity when compared to the 2.5 percent level, although this PC activity is still far superior to undoped TiO₂. These data suggest that the optimum doping concentration for the metals is near 2.5 percent under the doping conditions presented, and that non-compensated *n-p* codoping is an important factor in considering which dopants to use. Moreover, the relationship between absorbance and PC activity is complicated. While increased absorbance points to increased PC activity, there seems to be little correlation between the level of absorbance and the activity.

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Figure captions

Figure 1. Ball-and-stick diagram of the anatase phase of titanium dioxide.

Figure 2. SEM image of (Cu,N)TiO₂ particles produced by the hydrothermal method.

Figure 3. X-ray diffraction patterns of 2.5 percent (M,N)TiO₂ (M=Mn, Co, Ni, Cu) showing that anatase is the majority phase present in all samples. The presence of a weak peak near 30.1° 2θ indicates the presence of a small fraction of brookite phase TiO₂.

Figure 4. BET isotherm data revealing the mesoporous nature of the (Mn,N)TiO₂ and (Co,N)TiO₂ samples.

Figure 5. Diffuse reflectance spectra of 2.5% (M,N)TiO₂ [M=Mn, Co, Ni, Cu,] samples.

Figure 6. (a) Photocatalytic activity of (M,N)TiO₂ in the UV-visible portion of the spectrum as measured by the decay of methylene blue. (b) Photocatalytic activity (M,N)TiO₂ in the visible region as measured by the decay of methylene blue.

Figure 7. Calculated density of states for (M,N)-doped TiO₂. (a) (Cr,N)TiO₂, (b) (Ni,N)TiO₂, (c) (Cu,N)TiO₂, (d) (Mn,N)TiO₂

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7