Asian Journal of Chemistry; Vol. 23, No. 5 (2011), 2343-2346

ASIAN JOURNAL OF CHEMISTRY

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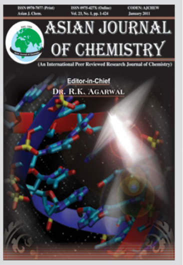

La,N-codoped TiO_2 Visible-Light Responsive Photocatalysts Prepared by Hydrolysis Precipitation Method†

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AJC-9565

La,N-codoped TiO_2 photocatalysts were synthesized *via* hydrolysis precipitation method and characterized by X-ray diffraction, X-ray photoelectron spectra and UV-vis diffuse reflectance spectra. The photocatalytic activity of the as-prepared samples under visible light irradiation was tested using methylene blue as a model organic pollutant. The results indicate that nitrogen and lanthanum ions are incorporated into the interstices of anatase titania nanocrystals, which induces the expected red-shift of absorption band edge, the suppression of the recombination of photo-induced electron-hole pairs and the enhanced photocatalytic activity under visible light irradiation. When N:La:Ti molar ratio is at 0.02:0.003:1, the photocatalytic activity of the codoped samples is the highest, which is about three times as high as that of pure titanium dioxide.

Key Words: La, N-codoped TiO_2, Photocatalyst.

INTRODUCTION

Titanium dioxide, which is well known as a cheap, non-toxic, efficient and the most promising photo-catalyst, has attracted much attention for past decades. In order to extend the light absorption from UV to visible light range and improve the efficiency of utilization of sunlight, great efforts had been focused on aspects of its modification with various ions. Since Asahi and co-workers[1] reported that nitrogen-doping of TiO_2 improved significantly the response to visible light, the non-metal-doping of TiO_2 has become the widespread concern[2]. However, it was found that non-metal doping couldn't well improve the quantum efficiency[3] and the appropriate rare earth doping could introduce the defect energy band structure, extend the light response scope of TiO_2 and reduce the recombination rate of excited electrons and holes, thus, effectively improving its quantum efficiency and photocatalytic activity[4]. Recently, some researchers considered that codoping of rare earth metals and non-metals could enhance greatly the utilization of sun energy and photocatalytic activity of TiO_2 *via* the synergetic effect.

Up to now, most of codoped TiO_2 photocatalysts was prepared using very toxic $TiCl_4$ as raw material and metal and non-metal were doped into TiO_2 in two steps. With a view to developing novel, environment-friendly and facile preparation methods, this paper reports herein, the preparation, structure and visible light photocatalytic performance of nitrogen and lanthanum codoped TiO_2 photocatalysts, La-N-TiO_2, using hydrolysis precipitation method where ammonia and lanthanum nitrate were used as nitrogen and lanthanum sources, respectively and codoping was finished in one step. The results indicate that codoping of N and La shifts significantly the absorption band edge of TiO_2 from UV to visible light region and improves its photocatalytic activity *via* the synergetic effect.

EXPERIMENTAL

Photocatalyst preparation: In this paper, all chemicals were analytical reagent and used as received without further purification. Tetrabutyl titanate, ammonia and lanthanum nitrate were used as titanium, nitrogen and lanthanum sources, respectively. La,N-codoped TiO_2 photocatalysts were prepared using hydrolysis precipitation method by the following procedure.

A certain amount of tetrabutyl titanate was mixed with ethanol under continuous stirring to obtain solution **1**, then mixing of ammonia with ethanol and water to obtain solution **2**. The original molar ratio was as follows:tetrabutyl titanate:ethanol:water = 1:18:4. Under water bath condition at room temperature, solution **2** was slowly added into solution

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†Presented to the 4th Korea-China International Conference on Multi-Functional Materials and Application.

1. After reaction of 2 h, the mixture was centrifugally separated and then the resulting solid was dried. The obtained powder was calcined in muffle furnace at 673 K for 2 h with the ramping rate of 4 K min^{-1} to result in only nitrogen-doped TiO_2 sample. When lanthanum nitrate was added into solution **2** following the same procedure (lanthanum nitrate needed to be dissolved completely in solution **2** before adding ammonia), lanthanum and nitrogen codoped TiO_2 samples was obtained. Undoped, nitrogen-doped and lanthanum, nitrogen codoped TiO_2 catalysts were labeled as TiO_2, N-TiO_2 and x-La-N-TiO_2, respectively, in which x denoted the mole ratio of La to Ti, *i.e*.; 0.1, 0.3 and 0.7 %.

Photocatalyst characterization: The UV-vis diffuse reflectance spectra (UV-vis DRS) of samples were measured by a SolidSpec-3700 DUV with scan range between 200 and 700 nm. The X-ray diffraction (XRD) patterns were recorded on a D/max-Rb X-ray diffractometer (Rigaku Corporation) equipped with CuK_α radiation source. The tube voltage, tube current, scan range and step were set at 40 kV, 50 mA, 20-70 and 0.02º, respectively. The X-ray photoelectron spectra (XPS) were determined by a Thermo ESCALAB 250 instrument. All the binding energies were referenced to the C1s peak at 284.6 eV of the surface adventitious carbon.

Photocatalytic activity[5]**:** Photocatalytic experiments were conducted in a self-constructed reactor with a 100 W incandescent lamp providing the visible light source and methylene blue as a model organic pollutant. In each experiment, 160.0 mg catalyst was added into 100.0 mL methylene blue solution (10.0 mg L^{-1}) to obtain a suspension and after stirring for 0.5 h in the dark to achieve adsorption equilibrium, the incandescent lamp was turned on, in which the vertical distance of the light source to the suspension was 12.0 cm. After each 0.5 h interval, 10 mL of solution was sampled from the reaction mixture and centrifugated for 15 min with 4000 rpm of rotation speed. The upper layer clear solution was collected to determine the concentration of methylene blue to calculate the rate of decolorization.

RESULTS AND DISCUSSION

XRD analysis: The X-ray patterns of the undoped, N-doped and different amounts of La,N-codoped TiO_2 are given in Fig. 1. As shown, all the samples have crystalline structure of only anatase, which is evidenced by the appearance of its characteristic peaks corresponding to 101, 004, 200, 105, 211, 204 crystal planes and the clear separation of 105 and 211 crystal plane diffraction peaks implies that the samples have perfect crystallinity.

Upon doping of N or La and N, the diffraction peaks become widening. Using Scherrer equation, $D = K\lambda/\beta \cos \theta$, where K is the Scherrer constant (K = 0.9), λ and θ the wavelength ($\lambda = 0.15418$ nm) and the incident angle of the X-rays and β the full-width at half-maximum (FWHM) of the 101 plane, the average crystallite sizes for TiO_2, N-TiO_2, 0.1 % La-N-TiO_2, 0.3 % La-N-TiO_2 and 0.7 % La-N-TiO_2 were calculated to be 8.48, 7.14, 7.05, 7.89 and 6.69 nm, respectively. The results show that the particle sizes of doped samples are smaller than those of undoped and doping can suppress the growth of TiO_2 crystallite particles.

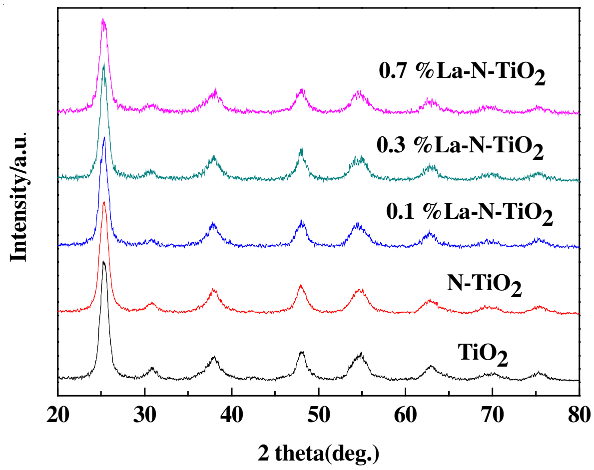
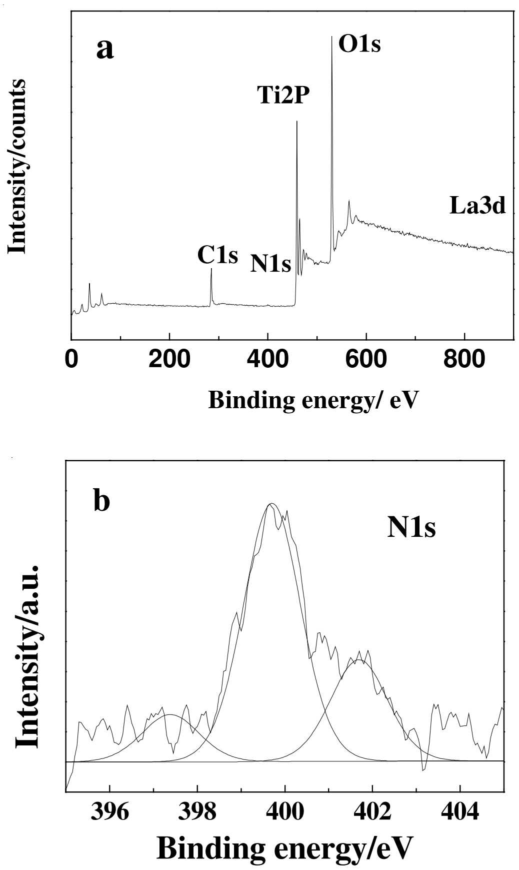


Fig. 1. XRD patterns of the TiO_2 samples

According to Pauling's principle, it is not possible for La^{3+} to replace Ti^{4+} to enter into the titania lattice because of its larger ion radius (0.108 nm) compared with that of Ti^{4+} (0.068 nm)[6]. The characteristic peaks of Ti-N and La_2O_3 phases aren't observed in the X-ray patterns of doped samples, which may be due to the reason that N and La have very small doping amounts and can not form separate phases. These results suggest that La^{3+} may be uniformly distributed in the interstices of titania lattice.

XPS analysis: To theoretically validate the main elements and chemical states on the surface of TiO_2, the global XPS spectrum ((Fig. 2(a)) and the high-resolution XPS of N, Ti, O and La (Fig. 2(b-e)) of the resulting La,N-codoped TiO_2 powder were recorded.



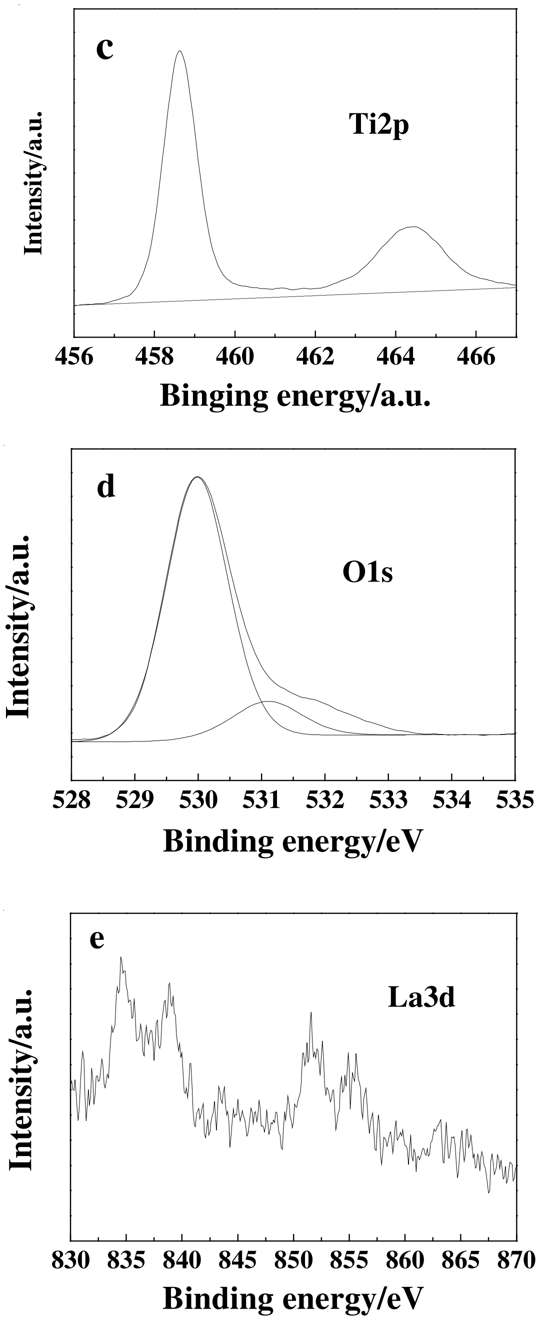


Fig. 2. XPS of the sample codoped with La (0.3 mol %) and N: (a) global spectrum; (b) Nls; (c) Ti2p; (d) O1s; (e) La3d

The shift of binding energy corresponding to the relative surface charge was calibrated using Cls level at 284.6 eV as the internal standard.

The global XPS spectrum indicates that the surface composition of the resulting codoped sample is Ti, O, La and N, unexpectedly, in which the peaks of Nls and La3d are almost absent. This is ascribed to the relatively low contents of N and La in the sample, which agrees with the results of XRD analysis.

The N1s binding energy peaks [Fig. 2(b)] appear at 397.3, 399.8 and 401.8 eV, of which 397.3 eV peak represents the replacement of lattice oxygen O in TiO_2 by N, thus forming N-Ti bond, the main reason of red-shift of absorption band edge of N-doped TiO_2[1], while the peaks in the range of between 399 and 404 eV correspond to binding energies of N in the forms of NO, NN and NHx in the TiO_2 lattice or its surface[7,8]. The nitrogen doped contents are detected to be 1.6 and 1.0 wt % for La,N-codoped and nitrogen-doped TiO_2 powders, respectively, confirming the existence of nitrogen in two powders.

In Fig. 2(c), there appears two binding energy peaks of Ti2p3/2 (458.4 eV) and Ti2p1/2 (464.1 eV) indicating that titanium ions exist in the form of Ti^{4+} in the lattice of the quartet[9]. The peak at 529.9 eV in Fig. 2(d) represents binding energy of O1s of TiO_2 whereas that at 531.1 eV is attributed to hydroxyl group on the titania surface[10].

In addition, the results of Fig. 2(e) and the fitted peak of O1s located at 529.9 eV in Fig. 2(d) suggest that La^{3+} may be uniformly distributed in the interstices of titania in the form of Ti-O-La rather than in the form of substitution of Ti^{4+} by La^{3+}, which further verifies the analysis of XRD.

UV-Vis diffuse reflectance spectra analysis: The UV-vis DRS of the TiO_2 samples are shown in Fig. 3. In comparison with the undoped TiO_2, the doped samples show different degrees of shift of absorption band edge to the longer wavelength region, especially for the codoped one. The formation of N2p level resulting from the replacement of the TiO_2 lattice oxygen atoms by N induces the response of TiO_2 in the visible light region[11]. However, in contrast to N-doped TiO_2, codoped sample has an even higher visible light response. The reason may be that the radius of doping La^{3+} ion is much larger than that of Ti^{4+}, which results in the lattice distortion and the corresponding increase of the lattice constant, so that the codoped samples have a more obvious visible light response.

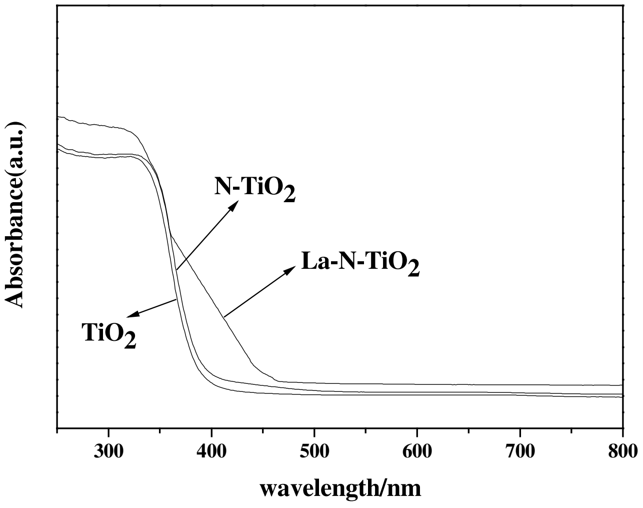


Fig. 3. UV-vis DRS of the TiO_2 samples

Photocatalytic activity: The photocatalytic activity of the TiO_2 samples was evaluated under visible light irradiation for 2 h using methylene blue as a model organic pollutant. and the results are presented in Fig. 4.

As shown, the sequence of decoloration rate of the prepared TiO_2 photocatalysts is as follows: La,N-codoped > N-doped > undoped and, especially for 0.3 % La-N-TiO_2, its decoloration rate is three times as big as that of undoped TiO_2 after 2 h of photocatalytic reaction, which implies that the improvement of photocatalytic activity is ascribed to the synergistic effects for La,N-codoping.

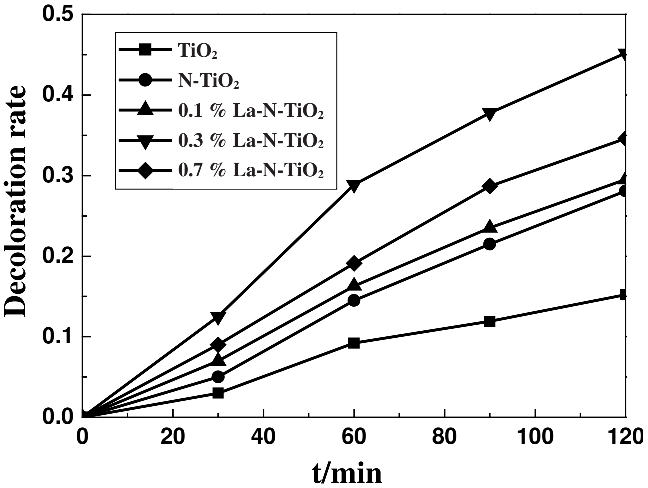


Fig. 4. Time dependence of decolorization rate of methylene blue for TiO_2 photocatalysts under visible light irradiation

It is worth noting that, when fixing the doping molar ratio of N to Ti, the photocatalytic activity of La-N-TiO_2 increases first and then decreases with the increase of the doping molar ratio of La to Ti. The mechanism for La to mediate the photocatalytic activity of TiO_2 can be proposed that: the radius of La^{3+} is obviously more than that of Ti^{4+} and only a very small amount of lanthanum ions can be incorporated into interstices of TiO_2 to result in the distortion induced lattice expansion, which partially contributes to the improved visible light response. The surface defects of TiO_2 increase with increasing of doping and a small quantity of defects can effectively suppress the recombination of photo-induced electron-hole pairs and improve the photocatalytic performance. However, when the doping amount of La is higher than 0.3 %, superabundant La can not enter into the interstices but only deposit onto the surface of TiO_2. As a result, the contact area of TiO_2 with illumination is reduced remarkably. Meanwhile, too much doping induces many defects and spaces that will become the center of recombination of electron-hole pairs. Hence the photo quantum efficiency and the photocatalytic activity are reduced.

Conclusion

Using tetrabutyl titanate, ammonia and lanthanum nitrate as titanium, nitrogen and lanthanum sources, respectively, La,N-codoped TiO_2 photocatalysts with anatase phase were prepared *via* hydrolysis precipitation method. The formation of N2p level resulting from the replacement of the TiO_2 lattice oxygen atoms by N induces the visible-light response, which is further strengthened by lattice distortion *via* La doping. The enhanced visible light respond and suppression of the recombination of photo-induced electron-hole pairs are two main factors for the improvement of photocatalytic activity of La,N-codoping TiO_2 in the visible light region. It is worth to note that, when N:La:Ti molar ratio is equal to 0.02:0.003:1, the photocatalytic efficiency of codoped samples is the highest, being about three times as high as that of pure titanium dioxide. The results of this study provide a method of potential value for the effective utilization of visible light, the largest fraction of solar energy in environmental protection.

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