

C-N-Codoped TiO₂ Synthesis by using Peroxo Sol Gel Method for Photocatalytic Reduction of Cr(VI)

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ABSTRACT

C-N-codoped TiO₂ (CNTO) photocatalysts were successfully synthesized by using “green” method peroxo sol-gel. XRD results revealed the presence of anatase phase only for all samples. The result of Scanning Electron Microscope-Electron Dispersive X-Ray (SEM-EDX) showed surface morphology of CNTO10 was spherical (44 nm) and homogeneous. Diffuse Reflectance Spectra UV-Vis (DRS UV-Vis) result showed red shift in absorbance indicating successful modification of TiO₂ by C and N. The result of photocatalytic activity in reducing Cr(VI) showed that the Cr(VI) reduction increase with the increase of irradiation time and photocatalyst's mass. The highest Cr(VI) reduction was 90.07% for CNTO10 sample. This is due to the synergistic effects of C and N dopants that improves TiO₂ photocatalytic activity under visible light irradiation.

Key word: photocatalyst, C-N-codoped TiO₂, peroxo sol gel, waste water treatment, Cr(VI)

INTRODUCTION

Cr(VI) is a toxic heavy metal ion and it has carcinogenic effect to living things. Nowadays, the presence of Cr(VI) in environment turned into environmental problem. Industrial processing such as electroplating, metallurgy, paint, pigment manufacturing, photography, chrome plating, leather tanning industry and wood processing discharge Cr(VI) in effluent streams and increase day by day [1-3]. Various materials and methods including physico-chemical [4], electrocoagulation [5], permeable reactivity walls [6], adsorption [7], biosorption [8], bioreduction [9] have been developed to perform effective remediation of Cr(VI) in aquatic environment but end up with high cost and not an effective procedural treatment. Compared to those methods, photocatalysis is more effective and low cost to reduce Cr(VI) [10,11].

A well-known photocatalyst, TiO₂ has attracted scientists for its application in reduction Cr(VI) due to good stability in light absorption, low cost and nontoxicity. Unfortunately, pure anatase TiO₂ can only be activated under UV light irradiation due to its wide band gap (3.2 eV). Therefore, some methods have been developed to extend the band gap absorption to visible light region including doping or codoping with transition metal such as Cr, Fe, Mn, V, and non-metal atoms such as N, S, C. In the previous research C-N-codoped TiO₂ photocatalytic activity was found more effective compared to TiO₂. C-N-

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codoped has synergistic effect from dopant carbon and nitrogen in light absorption under visible light irradiation to enhance photocatalytic activity [1, 12-16].

Some techniques have been conducted to synthesis C-N-codoped TiO₂, including sol gel method. However, sol gel method always involves organic solvents and adding other expensive cost chemicals. Here, synthesis of C-N-codoped TiO₂ by peroxo sol gel was an effective way to solve above problems, became more efficient and environmental friendly due to using water only as the solvent [15]. Furthermore, a few publications have been published about photocatalytic activity reduction of Cr(VI) with multi-non-metal-codoped TiO₂ material under visible light irradiation. Therefore, in the present work, we focus on photocatalytic activity reduction of Cr(VI) by C-N-codoped TiO₂. The optimum carbon dopant concentration and photocatalyst mass for that application are also investigated.

EXPERIMENT

Chemicals and instrumentation

All chemicals were used directly without further purification. Titanium (IV) chloride, purchased from Merck was used as Ti source. Carbon powder was prepared from coconut shell as carbon source. Hydrogen peroxide (p.a), ammonia solution (p.a), sodium hydroxide, potassium dichromate, 1,5-diphenylcarbazide, acetone, and sulfuric acid (p.a) were obtained from Merck.

Samples were characterization by X-Ray Diffraction (XRD, Philips X'pert powder PANanalytical) instrument with Cu K α to identify crystal structure of samples. Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX, Phenon) was used to determine surface morphology, size and existence of carbon and nitrogen inside C-N-codoped TiO₂. Optical property of the photocatalyst was obtained using Diffuse Reflectance Spectra UV-Vis (DRS UV-Vis, Shimadzu UV-Vis 2450 Spectrophotometer). The concentration of Cr(VI)-DPC complex was measured by Spectrophotometer UV-Vis (Genesys 20, λ = 543 nm).

Procedure reaction

Carbon powder (10, 20 and 25 wt.% with respect to TiO₂) was added to 300 mL distilled water and ultrasonically treated for 1h. 3.6 mL of TiCl₄ was added drop-wise into the carbon suspension solution in ice bath under vigorous stirring. pH of solution was adjusted to 10 by drop wise addition of ammonia solution (3.0 M). After stirring for 24 h, the obtained precipitate was centrifuged and washed thoroughly with distilled water repeatedly until no Cl⁻ was detected. The precipitates were solved to 80 mL distilled water, 28 mL H₂O₂ was added drop-wise into the mixture under continuous stirring. The solvent was vaped by using rotary evaporator. The precipitates was dried then calcined in air at 500°C for 1 h. All samples were labelled as CNTO10, CNTO20 and CNTO25. Ammonia solution was replaced by NaOH solution for preparing un-doped TiO₂ and C-doped TiO₂ (CT) [15, 17].

Photocatalytic activity test

Photocatalyst (0.01; 0.03; and 0.05 g) was added into 60 mL solution containing Cr(VI) with concentration at 5 mg/L, solution pH was adjusted to 2 using H₂SO₄ 6 N [1]. Prior to reach absorption-desorption equilibrium, mixture solution was stirred for 30 min in the dark then 10 mL aliquot was taken. The procedure was continued by irradiated the mixture under 24 W LED lamp as light source for 150 minutes (interval 30 minutes). The absorption spectrum of the filtrate solution was recorded using Genesys 20 Spectrophotometer UV-Vis. Reduction of Cr(VI) percentages were determined colorimetrically at 543 nm using 1,5-diphenylcarbazide as color agent.

RESULT AND DISCUSSION

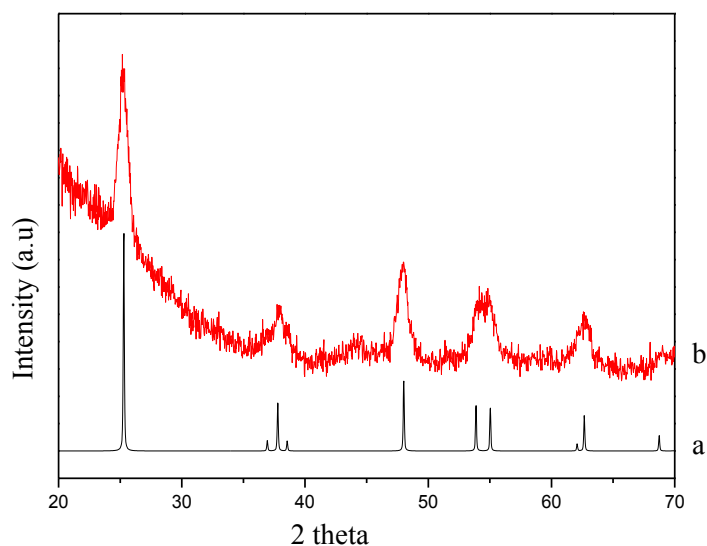


Figure 1. The comparison XRD pattern of (a) TiO₂ standard ICSD no. 82084 and (b) TiO₂ as-prepared

Figure 1 shows the typical XRD pattern of as-prepared TiO₂ that has peaks at 2θ values of 25.18° , 37.97° , 47.92° , 54.26° , 54.87° , and 62.65° . Those peaks show the presence of only anatase phase (ICSD no. 82084). In order to investigate the effect of carbon concentration on the crystal structure of TiO₂, the XRD patterns of CNTO10, CNTO20, CNTO25 samples were recorded as shown in Figure 2. It can be seen that the phase of all samples C-N-codoped TiO₂ did not change but the crystallinity of the samples steeply increase due to the increase of C dopant concentration. There is no shift of peak position for CNTO10, CNTO20 and CNTO25, in spite of TiO₂ which probably because C or/and N do not substitute the atoms in TiO₂ lattice or the concentration of C or/and N substituted in TiO₂ lattice is low [17].

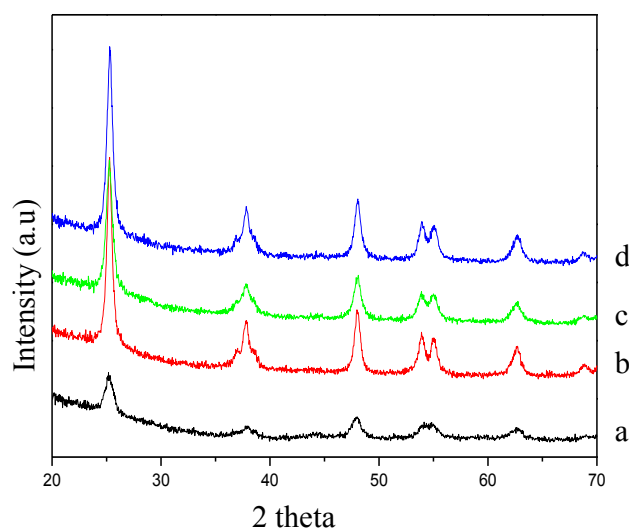


Figure 2. XDR pattern of (a) TiO₂, (b) CNTO10, (c) CNTO20 and (d) CNTO25

SEM-EDX characterization was done to determine the surface morphology and compositions of Ti, O, C and N inside CNTO10. CNTO10 was representing as prepared codoped TiO_2 due to its highest photocatalytic activity for Cr(VI) reduction under visible light irradiation. From Figure 3(a), it could be clearly observed that CNTO10 were nanospheres (44 nm) and homogeneous. EDX spectra in Figure 3(b). shows Ti, O, C and N atom peak of CNTO10. The peak of C and N atom proves that TiO_2 was successfully modified by C and N atom.

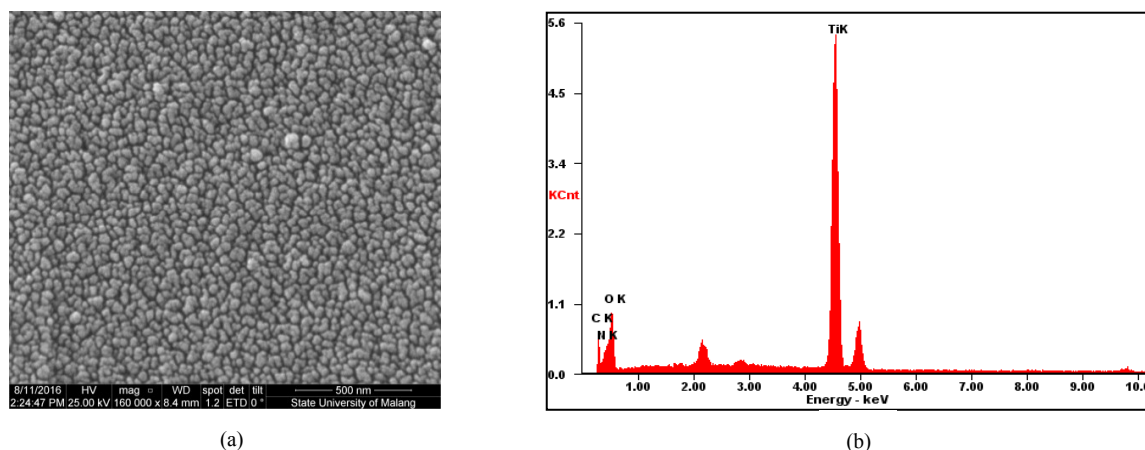


Figure 3. (a) SEM images of CNTO10, (b) EDX spectra of CNTO10

Photocatalysts were characterized by Diffuse Reflectance Spectra UV-Vis (DRS UV-Vis) to measure the absorption characteristic. Then, it was used to determine the band gap and the shift of absorption edge after modification. Absorption intensities of CNTO were higher significantly than controls (NT, CT and undoped- TiO_2), as shown in Figure 4. Absorption edge of CNTO10, CNTO20, CNTO25, CT, and NT extended into visible region which attribute to the successness of TiO_2 modification compared to TiO_2 which is active only in UV region.

The shift of absorption edge was caused by narrowing band gap due to mixed C or/and N 2p states with O 2p states in valance band or the intergap localized states of C and/or N together contribute to the shift of absorption edge [18]. The band gap of CNTO10, CNTO20, CNTO25, NT, CT, and undoped- TiO_2 calculated by using Plank formula were 2.87 eV, 2.86 eV, 2.71 eV, 2.97 eV, 3.02 eV and 3.09 eV, respectively. The decreased of band gap proved that C and N successfully modified TiO_2 due to the synergistic effect of N and C[13]. The absorption intensities of CNTO in the visible region increase with increase of the concentration of carbon black. However, the absorption intensity of CNTO20 showed no obvious difference in the visible light region compared with that of CNTO10, even though the concentration of carbon doping in CNTO20 is higher than CNTO10 due to the increase of C dopant concentration in CNTO20 was not enough to shift the absorption edge of TiO_2 . The shift of absorption edge was caused by narrowing band gap due to mixed C or/and N 2p states with O 2p states.

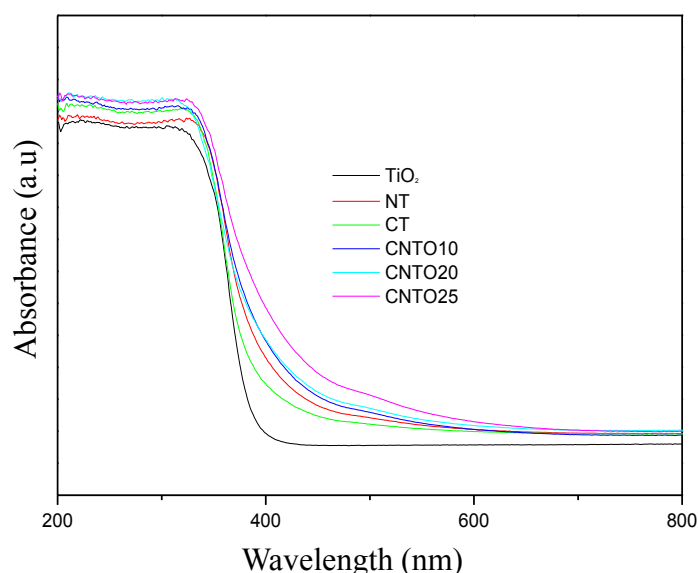


Figure 4 DRS spectra as-prepared samples as photocatalyst

Figure 5 (a), (b) and (c) show photocatalytic reduction of Cr(VI) under visible light irradiation using as-prepared photocatalysts. The highest photocatalytic reduction of Cr(VI) using 0.01 g, 0.03 g and 0.05 g as-prepared photocatalysts is done by CNTO10 with reduction efficiency of Cr(VI) are 35.99%, 72.54% and 90.07% ($t=150$ mins), respectively, then followed by CNTO20, NT, CT, CNTO25, and TiO_2 . The average of absorption efficiency for all samples is 11-20% ($t=30$ min).

Based on mass and time variation, it can be seen reduction efficiency of CNTO is much better than controls (NT, CT and undoped- TiO_2) due to TiO_2 modification by C and N which successfully narrowed TiO_2 band gap, in addition TiO_2 was activated under visible light irradiation and Cr(VI) reduction was more efficient. Photocatalytic CNTO10 is better than CNTO20 and CNTO25 which means the optimal concentration of carbon in CNTO is 10 wt%. Photocatalytic activity was decreased with the increase of carbon concentration due to the increase of dopant would increase the electron hole recombination rate of charge carriers which affected the rate of photocatalytic process [19].

The most effective as-prepared photocatalysts mass in photocatalytic reduction of Cr(VI) was 0.05 g (as shown in Figure 5(c)). The increase of mass and irradiation time were increased the coalition between photocatalysts, visible light and Cr(VI) solution as the result the reduction efficiency was higher. Chromate/dichromate ion, strong oxidator in acid solution is easy to be reduced by TiO_2 which has more negative potential reduction than Cr(VI) ion. The total reaction can be written down as:



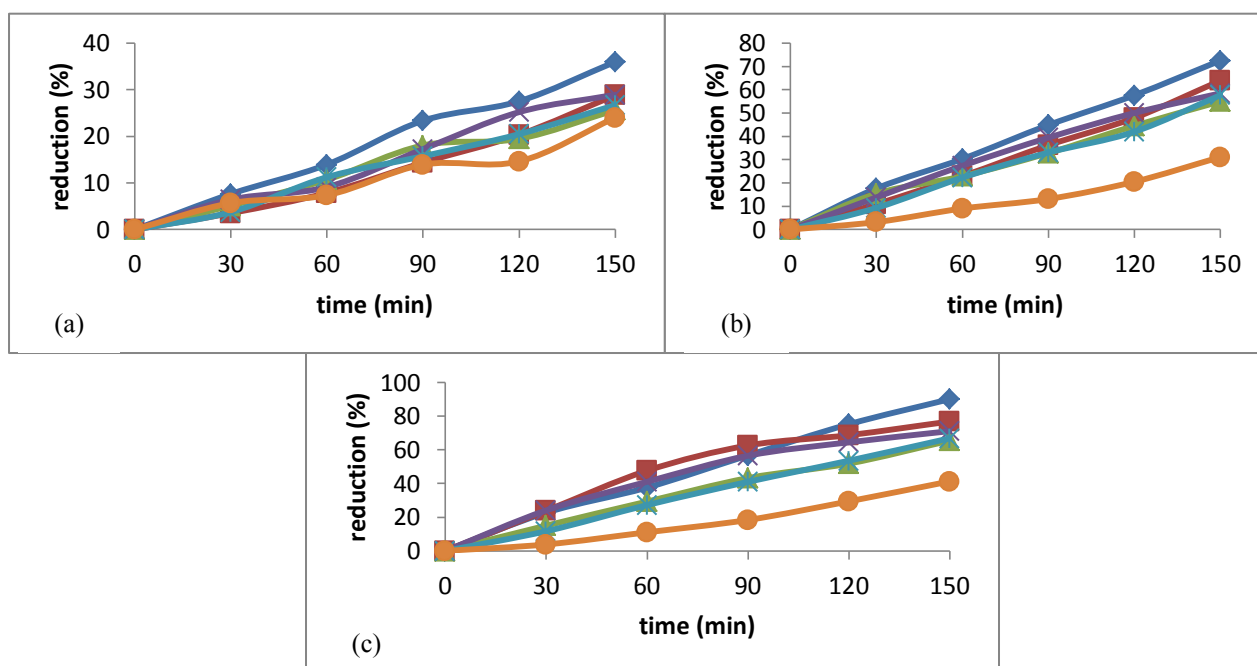


Figure 5. Reduction efficiency of Cr(VI) solution with various photocatalyst mass (a)0.01 g, (b)0.03 g. and (c)0.05 g.

Note : (◇) CNT010 (□) CNT020 (Δ) CNT025 (X) NT (*) CT (●) TiO₂

CONCLUSION

The C-N-codoped TiO₂ samples with carbon concentration variation have been successfully synthesized by using “green” method peroxo sol gel. TiO₂ was successfully modified by N and C, narrowed TiO₂ band gap, and increased photocatalytic activity in reduction of Cr(VI) solution. The optimal carbon concentration for synthesizing C-N-codoped TiO₂ was 10 wt% due to its excellent reduction efficiency under visible light irradiation (90.07% in 150 min). The most effective C-N-codoped TiO₂ mass in reduction of 5 mg/L Cr(VI) solution was 0.05 g. It can be attributed to synergic effect of C and N inside TiO₂ under visible light irradiation.

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REFERENCES

- [1] Lei, X.F., Xue, X.X., Yang, H., Chen, C., Li, X., Pei, J.X., Niu, M.C., Yang, Y.T. and Gao, X.Y., *J. Alloy. Compd.*, **2015**, 646, 541-549.
- [2] Alanis, C., Natividad, R., Barrera-Diaz, C., Martínez-Miranda, V., Prince, J., & Valente, J. S., *Appl. Catal. B-Environ.*, **2013**, 140, 546-551.
- [3] Cai, L., Xiong, X., Liang, N., & Long, Q., *Appl. Surf. Sc.*, **2015**, 353, 939-948.
- [4] Kurniawan, T. A., Lo, W. H., & Chan, G. Y., *J. Hazard. Mater.*, **2006**, 129(1), 80-100.
- [5] Adhoum, N., Monser, L., Bellakhal, N., & Belgaied, J. E., *J. Hazard. Mater.*, **2004**, 112(3), 207-213.
- [6] Blowes, D. W., Ptacek, C. J., & Jambor, J. L., *Environ. Sci. Technol.*, **1997**, 31(12), 3348-3357.
- [7] Selvi, K., Pattabhi, S., & Kadirvelu, K., *Bioresour. Technol.*, **2001**, 80(1), 87-89.

- [8] Gupta, V. K., Shrivastava, A. K., & Jain, N., *Water. Res.*, **2001**, 35(17), 4079-4085.
- [9] Han, X., Wong, Y. S., Wong, M. H., & Tam, N. F. Y., *J. Hazard. Mater.*, **2007**, 146(1), 65-72.
- [10] Diao, Z. H., Xu, X. R., Liu, F. M., Sun, Y. X., Zhang, Z. W., Sun, K. F., Wang, S. Z. & Cheng, H., *Sep. Purif. Technol.*, **2015**, 154, 168-175.
- [11] Wang, C. C., Du, X. D., Li, J., Guo, X. X., Wang, P., & Zhang, J., *Appl. Catal. B-Environ.*, **2016**, 193, 198-216.
- [12] Lei, X. F., Xue, X. X., & Yang, H., *Appl. Surf. Sc.*, **2014**, 321, 396-403.
- [13] Guo, M., & Du, J., *Int. J. Mod. Phys. B.*, **2013**, 27(23), 1350123.
- [14] Devi, L. G., & Kavitha, R., *Appl. Catal. B-Environ.*, **2013**, 140, 559-587.
- [15] Xu, Q. C., Wellia, D. V., Amal, R., Liao, D. W., Loo, S. C. J., & Tan, T. T. Y., *Nanoscale*, **2010**, 2(7), 1122-1127.
- [16] Li, L. H., Lu, J., Wang, Z. S., Yang, L., Zhou, X. F., & Han, L., *Mater. Res. Bull.*, **2012**, 47(6), 1508-1512.
- [17] Xu, Q. C., Wellia, D. V., Yan, S., Liao, D. W., Lim, T. M., & Tan, T. T. Y., *J. Hazard. Mater.*, **2011**, 188(1), 172-180.
- [18] Xu, Q. C., Wellia, D. V., Yan, S., Liao, D. W., Lim, T. M., & Tan, T. T. Y., *Appl. Catal. B-Environ.*, **2010**, 100(1), 355-364.
- [19] Rehman, S., Ullah, R., Butt, A. M., & Gohar, N. D., *J. Hazard. Mater.*, **2009**, 170(2), 560-569.