Local structure of Mo-doped TiO₂ photocatalysts investigated by X-ray absorption fine structure

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Abstract. The local structures of Mo-doped TiO₂ photocatalysts are investigated by X-ray absorption fine structure spectroscopy (XAFS) combined with X-ray diffraction (XRD). The XRD patterns show that all the Mo-doped TiO₂ samples maintain the high qualitative anatase TiO₂ structure without any visible diffraction peak related to Mo. The detailed XANES and EXAFS analysis reveal that all of the Mo atoms substitute Ti atoms in the anatase lattice as Mo⁶⁺ with doping concentration as high as 6 atom %. Combined with theoretical calculation, we suggested that the high electron density of Mo-O causes the strong shrinkage of ~0.1 Å for Mo-O bond length in Mo-doped TiO₂.

1. Introduction
Titanium dioxide has attracted considerable attentions in recent years, due to its strong catalytic activity, high chemical stability, a long lifetime of photo-generated carriers, and water splitting under ultraviolet light as well as potential commercial in environmental cleanup and solar energy utilization. However, the band gap of TiO₂ absorbs only small portion in the ultraviolet region of solar spectrum, which inhibits its photoreaction efficiency under natural sunlight [6, 7, 9]. In order to increase the limited optical absorption of TiO₂ under sunlight, many researchers have studied TiO₂ by adding controlled metal [1, 4, 6, 7, 9] or nonmetal [2, 3, 14]. Several groups have studied the Molybdenum (Mo) ions doped TiO₂, both from experimental and theoretical points of view. For example, Stengl et al. have reported Mo-doped TiO₂ with the Mo content varying from 0 up to 4.7 atom % [12]. Devi et al. have reported Mo doped TiO₂ with the Mo content varying from 0 up to 0.1 atom % [5]. Jeon et al. have studied nanosized Mo doped TiO₂ with the Mo content varying from 0 up to 2.5 atom% [8]. Typically, X-ray diffraction (XRD) was utilized to investigate the structure of Mo doped TiO₂ to confirm the possibility of Mo substitution in TiO₂ lattice [5]. However, those results could hardly
provide effective information on the exact formation of Mo ions occupy sites in the TiO₂ matrix. Theoretically, Yu et al. have performed that the substitutional site Mo ions and the interstitial site Mo ions in the matrix have different impacts on the electronic/optical properties of anatase TiO₂, and substitutional Mo doping is effective in reducing the bandgap of TiO₂ and the redshift is significantly enhanced through increasing Mo concentration [15]. Considering that the optical and electrics of the Mo doped TiO₂ strongly depend on the concentration and the existence sites of the Mo ions in the host structure, it is necessary to investigate the local structural of the Mo atoms in the TiO₂ matrix.

In this work, the photocatalysts Mo doped TiO₂ with high concentration of Mo were synthesized through a co-deposition method. The x-ray absorption fine structure (XAFS) and x-ray diffraction (XRD) techniques were combined to investigate the atomic structure in Mo doped TiO₂ samples. With the advantage of the sensitivity of the XAFS spectroscopy to the local structure around Mo ions, in conjunction with the theoretical calculations, the results reveal that the Mo ions occupied the Ti sites in the TiO₂ lattice and substitutionally doped in TiO₂ matrix.

2. Experimental

The Mo doped TiO₂ samples Ti₁ₓMoₓO₂ (x = 0.03, 0.06) were prepared via a co-deposition method, briefly, using a solution containing Ti (solution A) and a solution containing Mo (solution B). To prepare solution A, 30 mL tetrabutyl titanate and 5 mL acetylacetone were added into 90 mL ethanol. And a ethanolic solution of nitric acid (10 mL stilled water and 0.55 mL nitric acid in 45 mL ethanol) was dropped in and the solution was stirred for 60 min. Solution B is MoO₃ powder with different amount (0.407 g for 3%, and 0.806 g for 6%) dissolved in 0.55 mL nitric acid, and 25mL aqueous ammonia was added in. Solution B was dropped into solution A during 30 min under stirring and the stirring lasted for another 120 min. After aging of 48 h, the wet gel was dried under vacuum and calcined at 600°C for 12 h. The final products were gray powder.

The crystal structures of the samples were determined by an X-ray diffractometer operated at 60 kV and 55 mA, using Cu Kα radiation with a 0-2θ scan mode. The Mo K-edge and Ti K-edge XAFS spectra of the prepared samples were collected respectively at beamline BL14W1 of Shanghai Synchrotron Radiation facility (SSRF, China) and beamline U7C of National Synchrotron Radiation Laboratory (NSRL, China). At all the beamlines, a Si (111) double crystal monochromator was used. XAFS data were analyzed by the UWXAFS3.0 software package [13].

![Figure 1. XRD patterns of prepared Ti₀.₉₇Mo₀.₀₃O₂, Ti₀.₉₄Mo₀.₀₆O₂ and anatase TiO₂ samples.](image-url)
3. Results & Discussion

The XRD patterns of Ti_{1-x}Mo_{x}O_{2} (x=0, 0.03, 0.06) are showed in Figure 1. From Figure 1, it can be seen that only six peaks as the characteristic of the anatase TiO_{2} ([101], [004], [200], [105], [211] and [204] crystalline faces) can be observed without any visible diffraction peak related to Mo. They point out that all the samples have a good crystallinity with anatase structure, almost consistent with previous studies [5]. In order to determine the detailed structure of Mo atoms in TiO_{2}, a further study using XAFS is necessary.

Figure 2. (a) Schematic diagrams of anatase TiO_{2} lattice (model I), substitutional Mo (model II, Mo\textsubscript{Ti}) and interstitial Mo (model III, Mo\textsubscript{i}); (b) Mo K-edge EXAFS FTs spectra of Ti_{0.97}Mo_{0.03}O_{2}, Ti_{0.94}Mo_{0.06}O_{2}, the reference materials of crystalline MoO\textsubscript{3} and Mo metal as well as the calculated spectra for two model structures: substitutional Mo (model II, Mo\textsubscript{Ti}) and interstitial Mo (model III, Mo\textsubscript{i}); Ti K-edge EXAFS FTs spectra of anatase TiO_{2}.

In Figure 2a, we show schematically three representative models built by anatase TiO_{2} lattice: anatase TiO_{2} lattice (model I), substitutional Mo (model II, Mo\textsubscript{Ti}) and interstitial Mo (model III, Mo\textsubscript{i}) respectively. All the calculations were performed within the supercells constructed from a 2× 2× 2 standard unit cell of anatase TiO_{2} lattice and the optimization of total energy was used to calculate the theoretical Mo K-edge EXAFS spectra of substitutional Mo (model II, Mo\textsubscript{Ti}) and interstitial Mo (model III, Mo\textsubscript{i}).

Figure 2b displays Mo K-edge Fourier transforms (FTs) of EXAFS spectra for Ti_{0.97}Mo_{0.03}O_{2} and Ti_{0.94}Mo_{0.06}O_{2} samples. As references, the Mo K-edge functions of Mo foil, MoO\textsubscript{3}, Mo\textsubscript{Ti} model, Mo\textsubscript{i} model, and Ti K-edge EXAFS spectrum of anatase TiO_{2} are also displayed in Figure 2b. It can be seen that the FT features of Ti_{0.97}Mo_{0.03}O_{2}, Ti_{0.94}Mo_{0.06}O_{2} samples, and Mo\textsubscript{Ti} are very close to that of anatase TiO_{2} powder, presenting strong peaks at around 1.5 Å corresponding to the nearest Mo-O and two weak peaks B and C from 2.0 Å to 3.5 Å corresponding to the next-nearest Mo-Ti neighbors. These peaks are distinctly different from those of MoO\textsubscript{3} bulk, Mo metal and model Mo\textsubscript{i}. Therefore, the existence of MoO\textsubscript{3}, Mo metal and Mo occupying the interstitial sites can be easily excluded. This indicates that Mo ions in Mo doped TiO_{2} samples occupy the Ti sites in TiO_{2} lattice with the doping concentration from 0.03 to 0.06. It is notable that peak A in Mo doped TiO_{2} samples presents an evident shift of ~ 0.1 Å toward low R compared with pristine TiO_{2}. Therefore, it can be deduced that the bond length of Mo-O bond significantly shrinks than that of Ti-O bond.

To further obtain the quantitative structural information, we quantitatively fit the nearest Mo-O coordinations using the basic EXAFS formula [10]. The best fit of the structural parameters obtained for the samples are summarized in the Table I and the results of the fit are shown as empty circles in
Figure 2b. Table I shows that for the Mo atoms in Ti_{1-x}Mo_{x}O_{2}, there are 4 Mo-O in 1.80 ~ 1.81 Å and 2 Mo-O in 1.85 ~ 1.86 Å, respectively. They are obviously shrink ~ 0.1 Å as to be considered in comparison with the distance of anatase TiO_{2} (R_{Ti-O}=1.90, 1.95). The goodness of the fits provides evidence that the real structure of Mo doped TiO_{2} can be modeled by the substitutional Mo in TiO_{2}. However, due to the less thermodynamically stable than the pure phase, Mo doping will enhance structural distortion [12].

![Figure 3](image)

**Figure 3.** Mo K-edge XNAES spectra of Ti_{0.97}Mo_{0.03}O_{2}, Ti_{0.94}Mo_{0.06}O_{2}, and MoO_{3}.

The Mo K-edge X-ray absorption near-edge structure spectra (XANES) of Ti_{0.97}Mo_{0.03}O_{2} and Ti_{0.94}Mo_{0.06}O_{2}, along with the reference materials of crystalline MoO_{3} are presented in Figure 3. The absorption edge positions of both Mo doped TiO_{2} samples are similar to that of MoO_{3}, suggesting the existence of Mo^{6+}.

Due to the similarity in the ionic radii of Mo^{6+} (0.062 nm) and Ti^{4+} (0.068 nm), Mo^{6+} can replace Ti^{4+} in the lattice [11]. Figure 4 depicts the electron density distribution of Mo-doped TiO_{2} calculated using Density-functional theory (DFT) with generalized gradient approach (GGA). It is clearly that the electron density in Mo-O bonds is higher than that in Ti-O bonds, which may arise from that the Mo^{6+} fetches more electrons from O^{2-} than Ti^{4+} due to its high charge. Therefore, we can induce that the larger intensity of Mo^{6+} attracting O^{2-} than that of Ti^{4+} is the origin of shrinkage in Mo-O band length, which is consistent with the calculated results of model Mo_{II}.

![Figure 4](image)

**Figure 4.** The electron density distribution of substitutional Mo (Mo_{II}) calculated using Density-functional theory (DFT) with generalized gradient approach (GGA).

| Sample | Coordination | Coordination numbers (N) | R(Å) | σ^(2) (Å^2) |
|--------|--------------|--------------------------|------|-------------|
| Theoretic TiO | 4 | 1.92 | 0 |
| Anatase TiO_{2} | 2 | 1.97 | 0 |
| Anatase TiO_{2} | Ti-O | 3.9 | 1.90±0.01 | 0.0031±0.0001 |
| | | 2 | 1.95±0.01 | 0.0035±0.0001 |
| Ti_{0.97}Mo_{0.03}O_{2} | Mo-O | 3.9±0.1 | 1.81±0.02 | 0.0045±0.0001 |
| | | 1.9±0.1 | 1.86±0.01 | 0.0044±0.0002 |
| Ti_{0.94}Mo_{0.06}O_{2} | Mo-O | 3.9±0.1 | 1.80±0.01 | 0.0050±0.0003 |
| | | 1.9±0.1 | 1.85±0.01 | 0.0050±0.0002 |
| Calculated Mo-O | 4 | 1.85 | 0 |
| model Mo_{II} | 2 | 1.90 | 0 |

**Table I.** Structure parameters for Theoretic Anatase TiO_{2}, Anatase TiO_{2}, Ti_{0.97}Mo_{0.03}O_{2}, Ti_{0.94}Mo_{0.06}O_{2} Samples, and calculated substitutional Mo (model II, Mo_{II}).
4. Conclusions

Using XAFS spectroscopy combined with XRD and theoretical calculation, we studied Mo doped TiO$_2$ samples with different Mo concentration by co-deposition method. The detailed XANES and EXAFS analysis shows that all of the Mo atoms substitute Ti atoms as Mo$^{6+}$ in the anatase TiO$_2$ lattice at the higher Mo concentration of 6 atom%. The high electron density of Mo doping causes $\sim$ 0.1 Å shrinkage of Mo-O bond length, which is consistent with the results of calculated model structure of Mo$_7$Ti.

Acknowledgments

This work was supported by the National Basic Research Program of China (No. 2012CB825801 and 2012CB825801), the National Natural Science Foundation of China (No. 11135008, 10725522, 10905058, and 11179004). The Authors would like to thank the SSRF and NSRL facilities for the beam time. A special acknowledgement is due to Prof. Yuying Huang, Prof. Zheng Jiang, Dr. Lina Li, and Mr Hongliang Bao for their invaluable support.

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