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Structure and photocatalytic property of Mo-doped TiO$_2$ nanoparticles

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Abstract

Mo-doped TiO$_2$ nanoparticles were prepared by sol-gel technique. The as-synthesized samples were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), TEM and FE-SEM. UV-Vis absorption spectrum and the Kubelka–Munk transformation were used to measure the absorption curves and band gap. Their photocatalytic activities were evaluated by the photo-degradation of methyl orange (MO) under irradiation of UV-Visible light and simulated solar light. The results show that Mo$^{6+}$ ions have been doped into anatase TiO$_2$ lattice. Mo doping in TiO$_2$ narrows the band gap (from 3.19 eV of TiO$_2$ to 3.05 eV of Ti$_{0.97}$Mo$_{0.03}$O$_2$) and efficiently increases the optical absorption in visible range. The density functional theory (DFT) calculation of Ti$_{1-x}$Mo$_x$O$_2$ ($x = 0.02$) explains that Mo atom behaves as an abundant donor in TiO$_2$ and can narrow the band gap, since it has two more valence electrons. Therefore, Mo-doped TiO$_2$ nanoparticles exhibit improved photo-degradation ability and the optimal ability of TiO$_2$ nanocrystals is achieved by 2.0 at% Mo-doping.

Keywords: nanoparticle; Mo-doping; red-shift; electronic structure; solar-driven photocatalysis

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1. Introduction

Titanium oxide (TiO$_2$) has been widely studied and used as a photocatalyst in virtue of its strong photocatalytic activity, chemical stability, nontoxicity, favorable optoelectronic property and low cost. But only a small ultraviolet (UV) fraction of solar light (3–5%) can be used because of the wide band gap of TiO$_2$ [1]. In the last decade, great efforts have been made to modify the band structure of TiO$_2$ to shift its light absorption towards the visible region and thus improve its photocatalytic efficiency. One way of doing so is to dope TiO$_2$ with various metal and nonmetal elements, such as Fe [2], La [3], Ce [4], N [5,6], C [7-9], F [10], respectively, or even choosing two proper elements to co-dope TiO$_2$. This approach is able to introduce a carrier trap to prolong the lifetime of photogenerated electron/hole pair and reduce the band gap of TiO$_2$ to some extent. Nowadays transition metals have been reported extensively as the dopant in TiO$_2$. However, researchers have mainly focused on those elements of creating deep donor levels.

Li et al. [11] have found that Mo introduces only a shallow donor level below the CBM and it can be an ideal n-type dopant causing little perturbation on the CBM. Also, unlike some transition metals, which suffer from the formation of strongly localized d states within the band gap and therefore significantly reduce the mobility of the carriers, the shallowness of 4d orbital energy compared to that of 3d orbit presents more nonlocalized character of the 4d orbit [12-13].

In the present work, we attempt to study the influence of shallow impurity doped in TiO$_2$ on the photocatalytic activity. Consequently we will dope Mo into TiO$_2$ and investigate the effects of doping concentration on the photocatalytic activities. Meanwhile, the electronic structures and properties of Mo doped TiO$_2$ will be theoretically investigated based on density functional theory calculations, in order to give reasonable explanations of the possible electronic structure and catalytic mechanisms.
2. Experiments

2.1 Synthesis of undoped and Mo-doped TiO₂ nanoparticles

Mo-doped TiO₂ nanoparticles were synthesized by sol-gel route. 10ml tetrabutyl titanate was added with vigorous stirring into a vessel containing 30 ml ethanol and 1ml acetylacetone to form a solution A. Meanwhile, another solution B containing 10 ml ethanol, 2 ml deionized water, 1 ml hydrochloric acid and molybdenum pentachloride with different concentrations of Mo from 1.0 at% to 3.0 at% (the weight of molybdenum pentachloride were 0.04 g, 0.08 g and 0.12 g, respectively) was prepared. Then, solution B was dropped into solution A with stirring to form Mo-contained sol. After being stilled for 48 h, the gel was formed and kept in an oven at 80°C to produce dried gel powders, and then the powders were calcined in a muffle furnace at 450°C to acquire Mo-doping TiO₂ nanoparticles.

2.2 Characterization

The crystal structure of the powders was analyzed by XRD (Rigaku D/MAX 2500PC) with a Cu target and a mono-chronometer at 40 kV and 250 mA. The scanning range was from 20° to 70°. X-Ray Photoelectron Spectrum (XPS) with an ESCALAB Mk II (Vacuum Generators) spectrometer using unmonochromatized Al Kα X-rays (240 W) was used to detect complementary information on the chemical combination states of various elements of Mo doped TiO₂. Cycles of XPS measurements were done in a high-vacuum chamber with a base pressure of 10⁻⁸ Torr. TEM (JEM-2000EX) was employed to observe the grain size and microstructure of the TiO₂ powders. And FE-SEM (JSM-6700F) was used to observe the morphology of the nanoparticles.
2.3 Photocatalytic activity

The photocatalysis of the powders were characterized by the degradation of 20 mg/L methyl orange under the irradiation of UV-Vis light (wavelength range from 350 nm to 450 nm) derived from a 250 W high-pressure mercury lamp and simulated solar light derived from a 300 W xenon lamp with an AM 1.5 filter. The photodegradation of methyl orange was performed in air at ambient temperature. 10 mg TiO₂ powders were used to degrade a 30 ml solution of methyl orange with concentration of 20 mg/L. The solution was stirred by bubbling air at a flux of 50 mL/min into the beaker. The decolorization of methyl orange solution at its maximum absorption wavelength (464 nm) was recorded by UV–visible spectrometry as a function of exposure time. The experimental results are the average of three repeated experiments. The UV–Vis spectrophotometer was also used to measure the absorbance spectrum of the powders.

2.4 Computational methodology

Density functional theory (DFT) calculation was performed using the Cambridge serial total energy package (CASTEP) code. Exchange and correlated effects were described by the generalized gradient approximation (GGA) [14]. A plane wave cutoff of 500 eV and a 3×3×3 k-point mesh were found to give sufficient convergences. A supercell containing 144 atoms with 48 titanium atoms and 96 oxygen atoms was used as the simulation model. The band gap was estimated after a self-consistent calculation that could generate high quality charge density with the optimized geometrical structure.
3. Results and discussion

3.1 Phase of TiO$_2$ nanoparticles with various Mo-doped concentrations

XRD patterns of TiO$_2$ powders calcined at 450°C for 2 h are shown in Fig.1. All the diffraction peaks of TiO$_2$ and Mo doped TiO$_2$ are attributed to anatase phase, and there is no other phase detected. Moreover, the XRD patterns reveal that the intensity of diffraction peaks decreases with increasing Mo-doped concentration, which may reflect the decrease in the crystalline quality of anatase TiO$_2$ due to the doping of Mo element. The Mo ions should substitute the position of Ti ions in the TiO$_2$ lattice. As the radius of Mo ion (0.62 nm) is very similar to that of Ti ion (0.68 nm), it is much easier for Mo to occupy the lattice position of Ti instead of interstitial position. Mo doped TiO$_2$ nanoparticles are also observed with TEM, the TEM image of 2.0 at% Mo-doped TiO$_2$ powders is shown in Fig.2 (a), the insert is the HRTEM image of a TiO$_2$ particle, the measured lattice spacing of 0.382 nm is in coincidence with the spacing distance of (101) plane. This observation is confirmed by the diffraction pattern position of 2.0 at% Mo-doped TiO$_2$' (101) peak shown in Fig.1. The corresponding SAED pattern of 2.0 at% Mo doped TiO$_2$ is shown in Fig.2 (b), the diffraction rings could be ascribed to (101), (004), (200), (211), (204), and (116) crystalline planes of anatase TiO$_2$. So both the XRD and HRTEM observations present the coincident results and show that the as-synthesized particles are nanocrystalline anatase TiO$_2$. Fig.3 shows the FE-SEM pictures of the as-synthesized nanoparticles. All the particles show round or polyhedron shape with grain size in the range of about 30~40 nm, although the doping of 2 at% Mo in TiO$_2$ (Fig. 3 b) may induce a slight decrease in grain size compared with that of undoped TiO$_2$ (Fig. 3 a).

The XPS survey spectra of TiO$_2$ and 2.0 at% Mo doped TiO$_2$ nanopowders were measured. As shown in Fig.4 (a), the peaks located at binding energy (BE) of 458.57 eV and 464.27 eV correspond
to Ti 2p3/2 and Ti 2p1/2 states of stoichiometric TiO2, respectively, which are consistent with the values of Ti4+ in TiO2 lattice [15]. For 2.0 at% Mo-doped TiO2, the binding energies of Ti 2p3/2 and Ti 2p1/2 are 458.78 eV and 464.48 eV, respectively; a little right-shift movement of 0.21 eV is caused by Mo doping, which may be an indication that molybdenum atoms indeed substituted titanium atoms in anatase lattice.

Mo 3d3/2 and 3d5/2 peaks of 2.0 at% Mo-doping TiO2 sample are shown in Fig.4 (b). The range of binding energies of Mo 3d electron in the spectrum show the presence of a doublet peak structure at 232.5 eV and 235.7 eV characteristic for Mo6+ ion [16]. The separation between the two peaks is 3.2 eV, in agreement with the values reported in the literatures [17-21]. The other signals at binding energy of 231.8 eV and 235 eV are attributed to Mo5+ ion. The BE difference between Mo6+ state and Mo5+ state is 0.7 eV in our work, which is in agreement with an early reported value of 0.8 eV [22]. The area ratio of the two fit peaks is 4.81:1.00, which presumes that the atomic percentages of Mo6+ and Mo5+ would be 82.79% and 17.21%, respectively. That is, most doped Mo ions exist as Mo6+ ions in TiO2 lattice, but a small part of Mo ions exist as Mo5+ ions. The presence of Mo5+ ions signifies that no adequacy oxygen in anatase TiO2 lattice to support Mo being as completed oxidation state of Mo6+ ions. So, the existence of Mo5+ ions also implies that 2 at% Mo-doped TiO2 nanoparticles are in an oxygen deficiency state.

It is interesting to note that the state of O element in Mo-doped TiO2 nanopowders is also different from that of undoped TiO2. The O 1s peaks of undoped TiO2 and Mo-doped TiO2 are shown in Fig.5 (a) and (b), respectively. For the undoped one, the O 1s spectrum can be decomposed into two peaks, the main peak located at about 530.2 eV is assigned to the binding energy of O2− in TiO2 lattice [23,24]; and the small left shoulder peak at about 532.0 eV is attributed to adsorbed
oxygen. But for Mo-doped TiO$_2$, three peaks appear. Beside the O$^{2-}$ peak located at about 530.0 eV, the one at 532.2 eV corresponds to adsorbed oxygen and the peak at about 533.5 eV only shown in Mo-doped TiO$_2$ is attributed to adsorbed water and hydroxyl groups. The comparison between Fig.5 (a) and (b) reveals that there is much more “absorption O” on the surface of 2 at% Mo-doped TiO$_2$ than that on undoped TiO$_2$. After doping of Mo into TiO$_2$, the TiO$_2$ lattice is in the oxygen deficiency state (as one titanium atom needs two O atoms but one molybdenum atom needs three O atoms. And as mentioned above, the existence of Mo$^{5+}$ ions is also a signal of oxygen deficiency), the surface deficiency of O can be complemented by aborting more O atoms, so more absorbed O can be detected on the surface of Mo doped TiO$_2$ in comparison with that of undoped TiO$_2$.

3.2 Optical property of Mo doped TiO$_2$ nanoparticles

Fig. 6 illustrates the Ultraviolet–visible absorbance spectra (converted from diffuse reflectance spectra) for TiO$_2$ with different Mo-doping concentrations. Optical band gap can be calculated from the absorption spectrum. Kubelka–Munk transformation of the absorption curves is shown in the top-right inset. The Kubelka–Munk equation for an “infinitely thick” layer is shown in Eq. 1 [25].

$$f(R_s) = \frac{(1 - R_s)^2}{2R_s} = \frac{k}{s}$$  \hspace{1cm} (1)

where $R_s$ is the absolute reflectance of the layer, $s$ is the scattering coefficient and $k$ is the molar absorption coefficient. The band gap energy can be measured by the Kubelka–Munk plots of $(1 - 2R_s)^2 / 2R_s$ versus energy. The measured band gap energies and the absorption thresholds of these TiO$_2$ nanocrystals are listed in Table 1. Undoped TiO$_2$ gives a band gap value of 3.19 eV, which is in agreement with the typical value of bulk TiO$_2$ (3.2 eV). Doping of 2~3 at% Mo induces a decrease of bang gap to 3.10 ~3.05 eV, i.e., the light absorption threshold moves to violet light range.
(~400 to 410 nm). It is also worth to notice that for 2~3 at% Mo doped TiO₂ the light absorption in both UV and visible regions are greatly increased. The effective red shift of band gap and the evidently enhanced light absorption in UV-visible region are beneficial to the photocatalytic activity of Mo-doped TiO₂.

3.3 Electronic structures and Mo doping modification

The above results should depend on the electronic structure of the materials. The electronic structures of TiO₂ and Ti₁₋ₓMoₓO₂ (x = 0.02) were calculated by density functional theory (DFT) using the Cambridge serial total energy package (CASTEP) code. Fig. 7 shows the band structure (along high symmetry lines in the Brillouin zone) and the partial density of states (PDOS) for TiO₂ (Fig. 7 (a)) and Ti₀.₉₈Mo₀.₀₂O₂, (Fig. 7 (b)) calculated by GGA approach. For TiO₂, the main component in the valance band maximum (VBM) is the O 2p state and the HOMO levels are solely localized on the O 2p states, as shown in Fig. 8 (a). On the other hand, the conduction band maximum (CBM) is characterized by Ti 3d state, and the LUMO levels are solely localized around Ti atoms, as shown in Fig. 8 (b). The band structure and PDOS of Ti₀.₉₈Mo₀.₀₂O₂ are similar to those of TiO₂, but Mo-doping induces some splits in VB and CB due to the breaking of symmetry. To act as a donor impurity, the introduction of Mo atom indistinctively modifies the CBM of TiO₂ and its Fermi level shifts upward into the CB. The electron density contour maps for HOMO and LUMO levels of the Ti₀.₉₈Mo₀.₀₂O₂ are shown in Fig. 8 (c) and (d). Mo-doping in TiO₂ significantly changes the distribution of LUMO which are mainly localized around Mo atom and adjacent metal atoms, which effectively promotes the separation of electrons and holes, thus reduces their recombination probability. Calculated results show a slight decrease or red-shift of band gap from 2.164 eV to 2.138 eV. The prediction of red-shift is reasonable but the calculated band gap values are underestimated.
Comparing to the energy band structure of TiO$_2$, the Mo-doping introduces an impurity level in the band gap, which is near the bottom of the conduction band, because the orbital energy of Mo 4d is close to that of Ti 3d [11]. Therefore, the Fermi level moves upward and would lead a relatively systematic narrow between the valence band and conduction band for n-type semiconductor. In our study, the red-shift is enlarged with increased Mo concentration, and the optical absorption is wholly improved by Mo doping. For Mo-doped TiO$_2$, the incorporation of Mo ions into TiO$_2$ lattice is usually accompanied by vacancy in oxygen site [26], the lattice cycle potential field was disarranged with Mo-doping, so the impurity absorption and the absorption of crystal defects increased greatly [27]. The optical absorption in the UV range is mainly associated to the O$^{2-}$ (2p)→Ti$^{4+}$ (3d) charge transfer process. Those excitations from optical absorption above 380 nm may be corresponding to the shifting of electrons from O 2p to Mo 4d states or sub-band transitions closely related to the ionized oxygen vacancies [28], and the light absorption in the low energy region in Mo-doped TiO$_2$ may be attributed to intra-band transition of between Mo 4d and Ti 3d states [29]. More growth defects will be introduced as the amount of Mo increases, as a result, the ability of light absorption enhances greatly. The optical absorption of Mo-doped TiO$_2$ increases obviously, which is an important factor causing significant photocatalystic activity.

3.4 Photocatalytic activities of Mo doped TiO$_2$ nanoparticles

Fig. 9 (a) and (b) show the photocatalytic activities of TiO$_2$ and Mo-doped TiO$_2$ with different Mo concentrations on the degradation of 20 mg/L methyl orange (MO) under the irradiation of UV-Visible light and simulated solar light, respectively. From the comparison, it is seen that the TiO$_2$ nanoparticles already show good UV-Visible photo-degradation, the decomposition of MO reaches to about 50% while the degradation rate is only 36% for simulated solar-driven photocatalysis after 150
minutes. It indicates that TiO₂ is a better photocatalyst in UV light than in solar light. Mo doping have improved the photocatalytic performance, the 2.0 at% Mo-doped TiO₂ performs best photocatalytic activity with the decomposition of MO reaching to about 75% and 73% under UV-Visible light and simulated solar sources, respectively, after irradiating for 150 minutes. So, the degradating efficiencies of 2.0 at% Mo-doped TiO₂ increases by about 50% and 100% for UV-Visible and solar-driven photocatalysis, respectively, in comparisons with those of undoped TiO₂. However, further increase of Mo-doping concentration to 3.0 at% induces a certain decline of the degradating efficiency, although its performance is still better than those of undoped and 1.0 at% Mo-doped TiO₂ nanoparticles, and this ordering is the same for both photocatalytic activies. The results demonstrate that Mo-doped TiO₂ is a more effective photocatalyst under solar or visible light than under UV irradiation.

Phenomenological, due to the narrower band gap of TiO₂ caused by Mo-doping as shown in Figure 6 and Table 1, the absorption of photons from solar-driven light illumination can be effectively enhanced, which promotes the separation of photogenerated electron-hole pair and facilitates the interfacial electron transferred to improve the photocatalytic activity. Furthermore, Mo⁶⁺ ions replacing Ti⁴⁺ ions in the lattice act as electron traps to promote the charge separation and to reduce the recombination rate of the photogenerated carriers. The photogenerated electrons trapped by Mo⁶⁺ are transferred to the oxygen molecules, and in that case, the oxygen molecules could obtain the electrons to form H₂O₂, HO₂⁻ and O₂⁻ [30]. Meanwhile, in the analysis of XPS, there should be a certain amount of oxygen vacancy (V₀) on the surface of Mo-doped TiO₂, which means that V₀ likewise plays a role as another separating site of electron. Because the presence of V₀ could trap the photogenerated electron thus the trapped electron could transfer to the surface of TiO₂ to
react with the oxygen molecules. These active species go through a series of reactions to produce a superoxide radical (·O$_2^-$), which could promote the photocatalytic oxidation reaction. Moreover, the increasing water molecules and hydroxyl groups adsorbed on the surface of Mo doped TiO$_2$ (see Fig. 5 (b)) could interact with the photogenerated holes to produce surface hydroxyl radical (·OH), which is responsible for the degradation of MO into H$_2$O and CO$_2$.

Mo ions could capture the photogenerated carriers to prolong the lifetime of carriers or quicken the separation of carriers [31], and the TiO$_2$ nanoparticles with appropriate Mo-doping concentration possess the best separate efficiency of electron/hole pair. However, because the concentration of holes on the valence band increases with the increasing of Mo$^{6+}$ ions, overmany Mo$^{6+}$ ions would cause the carriers recombination. As a result, the recombination of photogenerated electron/hole pair exceeds the carrier transition to the surface of photocatalysts. Once the concentration of Mo is beyond an optimum quantity, Mo$^{6+}$ ion’s role as a carrier recombination center would counteract its role of trapping carriers and prolonging carrier lifetime. So a decline of photocatalytic activity is observed.

4. Conclusions

Mo-doped TiO$_2$ nanoparticles of 30~40 nm were prepared by sol-gel technique and several conclusions can be derived.

1. 2.0-3.0 at% Mo doping in TiO$_2$ lattice induces a slight red shift of the band gap to 3.10 ~3.05 eV, which is attributed to the Fermi level moving upward into the conduction band, because donor Mo indistinctively modifies the CBM of TiO$_2$.

2. Mo doping also improves the light absorption in both UV and visible ranges. The enhanced optical absorption in UV range is mainly associated to the O$^{2-}$ (2p)$\rightarrow$Ti$^{4+}$ (3d) charge transfer process,
and absorption in visible light may be attributed to the shifting of electrons from O 2p to Mo 4d states and the intra-band transition of between Mo 4d and Ti 3d states.

3. Mo doped TiO₂ nanocrystals show an evident improvement in photo-degradation of methyl orange (MO) with a more significant increase on degradating efficiency under simulated solar irradiation than that under UV-Visible irradiation and the best performances are observed from 2.0 at% Mo-doped TiO₂ nanoparticles.

Acknowledgement

This work was supported by the Foundation of National Key Basic Research and Development Program (No.2010CB631001), National Nature Science Foundation (Grant No. 50871046) and the Program for Changjiang Scholars and Innovative Research Team in University.
Reference


Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7
Figure 9
Fig. 1. XRD patterns of TiO$_2$ with different concentrations of Mo-doping calcined at 450°C for 2h.

Fig. 2. (a) TEM image of 2.0 at% Mo-doped TiO$_2$ and the insert HRTEM photo showing (101) plane of anatase TiO$_2$. (b) The selected area electron diffraction (SAED) patterns of 2.0 at% Mo-doped TiO$_2$.

Fig. 3. FE-SEM micrographs of TiO$_2$ nanoparticles of (a) TiO$_2$ and (b) 2.0 at% Mo-doped TiO$_2$.

Fig. 4. (a) XPS spectra of Ti 2p of TiO$_2$ (up line) and 2.0 at% Mo-doped TiO$_2$ (down line) nanoparticles; (b) XPS spectra of Mo 3d of 2.0 at% Mo-doped TiO$_2$ nanoparticles, showing Mo ions were doped in the nanoparticles.

Fig. 5. XPS spectra of O 1s of (a) TiO$_2$ and (b) 2.0 at% Mo-doped TiO$_2$ nanoparticles.

Fig. 6. UV-Vis light absorption spectra of TiO$_2$ with different Mo-doping concentrations; the insert shows the conversion curves based on the Kubelka–Munk transformation, which gives the optical band gap.

Fig. 7. Band structures of (a) TiO$_2$, and (b) Ti$_{0.98}$Mo$_{0.2}$O$_2$. The band energies are referenced to the top of valence band. The Fermi levels at 0 eV, and 2.856 eV, respectively, are indicated by a horizontal dotted line.

Fig. 8. Electron density contour map of (a) the top of the valence (HOMO), (b) the bottom of the conduction band (LUMO) of TiO$_2$; (c) HOMO, (d) LUMO of Ti$_{0.98}$Mo$_{0.02}$O$_2$, which are along (111) crystal plane, and (e) top view of LUMO for Ti$_{0.98}$Mo$_{0.02}$O$_2$. Red spheres represent O atoms, grey spheres represent Ti atoms. (HOMO: Highest Occupied Molecular Orbital; LUMO: Lower Unoccupied Molecular Orbital.)

Fig. 9. The photocatalytic degradation of methyl orange by TiO$_2$ and Mo doped TiO$_2$ nanoparticles under (a) UV-Visible irradiation and (b) simulated solar-driven irradiation, respectively.
Table 1 The band gap energy of TiO$_2$ and Mo doped TiO$_2$ samples calculated from Kubelka–Munk plot

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_g$ (eV)</th>
<th>$\lambda$ (nm)</th>
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<tbody>
<tr>
<td>TiO$_2$</td>
<td>3.19</td>
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</tr>
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<td>1.0% Mo-TiO$_2$</td>
<td>3.12</td>
<td>397</td>
</tr>
<tr>
<td>2.0% Mo-TiO$_2$</td>
<td>3.10</td>
<td>400</td>
</tr>
<tr>
<td>3.0% Mo-TiO$_2$</td>
<td>3.05</td>
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Graphical Abstract

The Mo-doped TiO$_2$ nanoparticles exhibit improvements in the photo-degradation of methyl orange under UV-Visible irradiation and simulated solar-driven irradiation, respectively, due to the considerable optical absorption in both UV and visible ranges. For optimum 2.0 at% Mo-doped TiO$_2$, the degrading efficiency enhances more significantly under solar-driven or visible light than under UV light.
Highlights:
- The TiO$_2$ and Mo-doped TiO$_2$ nanoparticles were prepared by sol-gel route.
- The structure of TiO$_2$ was all anatase phase with the crystalline size about 30 nm.
- The light absorption was improved efficiently by Mo doping, even in the visible light region.
- The bandgap of TiO$_2$ was narrowed by Mo doping, corresponding with the analysis of electronic structure.
- The photocatalytic activity of TiO$_2$ nanopowders has been promoted by Mo doping.