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Synergetic effect of TiO<sub>2</sub> as co-catalyst for enhanced visible light photocatalytic reduction of Cr(VI) on MoSe<sub>2</sub>

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#### **Graphical Abstract**



**Research Highlights** 

- MoSe<sub>2</sub>-TiO<sub>2</sub> composites were synthesized via a facile solvothermal method.
- TiO<sub>2</sub> acts as co-catalyst to separate the photo-generated electron-hole pairs.
- MoSe<sub>2</sub>-TiO<sub>2</sub> composites exhibited enhanced photocatalytic activity.
- A high Cr(VI) reduction rate of 91% was achieved under visible light irradiation.

#### Abstract

MoSe<sub>2</sub>-TiO<sub>2</sub> composites were successfully synthesized via a facile solvothermal method. Their morphology, structure and photocatalytic activity in the reduction of Cr(VI) were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, UV-Vis absorption spectroscopy, X-ray photoelectron spectroscopy and electrochemical impedance spectra, respectively. The results show that the introduction of TiO<sub>2</sub> into MoSe<sub>2</sub> boosts the light harvesting efficiency and charge separation and transfer due to their synergistic effect, thus enhancing the visible light photocatalytic activity of MoSe<sub>2</sub> with a maximum Cr(VI) reduction rate of 91% at 120 min compared with pure MoSe<sub>2</sub> (61%) and TiO<sub>2</sub> (5%).

Keywords: Transition metal dichalcogenides; MoSe2; TiO2; Cr(VI); photocatalysis

#### **1. Introduction**

Semiconductor photocatalysis has attracted considerable attention owing to its wide potential in environmental and energy related applications, such as oxidation of organic pollutants [1-6], reduction of carbon dioxide [7-9], evolution of hydrogen or oxygen gas [10-15]. Currently, various semiconductors including metal oxides, sulphides and nitrides have been explored for photocatalytic reaction. However, these materials suffer from shortcomings such as the relatively low solar energy conversion efficiency, instability, high cost, and so on. Therefore, exploring novel visible light-sensitive photocatalysts with high efficiency and good stability remains a great challenge [16-22].

Transition metal dichalcogenides (TMDs) have attracted great interest recently due to their unique structural, electronic, and optical properties [23,24]. As an important member of TMDs, MoSe<sub>2</sub> with a narrow band gap of ~1.4 eV, has been employed as a good candidate for visible light photocatalysis [25-27]. Nevertheless, the photocatalytic activity of MoSe<sub>2</sub> is limited due to the relatively high recombination of photo-generated charge carriers. Currently, constructing unique structures has been suggested to overcome the aforementioned problems. Highly ordered mesoporous crystalline MoSe<sub>2</sub> prepared via a nanocasting strategy using mesoporous silica SBA-15 as a hard template was reported to exhibit higher visible light photocatalytic activity in the degradation of Rhodamine B compared to the bulk MoSe<sub>2</sub> due to its larger surface area and pore volume [28]. However, the quick recombination of photo-generated charge carries still exists for pure MoSe<sub>2</sub>. Another

particularly attractive strategy is to design and develop hybrid composites based on semiconductor oxides, which could offer the driving forces to separate and transfer photo-generated charge carriers [29]. TiO<sub>2</sub>-based composites have been demonstrated with excellent photocatalytic activity [30]. Recently, the hybrid density functional calculation shows that in the MX<sub>2</sub>-TiO<sub>2</sub> (M=Mo and W; X=S and Se) composites, MX<sub>2</sub> and TiO<sub>2</sub> serve as an efficient photo-sensitizer and co-catalyst, respectively, and a built-in-potentials in the composites are generated, which is advantageous for the electron-hole separation from MX<sub>2</sub> to TiO<sub>2</sub> [31]. Therefore, development of composite materials based on MoSe<sub>2</sub> and TiO<sub>2</sub> should be a promising method to enhance the photocatalytic activity of MoSe2 due to the stepwise structure of band-edge levels constructed in the MoSe<sub>2</sub>-TiO<sub>2</sub> (MT) composite (Fig. 1). The conduction band (CB) of TiO<sub>2</sub> is -4.2 eV and valence band (VB) -7.4 eV (vs. vacuum) [32], while the corresponding values of MoSe<sub>2</sub> are -3.58 and -5.62 eV (vs. vacuum), respectively [33]. Such energy levels are beneficial to the transfer of photo-generated electrons from MoSe<sub>2</sub> CB to TiO<sub>2</sub> CB, which could efficiently separate the photo-induced electrons and hinder the charge recombination in the electron-transfer processes, thus enhance the photocatalytic activity. Unfortunately, up to now, the exploration on MT composites for photocatalysis has not yet been reported, especially in terms of photocatalytic reduction of Cr(VI).

Herein, a fast strategy was developed to synthesize the MT composites through a solvothermal method, and their photocatalytic activity in the reduction of Cr(VI) was investigated. The MT composites exhibit improved visible light photocatalytic activity

compared with pure MoSe<sub>2</sub> and TiO<sub>2</sub>. The possible mechanism that contributes to the improvement of photocatalytic activity was studied in terms of a series of characterization and controlled experiments using hole and electron scavengers.

#### 2. Experimental

#### 2.1 Synthesis

A certain amount of TiO<sub>2</sub> (P25, Degussa), 18 mmol Na<sub>2</sub>SO<sub>3</sub>, 4.5 mmol Se power, 2.25 mmol Na<sub>2</sub>MoO<sub>4</sub> and 4.5 mmol NaBH<sub>4</sub> were dissolved into 60 ml aqueous solution by sonication for 30 min to produce a uniform dispersion. A dilute HCl solution was dropped in the above solution to adjust the pH value to be 7, and the mixture was stirred for 30 min. Subsequently, the mixture was transferred into a 100 ml Teflon-lined stainless steel autoclave, and treated at 180 °C for 12 h. The obtained samples were isolated by filtration, washed three times with distilled water, and finally dried in a vacuum oven at 80 °C for 24 h. The weight ratios of MoSe<sub>2</sub> to TiO<sub>2</sub> were 1:0.25, 1:0.5, 1:1, and 1:2 during the preparation, and the corresponding obtained MT composites were named as MT-0.25, MT-0.5, MT-1 and MT-2, respectively. Pure MoSe<sub>2</sub> were also synthesized by the similar method in the absence of TiO<sub>2</sub>. For the electrochemical impedance spectra (EIS) testing, 90 mg sample with 0.2 ml 2.5 wt.% polyvinyl alcohol binder was homogenously mixed in water to form slurry. Then, the resultant slurries were coated on the graphite flake (2 cm  $\times$  2 cm). Finally, these prepared electrodes were dried in a vacuum oven at 60 °C for 24 h.

#### 2.2 Characterization

The morphology and structure of the samples were characterized by field-emission scanning electron microscopy (FESEM, Hitachi S-4800), high-resolution transmission electron microscopy (HRTEM, JEOL-2010), X-ray diffraction (XRD, Holland Panalytical PRO PW3040/60) with Cu Ka radiation (V=30 kV, I=25 mA), and energy dispersive X-ray spectroscopy (EDS, JEM-2100). Photoluminescence (PL) spectra at room temperature were examined by fluorescence spectrophotometer (HORIBA Jobin Yvon fluoromax-4). X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Thermo ESCALAB 250 Xi spectrometer with a monochromatic Al Ka X-ray source. The diffuse absorption spectra of the samples were recorded using a Hitachi U-3900 UV-Vis spectrophotometer equipped with an integrated sphere attachment by using BaSO<sub>4</sub> as a reference. EIS measurements were carried out on an electrochemical workstation (AUTOLAB PGSTAT302N) in dark conditions using a three electrode configuration with the as-prepared films as working electrode, a Pt foil as counter electrode and a standard calomel electrode as reference electrode. The electrolyte was 20 mg l<sup>-1</sup>Cr(VI) aqueous solution. EIS were recorded in the frequency range of 0.1 Hz-1 MHz, and the applied bias voltage and ac amplitude were set at open-circuit voltage and 10 mV, respectively.

#### 2.3 Photocatalytic experiments

The photocatalytic activity of the as-prepared samples was evaluated through the experiment of photocatalytic reduction of Cr(VI) under visible light irradiation. The

samples (1 g l<sup>-1</sup>) were dispersed in 80 ml Cr(VI) aqueous solutions (20 mg l<sup>-1</sup>). The suspensions were magnetically stirred in the dark for 30 min to reach the adsorption-desorption equilibrium. Under ambient conditions and stirring, the mixed suspensions were exposed to visible light irradiation produced by a 400 W metal halogen lamp ( $\lambda > 400$  nm) with a cut off filter. At certain time intervals, 2 ml of the mixed suspensions were extracted and centrifuged to remove the photocatalysts. The filtrates were analyzed by recording the UV-Vis spectra of Cr(VI) using a Hitachi U-3900 UV-Vis spectrophotometer. The photocatalytic activity of P25 was also investigated for comparison. A recycled photocatalytic activity test was carried out according to the above-mentioned procedure. After each run of photocatalytic reaction, the fresh Cr(VI) aqueous solution was injected, and the separated photocatalyst was washed with deionized water carefully and used again. To investigate the photocatalytic mechanism, trapping experiments were carried out to determine the main reactive species in the photocatalytic process. The experimental procedure was similar to the photocatalytic activity measurement except that the hole and electron scavengers were added into the reaction system.

#### 3. Results and discussion

#### 3.1 Characterizations

Fig. 2(a) and (b) show the FESEM images of MoSe<sub>2</sub> and MT-0.5. MoSe<sub>2</sub> displays the sheet nanostructure. When TiO<sub>2</sub> nanoparticles are introduced, they are

well distributed in MoSe<sub>2</sub> sheets in the MT composites, as shown in Fig. 2(b). The morphologies of MT-0.25, MT-1 and MT-2 (not shown here) are similar to that of MT-0.5. Furthermore, the morphology of MoSe<sub>2</sub> in the MT composites (MT-0.5) is similar to that of pure MoSe<sub>2</sub>, indicating that the introduction of TiO<sub>2</sub> does not affect the formation of MoSe<sub>2</sub>. Fig. 2(c) and (d) show the low-magnification and high-magnification HRTEM images of MT-0.5. It confirms the presence of TiO<sub>2</sub> nanoparticles contacting with MoSe<sub>2</sub> sheets, which could significantly increase the separation of photo-generated carriers, and ultimately contribute to the photocatalytic activity. The lattice spacing measured for the crystalline plane is 0.35 nm, corresponding to the (101) plane of TiO<sub>2</sub> (JCPDS 21-1272) [2]. No typical layer structure and lattice fringe of MoSe<sub>2</sub> can be observed due to the existence of its amorphous state in the composite. The composition of MT-0.5 was identified by EDS linked to HRTEM, as shown in Fig. 3. The peaks of Mo, Se, Ti and O in the EDS spectrum further confirm the existence of MoSe<sub>2</sub> and TiO<sub>2</sub> in the composite.

The XRD patterns of MoSe<sub>2</sub> and MT-0.5 are shown in Fig. 4. Pure MoSe<sub>2</sub> exhibits several diffraction peaks at 13.7°, 34.4° and 55.9°, corresponding to (002), (102) and (110) crystal planes of the hexagonal 2H-MoSe<sub>2</sub> phase with space group  $P6_3/mmc$  (JCPDS: 29-0914) [27]. No other impurity peaks appear for pure MoSe<sub>2</sub>, indicating high purity of the as-prepared sample [28]. However, the XRD patterns show relatively broad diffraction peaks, indicating that the as-prepared products are somewhat amorphous and have short range structural order [27,34]. The XRD analysis shows that the main diffraction peaks of the MT-0.5 composites are similar to

those of pure MoSe<sub>2</sub>, indicating that the presence of TiO<sub>2</sub> does not result in the development of new crystal orientations or changes in preferential orientations of MoSe<sub>2</sub>. Compared with pure MoSe<sub>2</sub>, the new peaks corresponding to anatase (JCPDS 21-1272) and rutile (JCPDS 21-1276) phases of TiO<sub>2</sub> appear in XRD pattern of MT-0.5, which further confirms the existence of TiO<sub>2</sub> in the composites.

The surface chemical composition of MT-0.5 was characterized by XPS measurements. Fig. 5(a) and (b) show the high resolution XPS spectra of Mo 3d and Se 3d. Two characteristic peaks located at 228.7 eV and 232.4 eV can be assigned to Mo  $3d_{5/2}$  and Mo  $3d_{3/2}$ , respectively, which is indicative of the reduction of Mo<sup>6+</sup> to Mo<sup>4+</sup> and the formation of MoSe<sub>2</sub> [35,36]. The peak at 55 eV is attributed to Se  $3d_{3/2}$ , which is similar to that reported in the literature [37]. Fig. 5(c) shows the high resolution XPS spectra of Ti 2p, displaying the spin-orbit split lines of Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$  at 458.4 and 464.6 eV, respectively, which is in good agreement with that in TiO<sub>2</sub>. As shown in Fig. 5(d), the O 1s spectrum of MT-0.5 is fitted to two peaks. The peak of O1s at 530 eV corresponds to lattice oxygen of TiO<sub>2</sub>, and a higher binding energy of 531.7 eV is assigned to mixed contributions from surface hydroxides. All of these results clearly confirm the formation of MT composites.

Fig. 6 shows the UV-Vis diffuse absorption spectra of MoSe<sub>2</sub>, P25, MT-0.25, MT-0.5, MT-1 and MT-2. MoSe<sub>2</sub> displays good absorption in visible light range of 400-700 nm. It is observed that the MT composites with an appropriate proportion of TiO<sub>2</sub> exhibit higher visible light absorbance and the intensity increases with the increase of TiO<sub>2</sub> content. Such an enhancement of light absorption is beneficial to the

increase of the photo-generated electrons and holes [2,38,39]. However, when the  $TiO_2$  content is further increased (MT-1 and MT-2), the absorption decreases due to the wide band gap of  $TiO_2$ , which is similar to those reported in the literatures [40,41]. In addition, compared to pure  $TiO_2$ , the absorption edges of the MT composites exhibit a red shift, which is also beneficial to the absorption of visible light.

The charge transfer and recombination behavior of the as-prepared samples was studied by analyzing the EIS spectra under visible light irradiation. Fig. 7(a) shows the typical Nyquist plots of MoSe<sub>2</sub>, MT-0.25, MT-0.5, MT-1 and MT-2 under visible light irradiation. The semicircle in the EIS spectra is ascribed to the contribution from the charge transfer resistance  $(R_{ct})$  and constant phase element (CPE) at the photocatalyst/electrolyte interface. The inclined line, resulting from the Warburg impedance Zw, corresponds to the ion-diffusion process in the electrolyte. The corresponding equivalent circuit is shown in the inset of Fig. 7(a). It can be observed that the  $R_{ct}$  decreases with the increase of TiO<sub>2</sub> content, which indicates that the introduction of TiO<sub>2</sub> into MoSe<sub>2</sub> favors the electron transfer and suppresses the charge recombination in MoSe<sub>2</sub> due to the stepwise energy level structure in the composites. The result is consistent with the theoretical calculation [31]. However, when the TiO<sub>2</sub> content is further increased (MT-1 and MT-2), the R<sub>ct</sub> increases, which may be because that excessive TiO<sub>2</sub> can act as a recombination center instead of providing an electron pathway and promote the recombination of electron-hole pairs in TiO<sub>2</sub>[42]. Fig. 7(b) shows PL spectra of MoSe<sub>2</sub>, MT-0.25, MT-0.5, MT-1 and MT-2 with the excitation wavelength at 365 nm. It can be clearly observed that the introduction of

TiO<sub>2</sub> markedly decreases the PL intensity, which further confirms that the recombination of photo-induced electrons and holes in MoSe<sub>2</sub> can be effectively inhibited.

#### **3.2 Photocatalytic properties**

Photocatalytic reduction of Cr(VI) by MoSe<sub>2</sub>, TiO<sub>2</sub>, MT-0.25, MT-0.5, MT-1 and MT-2 was performed under visible light irradiation, as shown in Fig. 8. The normalized temporal concentration changes  $(C/C_0)$  of Cr(VI) during the photocatalytic process are proportional to the normalized maximum absorbance  $(A/A_0)$ , which can be derived from the change in the Cr(VI) absorption profile during the photocatalysis process. It is observed that MT composites with an appropriate proportion of TiO<sub>2</sub> exhibit a better photocatalytic activity than pure MoSe<sub>2</sub> and TiO<sub>2</sub>. The photocatalytic activity of MT composites is dependent on the proportion of TiO<sub>2</sub> in the composites. The reduction rates of Cr(VI) for MoSe<sub>2</sub> and TiO<sub>2</sub> are 61% and 5% at 120 min, respectively. When TiO<sub>2</sub> is introduced into MoSe<sub>2</sub>, the reduction rate is increased to 80% for MT-0.25 and reaches a maximum value of 91% for MT-0.5 at 120 min. It is known that during photocatalysis, the light adsorption, and the charge transportation and separation are crucial factors [43,44]. The enhancement of the photocatalytic activity should be mainly ascribed to the increase in light absorption and the reduction in electron-hole pair recombination in MoSe<sub>2</sub> with the introduction of TiO<sub>2</sub> due to the stepwise energy level in the composites, which have been confirmed by the UV-Vis absorption and EIS measurements. However, when the TiO<sub>2</sub> content is further increased, the reduction rates decreases to 39% and 18% for

MT-1 and MT-2, respectively, which may be due to their increased recombination of photo-generated electron-hole pairs, decreased visible light absorption and high content of TiO<sub>2</sub> [45,46]. The turnover numbers of photocatalytic production are about 0.021, 0.002, 0.009, 0.017, 0.014 and 0.006 for MoSe<sub>2</sub>, TiO<sub>2</sub>, MT-0.25, MT-0.5, MT-1 and MT-2, respectively.

The values of rate constants (*k*), as shown in Fig. 9, can be obtained directly from the fitted straight-line plots of  $\ln(C/C_0)$  vs. reaction time *t* and follow the order: MT-0.5 (0.0141 min<sup>-1</sup>) > MT-0.25 (0.0114 min<sup>-1</sup>) > MoSe<sub>2</sub> (0.0078 min<sup>-1</sup>) > MT-1 (0.0041 min<sup>-1</sup>) > MT-2 (0.0017 min<sup>-1</sup>) > P25 (0.0004 min<sup>-1</sup>), where *C*<sub>0</sub> and *C* are the initial concentration and the concentration of Cr(VI) at reaction time *t*, respectively. The result shows that MT-0.5 exhibits a best photocatalytic activity under visible light irradiation.

It is well known that the stability and reusability of photocatalysts are very important for practical application. The reusability of MT composites (MT-0.5) was investigated under visible light irradiation with three times of cycling uses, as shown in Fig. 10. It is noteworthy that only insignificant decrease for photocatalytic activity is found, which may be due to the loss of photocatalyst during collection process [47]. Furthermore, the morphology and crystal structure of MT-0.5 after the photocatalytic reaction (labeled as irr-MT-0.5) were characterized by SEM and XRD. The SEM image of irr-MT-0.5 shows much rougher surface, which may be due to the photocatalytic reduction of Cr(VI), leading to the deposition of chromium compounds as Cr<sub>2</sub>O<sub>3</sub> or Cr(OH)<sub>3</sub> on surface of MT composites. Similar results were also reported

in the literatures [48,49]. The results of XRD indicated that the crystal structure of irr-MT-0.5 did not show obvious changes before and after the photocatalytic reaction (Fig. S2). All results confirm that the MT composites can retain their excellent photocatalytic stability and reusability activity under the studied conditions.

#### **3.3 Possible photocatalytic mechanism**

The possible mechanism for the photocatalytic reduction of Cr(VI) over MT composites is proposed. MoSe<sub>2</sub> is excited by the absorption of photons under visible light irradiation and electron-hole pairs are created. The photo-generated electrons can transfer from MoSe<sub>2</sub> CB to TiO<sub>2</sub> CB, leading to the separation of photo-generated charge carriers. Then the photo-generated charge carriers may migrate to the surface of MT composites and participate in the photocatalytic reduction and oxidation reactions. Cr(VI) can be reduced to Cr(III) by the photo-generated electrons. Meanwhile, the holes can oxidize the water to form oxygen in the photocatalytic process [50]. The major reaction steps are summarized as follows:

 $MoSe_{2} + hv \rightarrow h^{+} + e^{-}$   $Cr_{2}O_{7}^{2-} + 14H^{+} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_{2}O$   $2H_{2}O + 4h^{+} \rightarrow O_{2} + 4H^{+}$ 

To detect the reductive product, the bonding state of Cr 2p for irr-MT-0.5 was characterized by XPS. Fig. S3 show the high resolution XPS spectra of Cr 2p. Two peaks located at 577.3 and 586.9 eV correspond to Cr 2p<sub>1/2</sub> and Cr 2p<sub>3/2</sub> orbitals, respectively, which are attributed to Cr(VI) and Cr(III). This result confirms that both Cr(VI) and Cr(III) exist on the surface of irr-MT-0.5. The appearance of Cr(III) is

mainly due to the photocatalytic reduction of Cr(VI) on the surface of photocatalyst and the Cr(III) species can be precipitated on the surface of irr-MT-0.5 as  $Cr_2O_3$  or  $Cr(OH)_3$ , which is similar to those reported results [48,51]. Furthermore, the weak peak of Cr 2p indicates that the deposited Cr(III) species can be removed via simply washing the sample with deionized water or NaOH.

To confirm the role of the photo-generated electrons in the photocatalytic process, controlled experiments have been carried out with addition of hole (formic acid, FA) and electron scavengers (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>). As shown in Fig. 11, the addition of hole scavengers can enhance the photocatalytic activity of MT-0.5, while the activity decreases largely with the addition of electron scavengers. FA as a hole scavenger can capture photo-generated holes in the photocatalytic process, and thus suppress the recombination of photo-generated carriers, leading to the enhancement of photocatalytic activity of MT-0.5. However, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as an electron scavenger can capture photo-generated electrons, and thus decrease the number of photo-generated electrons to participate in the photocatalytic reaction, which is not beneficial to the photocatalytic activity. The results confirm that the photo-generated electrons govern the photocatalytic reduction of Cr(VI), which is consistent with the literatures [24,40].

#### 4. Conclusions

MT composites were successfully synthesized via a simple solvothermal method and their photocatalytic activities in the reduction of Cr(VI) were investigated. The

results indicate that (i) MT composites exhibit an enhanced photocatalytic activity than pure MoSe<sub>2</sub>; (ii) the photocatalytic activity of MT composites is dependent on the proportion of TiO<sub>2</sub> in the composites and the MT-0.5 achieves a highest Cr(VI) reduction rate of 91% at 120 min; (iii) the enhanced photocatalytic activity is mainly ascribed to the increase in light adsorption and the reduction in photoelectron-hole pair recombination with the introduction of TiO<sub>2</sub>.

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#### **Figure captions**

Fig. 1. Schematic diagram of energy levels of MoSe<sub>2</sub> and TiO<sub>2</sub>.

Fig. 2. FESEM images of (a) MoSe<sub>2</sub> and (b) MT-0.5; (c) low-magnification and (d) high-magnification HRTEM images of MT-0.5.

Fig. 3. EDS spectrum of MT-0.5.

Fig. 4. XRD patterns of MoSe<sub>2</sub> and MT-0.5.

Fig. 5. High-resolution XPS spectra of (a) Mo 3d, (b) Se 3d, (c) Ti 2p and (d) O 1s spectra for MT-0.5.

Fig. 6. UV-Vis diffuse absorption spectra of MoSe<sub>2</sub>, P25, MT-0.25, MT-0.5, MT-1 and MT-2.

Fig. 7. (a) Nyquist plots and (b) PL spectra of MoSe<sub>2</sub>, MT-0.25, MT-0.5, MT-1 and MT-2. Inset is the corresponding equivalent circuit model.

Fig. 8. Photocatalytic reduction of Cr(VI) by MoSe<sub>2</sub>, P25, MT-0.25, MT-0.5, MT-1 and MT-2 under visible light irradiation.

Fig. 9. Reaction constant *k* for Cr(VI) reduction by MoSe<sub>2</sub>, P25, MT-0.25, MT-0.5, MT-1 and MT-2 under visible light irradiation.

Fig. 10. Photo-stability of MT-0.5 by investigating its photocatalytic activity with three times of cycling uses.

Fig. 11. Photocatalytic reduction of Cr(VI) by MT-0.5 with the addition of hole and electron scavengers.









Fig. 3



Fig. 4







#### Fig. 6







Fig. 8



Fig. 9









