Sono-intercalation of CdS nanoparticles into the layers of titanate facilitates the sunlight degradation of Congo red

S. Sehatia, M.H. Entezaria,b,*

a Sonochemical Research Center, Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, 91779 Mashhad, Iran  
b Environmental Chemistry Research Center, Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, 91779 Mashhad, Iran

Graphical abstract

Abstract

In this paper, the degradation of Congo red (CR) as a dye was investigated by a new synthetic photocatalyst. The synthesis was done through the intercalation of CdS in the layers of titanate (K2Ti4O9) by the assistance of ultrasound. The photocatalyst was prepared via ion-exchange reaction and sulfuration processes in the presence of ultrasonic irradiation. The samples were characterized by the field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), ultraviolet–visible spectra (UV–Vis), and Fourier transform infrared spectroscopy (FTIR). The deposition of CdS nanoparticles on the surface and between the spaces of titanate layers led to the shift of absorption edge of titanate to the visible light region. The photocatalytic degradation mechanism of CR has been evaluated through the addition of some scavengers to the solution. In addition, the stability and reusability of the catalyst were examined in this work too.

1. Introduction

The new nanocomposites and evaluation of their novel properties have attracted special attention as an economic and environmentally safe option for air and water pollutions. The intercalation of organic or inorganic molecules into the interlayer spaces of layered materials through mechanisms include ion exchange, ion–dipole interaction, hydrogen bonding, redox...
reactions, and acid–base reactions have considered as an efficient way to produce new generation of nanocomposites [1–4]. Intercalation chemistry is a subject of remarkable interest because of its applications in many fields, such as those related to the catalysis, superconductors, magnetic determinations and supports for catalytic methods [5]. It is noticeable that most organic pollutants cannot penetrate into the interlayer space of the layered compound because of its narrow interlayer distance and rigid structure. Therefore, photocatalytic reaction can only occur on the external surface of the layered compound and leads to a low photocatalytic activity. The intercalating of layered compounds is one of the efficient approaches to prepare the stable photocatalyst with enhanced photocatalytic activity by increasing the interlayer space [6]. Among various inorganic layered compounds, the layered titanates (e.g., Na2Ti5O11, K2Ti6O13 and KTiNbO5) have been extensively investigated. This is due to their unique structural properties [7], the specially electronic and optical properties as well as the highly chemical stability, large surface areas and nontoxicity [8–11]. However, the wide band gap energy ($E_g$) of these compounds prevents trapping of visible light and hence limits its photo-efficiency with respect to solar energy. In order to overcome this problem, many efforts have been made to modify the band structure as well as to improve its photocatalytic performance [12]. In the proposed manners, the intercalation with narrow band gap semiconductors such as Fe2O3 [13], CdS [14], PbS [15] is considered as one of the most efficient method [16]. The narrow band gap semiconductor in the nanocomposite not only acts as the sensitizer, but also reduces the recombination rate of the photo-generated electron–hole pair that is a major limitation in normal semiconductors [17–19]. The intercalation process requires several steps and it is so complicated and often takes at least one week via a traditional methods due to the mass transfer limitation [20].

Ultrasonic irradiation has been widely used to produce nanoparticles with improved properties. Acoustic cavitation, arising from ultrasound irradiation into the liquid, involves the formation, growth and collapse of bubbles in the liquid medium and plays an important role to arise the physicochemical effects of ultrasound. The implosive collapse of bubbles in liquid generates high temperatures (several thousands of degrees) and high pressures (hundreds of atmospheres) and accelerate many chemical reactions [21]. Besides that, the active radicals such as H, OH and OOH can be produced from ultrasonic irradiation and act as an advanced oxidation reagents [22]. These unique properties have caused that ultrasound to be used as an efficient method in the preparation of intercalated nanoparticles. The shock waves, resulting from ultrasound irradiation, can promote the diffusion of some species into the interlayer spacing in the layered materials [23]. In addition, the presence of bubbles between layers and their vibrations in this area will increase the distance between the layers and facilitates the rapid intercalation process. Furthermore, the collapse of cavitation bubble near the surfaces is not spherically symmetric and a localized ‘micro-jet’ of liquid is driven into the surface at extremely high velocities. This micro-jet causes an irreversible change in the host which is responsible for the increased intercalation rates [24].

In this work a new and simple method was presented for preparing the visible active photocatalyst through the intercalation of CdS into the titane layers by the assistance of ultrasonic waves. The CdS/K2Ti4O9 photocatalyst was synthesized under ultrasound at ambient temperature and in a shorter time than conventional method. Ultrasound facilitated the intercalation process and caused a high capacity photocatalyst that can eliminate the water pollutants at very short time. Degradation of CR as a water pollutant was done with higher efficiency with sonosynthesized sample in comparison with the same sample prepared by conventional method. Besides that, several parameters were studied in order to enhance the removal rate of CR.

2. Experimental

2.1. Materials

The CDTS/Ti4O9 photocatalyst was synthesized under ultrasound at ambient temperature and in a shorter time than conventional method. The product was kept at 90–120 °C until the mixture was kept for 15 min. Then, the KOH solution was added while the temperature remained constant. The KOH solution was added while the temperature remained constant. The mixture was kept at 90–120 °C and vigorously stirred by a magnetic heating stirrer to eliminate the water. After addition of Ti(O-Bu)4, the mixture was stirred for 2 h until a homogenous transparent solution was formed. The solution was heated in a furnace in air atmosphere to 300 °C. At this temperature, the solution was ignited and the obtained black powders were calcined at 800 °C for 2.5 h and finally the white powder was obtained.

2.2. Catalyst preparation

2.2.1. Synthesis of K2Ti4O9

The K2Ti4O9 powders were prepared at relatively low temperature by using stearic acid [25]. (Ti(O-Bu)4) and KOH were used as the precursors and stearic acid as the solvent and dispersant in our experiment. The detailed procedure is as follows: the molar ratio of Ti(O-Bu)4: KOH, and stearic acid was 1: 1.5. At first, a reasonable amount of stearic acid powder was heated and melted. Then, the KOH solution was added while the temperature remained constant. The mixture was kept at 90–120 °C and vigorously stirred by a magnetic heating stirrer to eliminate the water. After addition of Ti(O-Bu)4, the mixture was stirred for 2 h until a homogenous transparent solution was formed. The solution was heated in a furnace in air atmosphere to 300 °C. At this temperature, the solution was ignited and the obtained black powders were calcined at 800 °C for 2.5 h and finally the white powder was obtained.

2.2.2. Replacement of K⁺ by H⁺

The as-prepared K2Ti4O9 powder was added into HCl solution (1 M) and stirred for 3 days at 60 °C in order to replace K⁺ with H⁺ in the layered K2Ti4O9. The product was washed with distilled water and dried in vacuum at 30 °C.

2.2.3. Incorporating of butylamine molecules

The n-butyamine was incorporated between the layers of H2Ti4O9 by dispersing of 1 g H2Ti4O9 powder into 100 mL 20 vol% of n-butyamine aqueous solution and refluxing at 60 °C for 4 days. The solid material was separated by centrifugation and further dried in vacuum at 30 °C.

2.2.4. Intercalating of CdS

To intercalate the CdS, 0.1 g of (butylamine)-Ti4O9 was dispersed into solution containing 50 mL NH3 (5 M) and 25 mL SC (CH3)(NH2)2 (0.1 M). The mixture was sonicated for 15 min. Then, 25 mL aqueous solution of Cd(NO3)2 (0.1 M) was added dropwise to the mixture under ultrasound for 2 h. The product was dried at 110 °C for 3 h, and subsequently calcined at 400 °C for 2 h.

Fig. 1 shows a schematic that represents the preparation process.
2.3. Characterization and equipment

The crystalline structure was identified by XRD and the patterns were collected on a diffractometer (PHILIPS PW1800). The morphology was determined with FESEM (Mira 3-XMU) and TEM (CM120-Philips). The FTIR measurements were carried out with a spectrometer (FTIR-4300 Shimadzu) at room temperature in KBr pellets. The absorption spectrum of CR and its derivatives were measured using a UV–Vis spectrophotometer (Unico 2800). The atomic absorption spectrophotometer (AAS, Varian, spectra-110 880/220-Australia Pty Ltd.) was used to determine the concentration of $K^+$ and $Cd^{2+}$ ions in the solution during the intercalation process and CR degradation. The ultrasonic irradiation was applied with equipment operating at 20 kHz (Branson Digital Sonifier, W-450 D).

2.4. Photocatalytic activities

The photocatalytic activities of the samples for CR degradation were examined in a Pyrex glass vessel containing 50 mL CR (50 mg L$^{-1}$). An appropriate amount of photocatalyst was added at natural pH of CR (pH = 6.5) and magnetically stirred under direct sunlight radiation in sunny days in Jun 2014 between 11 am and 5 pm (GPS coordinates: N = 36º18’41.6”, E = 59º31’54.2”). The temperature of the solution was kept in the range of 28–35 ºC. At given times, about 5 mL of suspensions was sampled and the solid phase was separated from the solution by centrifugation. The mentioned conditions were fixed for all experiments. The removal efficiency of CR was determined based on the absorption at 500 nm by UV–Vis spectrophotometer.

3. Results and discussion

3.1. Intercalation of CdS

3.1.1. Effect of sonication time

The loading value of the CdS nanoparticles into titanate is strongly dependent on the time of ultrasonic treatment. In fact, sonication can promote the intercalation of the nanoparticles. By using a cooling system, the temperature of the sonicated solution was controlled and kept between 25 and 30 ºC. The photocatalytic activity of the prepared photocatalysts was determined by photodegradation of CR in water under sunlight irradiation. It was found that with increasing sonication time, the amount of CdS on the surface and between layers should be increased due to the higher shift of spectrum to the visible range (Fig. 2). The degradation of CR was maximized in the case of 2 h sonication time (Fig. 3). It means that sonication for longer time has a negative effect on the degradation of CR. This behavior should be related to the proper ratio of CdS and titanate in 2 h sonication.

3.1.2. Effect of composite ratio

The intercalated composites of CdS/Ti$_4$O$_9$ were prepared with different amounts of butylamine–Ti$_4$O$_9$ as a host. As the amount of host molecule was increased from 0.05 g to 0.10 g (CdS concentration remained constant = 0.1 M), the CR degradation was increased too. Notably, the photocatalytic efficiency of the CdS/ Ti$_4$O$_9$ (prepared with 0.10 g host) was more than that of the other...
samples (Fig. 4). However, the photocatalytic degradation rate of CR was then decreased with increasing the amount of host molecule more than 0.1 g. These results also confirm that a proper ratio in the composite has the highest removal efficiency.

3.2. Catalyst optimization in degradation process

3.2.1. Degradation in dark and light

In order to investigate the photocatalytic activity of CdS/Ti4O9 in dark and light, one sample contains of photocatalyst and CR was magnetically stirred in dark for 60 min to attain adsorption-desorption equilibrium. Then, the concentration of CR was followed under sunlight irradiation. Another sample directly was taken place under sunlight without keeping in the dark. The results show that the process was much shorter with higher efficiency for the sample placed directly under sunlight (Fig. 5). Therefore, all experiments were directly exposed to the light from the initial time.

3.2.2. Effect of catalyst loading

The catalyst dosage is considered as one of the most important parameters in degradation studies [26]. In order to study the effect of amount of catalyst on the photodegradation efficiency of CR, different values in the range of 0.01–0.08 g were applied in constant dye concentration (50 mg/L) and the mixtures were taken place directly under sun light, the results are shown in Fig. 6. When the catalyst was exposed to the pollutant, the catalyst color changed from yellow to red owing to the adsorption of CR on the surface of the photocatalyst. With increasing the catalyst loading, the color removal from solution was enhanced due to the increase in available active sites for CR adsorption. Over the time and in complete photocatalytic process, the catalyst color changed to yellow because of decomposing of adsorbed CR on the surface of the catalyst (Fig. 7B). In fact, the rate of degradation continuously increases with increasing the amount of catalyst. This is due to the availability of more catalyst surface area for the absorption of photon and more interaction with pollutant [27]. Whereas at higher dosage (>0.05 g), there was no considerably change in removing of the dye. Therefore, the whole experiments were continued with 0.05 g of the catalyst.

It should be mentioned that, the phrase "colorless time" is the time that the color of the solution was completely removed but the surface catalyst color was still red. In addition, the phrase "degradation time" is the time that the color of solution and the catalyst surface color was removed and catalyst color changed to yellow.

3.3. Comparison of photocatalytic efficiency

The photocatalytic efficiency of different samples was compared with the photodegradation of CR under sunlight and the results are shown in Fig. 8. Without any photocatalyst, CR was hardly self-photodegraded. By addition of photocatalysts the degradation was increased remarkably as a consequence of the integration of semiconductor portions. For photocatalytic degradation of CR on K2Ti4O9, CR molecules cannot penetrate into the interlayer of K2Ti4O9 owing to the high layer charge and narrow interlayer space. Therefore, CR degradation only occurs on the external surface of K2Ti4O9, which consequently leads to the low photocatalytic activities [28]. In the case of CdS/Ti4O9, however, CdS pillaring results in expanded interlayer space, which is capable of hosting CR molecules, resulting in a higher photocatalytic activity compared with the host molecule. As a consequence, the
photocatalytic efficiencies of CdS/Ti4O9 sample was greater than that of the CdS and K2Ti4O9 as separate samples.

3.4. Characterization of the synthesized photocatalysts

3.4.1. FT-IR

Fig. S3A (see Supplementary material) is related to the infrared spectrum of K2Ti4O9 that contains different peaks in the 400–940 cm⁻¹ region and can be related to the Ti—O bond vibrations. K2Ti4O9 contains four different Ti sites and nine various O sites in either terminal or bridging configurations that are shown by prefix notation (a, b, c and d). The highest energy vibration (940 cm⁻¹) is allocated to terminal a-O—Ti bonds, those with intermediate energies (854–557 cm⁻¹) to b—O—Ti bonds, and those of lowest energy (486–440 cm⁻¹) to c—O—Ti and d—O—Ti bonds. This assignment is consistent with the trends observed for the terminal and bridging oxygen in metal oxocomplexes [29].

The cation exchange causes the peaks become broader (Fig. S3B). The terminal a—O—Ti peaks move slightly to the higher energy (955 cm⁻¹ in H2Ti4O9), whereas the d—O—Ti peaks are nearly unchanged. Besides that, the d—O sites are buried in the structure and are less accessible to protons and water molecules. The protonation causes the terminal a—O—Ti vibration shifts to higher energy [30]. The IR spectrum of butylamine intercalated into the layered H2Ti4O9 is compiled in Fig. S3C. The IR peaks at 2930 cm⁻¹ and 2858 cm⁻¹ were characteristic of methylene stretching vibration (related to butylamine). The IR peak at 1468 cm⁻¹ was assigned to the methylene deforming vibration. Since the IR spectra of particles are generally influenced by the particle size and morphology, the corresponding peak was shifted in the sonochemical synthesized sample [30,31]. Adding the peaks of methylene group in the protonated titanate (H2Ti4O9) peak, clearly demonstrate the intercalation of butylamine into the interlayers of H2Ti4O9. (Fig. S3D) shows the IR spectra of CdS–Ti4O9. The peaks of methylene group, related to butylamine is eliminated. The IR bands at 623 cm⁻¹ and 644 cm⁻¹ are ascribed to the Cd—S stretching vibration.
3.4.2. XRD
The XRD patterns of K$_2$Ti$_4$O$_9$, H$_2$Ti$_4$O$_9$, butylamine–Ti$_4$O$_9$, and CdS/Ti$_4$O$_9$ were shown in Fig. 9(A, B, C and D, respectively). The crystallized K$_2$Ti$_4$O$_9$ (Fig. 54) (see Supplementary material) is in agreement with that of K$_2$Ti$_4$O$_9$ (JCPDS32-0861) [25,32]. The crystalline phase of K$_2$Ti$_4$O$_9$ that synthesized by stearic acid route was formed at 800 °C. However for K$_2$Ti$_4$O$_9$, preparing by conventional solid state reaction, no crystalline phase was detected in the product calcined at 800 °C [25]. In fact, by using stearic acid method, the crystallized K$_2$Ti$_4$O$_9$ could be obtained at lower temperature. Based on the results from XRD patterns, when the product was calcined at 800 °C, the phases of K$_2$Ti$_4$O$_9$ and K$_2$Ti$_6$O$_{13}$ coexist. The pattern obtained for the proton exchanged phases (Fig. 9B) agrees with the reported pattern for the monohydrate H$_2$Ti$_4$O$_9$·xH$_2$O [33,34]. After replacing of H$^+$, the crystalline structure of H$_2$Ti$_4$O$_9$ was not changed. After acid exchanging, the interlayer space of H$_2$Ti$_4$O$_9$ was 0.90 nm, slightly larger than that of K$_2$Ti$_4$O$_9$ (0.89 nm). The slightly expanded interlayer space of H$_2$Ti$_4$O$_9$ is mainly attributed to the intercalation of H$_3$O$^+$ into the interlayer. The main peaks correspond to (200) of H$_2$Ti$_4$O$_9$ shifted significantly to lower 2$\theta$ angles. Fig. 9C indicates the expansion of the interlayer by incorporation of butylamine between the layers, corresponding to an interlayer space of 1.63 nm for the sample prepared by classical method. The characteristic diffraction peaks for CdS were indexed to hexagonal and cubic CdS (JCPDS 41–1049) [30]. After intercalating of CdS nanoparticles into the layered space of K$_2$Ti$_4$O$_9$, the absorption of H$_2$Ti$_4$O$_9$ and (Bu-amine)-Ti$_4$O$_9$ shift to the higher wavelengths that means a decrease of the band gaps. After coupling with CdS, the absorption edge of CdS–Ti$_4$O$_9$ is extended to visible range which is appropriate for the visible-light driven photocatalysts. The band gap energies of the composite are estimated to about 2.13 and 2.81 (Fig. S5) (see Supplementary material) that is proper for the degradation of organic pollutants in the visible range.

3.4.3. Optical absorption of catalyst by UV–Vis
The optical absorption of the as-prepared photocatalysts was investigated using a UV–Vis spectrophotometer (Fig. 10). It is found that K$_2$Ti$_4$O$_9$ only exhibits the fundamental absorption edge at 250–300 nm in the ultraviolet region, corresponding to the band gap of approximately 3.4 which cannot be responsive for the visible light. After intercalating of H$^+$ and amine group in the layered space of K$_2$Ti$_4$O$_9$, the absorption of H$_2$Ti$_4$O$_9$ and (Bu-amine)-Ti$_4$O$_9$ shift to the higher wavelengths that means a decrease of the band gaps. After coupling with CdS, the absorption edge of CdS–Ti$_4$O$_9$ is extended to visible range which is appropriate for the visible-light driven photocatalysts. The band gap energies of the composite are estimated to about 2.13 and 2.81 (Fig. S5) (see Supplementary material) that is proper for the degradation of organic pollutants in the visible range.

3.4.4. SEM
The SEM (Fig. 11) shows the surface morphology of the titanate after incorporating of the CdS nanoparticles. It proves the intercalation of CdS nanoparticles into the lamellar space and on the surface of the titanate. The pillaring of cadmium sulfide was done by sonication without causing any damage and destruction of titanate structure. However, some CdS nanoparticles formed separately due to high concentration of initial precursors.

Table 2 shows the elemental percentage, obtaining from EDX spectrum. The existing of K and Ti elements result from titanate, and Cd and S result from CdS, respectively. The decrease in K$^+$ ions content to 1.18%, indicating that K$^+$ was replaced during the treatment processes and thus the CdS particles were formed in layers space.

3.4.5. TEM
The TEM images (Fig. 12) present the intercalated CdS nanoparticles into the titanate layers. The cross-sectional view of the CdS/Ti$_4$O$_9$ nanocomposite exhibits a parallel lines representing
the titanate layers, confirming the formation of an alternately arranged structure of the titanate sheets and CdS nanoparticles. In all samples, the external and internal surfaces of the rod structure of titanate have been extensively covered by CdS nanoparticles.

Table 2

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>1.18</td>
</tr>
<tr>
<td>Ti</td>
<td>8.73</td>
</tr>
<tr>
<td>Cd</td>
<td>67.32</td>
</tr>
<tr>
<td>S</td>
<td>3.93</td>
</tr>
</tbody>
</table>

Fig. 11. SEM images of CdS intercalated into titanate.

Fig. 12. TEM images of CdS/Ti$_4$O$_9$ nanocomposite.
3.5. Evaluation of the optimized photocatalyst

3.5.1. COD analysis

The chemical oxygen demand (COD) values have been related to the total concentration of organics in the solution and their decrease reflects the degree of mineralization [35]. The COD analysis was carried out by standard acid dichromate method [36]. For measuring the residual contamination, first, the COD was determined for a dye solution (50 ppm) as a blank. Thereafter, the solution was used for photochemical treatment in different interval times. After separation, the COD of the remaining solution was determined and the results are shown in Fig. 13. The COD at time zero for blank solution was about 310 (mg/L) and this value decreased with increasing the time of irradiation. The COD has totally disappeared in 3.5 h and the dye in solution was completely mineralized in the photocatalytic degradation process. As the results show, the photocatalytic degradation efficiency is clearly higher than the COD removal efficiency. This is due some intermediates that formed during the mineralization of CR on the surface and in the solution.

3.5.2. Reusability of the photocatalyst

For the purpose of practical performance, it is essential to evaluate the reusability of the catalyst. Fig. 14 shows the repetitive photocatalytic degradation of CR during the five sequential cycles with the same 0.05 g catalyst at 50 mg L⁻¹ dye concentration. After each cycle, the photocatalyst was separated, washed with distilled water, dried and followed by adding fresh solution of CR before each photocatalytic run. The degradation rates for the 5 consecutive cycles were 100%, 98%, 95%, 80% and 75%, after 15 min irradiation, respectively. The results showed that the catalytic activity of the CdS/Ti4O9 had a slight decrease in initial cycles. The loss of the catalyst during the washing and filtrating may also have an effect on the reduction of the catalyst activity. As far as the stability of photocatalyst is concerned, the recycle of CdS/Ti4O9 photocatalyst can confirm the relative stability of the CdS/Ti4O9 nanocomposite.

3.5.3. Photostability of the photocatalyst

It has been proved that the recombination of photogenerated electron–hole pairs in CdS is so fast and is particularly prone to photocorrosion. This is an inherent disadvantage of CdS photocatalyst and it considers as a defect for its cyclic operation and in environmental applications [37,38]. In order to improve the photoactivities and photostabilities of CdS semiconductor, some efforts have been devoted to producing CdS-based nanocomposites [39,40]. In fact, composites with CdS acted as acceptors for the photogenerated electrons and promoting charge separation and leaving holes on the CdS to cause photocorrosion. The separation of hole and electron can lead to the enhancement of photoreaction efficiency and significant inhibition of photocorrosion. The anti-photocorrosion and photostability behavior of CdS/Ti4O9 nanocomposite in comparison with CdS was evaluated through the measurement of the Cd²⁺ released in solution after photocatalytic degradation of CR. The results in Fig. 15 confirmed that the amount of Cd²⁺ released in solution in the case of nanocomposite was declined to 75.5% of the case of the CdS.

In order to further prevent photocorrosion of CdS, the role of sacrificial reagents was investigated. Photocorrosion of CdS occurs as follows Eq. (1):

\[
\text{CdS} + 2\text{H}^+ \rightarrow \text{Cd}^{2+} + \text{S} \quad (1)
\]

Some inorganic ions such as S²⁻/SO₃²⁻ [41], were used as sacrificial reagents for inhibiting of CdS photocorrosion. Serving as a sacrificial reagent, S²⁻ can react with 2 holes to form S and therefore, photocorrosion of CdS is prevented. The influence of the concentration of the sacrificial reagent such as Na₂S was investigated on the photocatalytic efficiency. The release of Cd²⁺ into the solution was measured and the results were shown in Fig. S6 (see Supplementary material) and Fig. 16. With increasing the amount of Na₂S to 0.1 M, the degradation of CR was increased in the presence of CdS/Ti4O9. Based on this observation, an optimum concentration of 0.1 M Na₂S was determined for degradation. In general, the diffusion of reactants to the surface of photocatalyst can be promoted by the concentrated sacrificial reagents [42]. This explains the observed presence of an optimum concentration of sacrificial reagents. Besides that, the amount of Cd²⁺ released in solution was behaved the same as Na₂S concentration on the degradation.

3.5.4. Mechanism of photocatalytic activity

The mechanism of photodegradation process under sunlight irradiation is shown in Fig. 17. In the prepared CdS/Ti4O9 photocatalyst, two semiconductors are in contact with different redox...
energy levels of their CB and VB. The efficiency of photo generated e− and h+, separation and the interfacial charge transfer can be increased in this combination. When the intercalated composite is exposed to sunlight, CdS with smaller band gap can absorb the photons and leads to e− and h+. The electric field creates at the CdS/Ti4O9 interface pushes the photo-generated electrons toward the conduction band of K2Ti4O9, and the electrons further migrate into the inner surface of the layered titanate. While the photo-generated holes stay on the CdS valence band. Therefore, the photo excited electrons can be effectively collected by titanate, and the holes by CdS.

Some experiments were designed to confirm the photodegradation mechanism of CR in the presence of sunlight. The effect of different scavengers was studied on the degradation mechanism as shown in Figs. S7 and S8 (see Supplementary material).

Iodide and fluoride ions are scavengers with redox potential of 1.3 V for the couple I/I− [44] and 3.6 V for the couple F/F− [45], respectively. They could react with h+ and OH and consumes the oxidizing species available at the surface of the catalyst. When 20 mM KI and NaF were added, the degradation was inhibited slightly as shown in Fig. S7.

As far as electron scavenging is concerned, addition of NaN3 as an external oxidant/electron acceptor into a photocatalyst/dye suspension caused a decrease in CR removal during photocatalytic process (Fig. S8). Elimination of e− by scavenger caused the O2 species and thus OH were not formed and the degradation of CR was declined. In addition of K2S2O8 as an oxidant group, the photocatalytic activity was increased slightly. This is due to the generation of OH through the reaction of SO2− with H2O, Eqs. (2) and (3) that can degrade the pollutant directly.

\[
\begin{align*}
S_2O_2^{2−} + e^- & \rightarrow SO_4^{−} + SO_4^{2−} & (2) \\
SO_4^{2−} + H_2O & \rightarrow OH + SO_4^{2−} + H^+ & (3)
\end{align*}
\]

Based on the results, both e− with progressing the reaction through the reduction in double band (N=N) of dye molecule and h+ with pushing the photocatalytic reaction through oxidation and active species like OH and O2, are involved in photocatalytic activities. In addition, the effect of different scavengers on photocatalytic activity is almost negligible. This effect can be attributed to the low access of scavengers to electrons and holes into the structure of intercalated compound.

4. Conclusion

The CdS/Ti4O9 photocatalyst was successfully synthesized under the assistance of ultrasonic irradiation. The photocatalytic and absorption edge of CdS/Ti4O9 was predominantly improved with intercalating of CdS in the layered space of titanate. The Congo red dye in its natural medium was successfully degraded in the presence of mentioned photocatalyst and sunlight irradiation. The photocatalytic reaction conditions such as the dosage of catalyst and the concentration of sacrificial reagents were optimized. The amount of released Cd2+ by photocorrosion of CdS which intercalated into layered titanate was much less than that of released from pure CdS. The synthesized photocatalyst was stable and reusable under visible light irradiation in several cycles. The mechanism of separation of the photogenerated electrons and holes at the CdS/Ti4O9 composite was discussed.
Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2015.09.070.

References