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Vanadium doping of strontium germanate and their visible photocatalytic properties

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Vanadium doped strontium germanate with rod-shaped morphology and different vanadium contents has been synthesized by a facile hydrothermal process. The obtained vanadium doped strontium germanate has been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and ultraviolet (UV) diffuse reflectance spectra. The phase of the vanadium doped strontium germanate depends on the vanadium content. SEM observations show that the vanadium doped strontium germanate are composed of rod-shaped morphology with the diameter and length of nanoscale, microscale size and longer than 10 μm, respectively. The band gap of the vanadium doped strontium germanate depends on the vanadium content and increases obviously from 2.74 eV to 3.02 eV with the vanadium content increasing from 1wt.% to 10wt.%. Vanadium doped strontium germanate shows highly efficient photocatalytic activity for the degradation of methylene blue under sun light irradiation. The results show that vanadium doped strontium germanate is very promising for visible light photocatalytic application.

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Introduction

Strontium germanate with orthorhombic $SrGeO_3$ phase belongs to typical semiconductor with perovskite ABO_3 structure. ABO_3-type perovskite structure has been showed to have good photocatalytic activity for the degradation of various organic pollutants.[1,2] In our previous research, single crystalline strontium germanate nanowires have been synthesized by a facile hydrothermal process without any surfactants.[3] The strontium germanate nanowires with $SrGeO_3$ phase exhibit good photocatalytic activity for methylene blue (MB) under UV light irradiation. However, strontium germanate nanowires are poor absorbers of the photons in sun light owing to the wide band gap with the value of 3.67 eV which is larger than that of ZnO and TiO_2.[4,5] Great effort has been devoted to the research for improving the photocatalytic activity of the photocatalysts with wide band gap under visible light. It has been proved that the photocatalytic activity of the photocatalysts can be improved by doping with transition metal elements. Chen *et al.*[6] reported the strategy for the enhancement of photocatalytic H_2 evolution by doping La into the depletion layer of $Cd_{0.6}Zn_{0.4}S$. It is reported that ZnO can be doped by several elements, such as Co,[7] La[8] and Ta[9] to improve its photocatalytic activity. TiO_2 can also be doped by different elements, such as La,[10] Si and Fe,[11] Fe and N[12] for the photocatalytic degradation of various pollutants under visible light. In these transtion metal elements, the photocatalytic activity of ZnO and TiO_2 can be greatly improved under visible light irradiation by vanadium doping because vanadium can lead to conspicuous absorption in visible light region and increases carrier lifetime.[13-15] The photocatalytic performance of the semiconductor photocatalysts can be greatly enhanced by the vanadium doping. Similar to the semicondutors with wide band gap, such as $Cd_{0.6}Zn_{0.4}S$, ZnO and TiO_2, it is of great significance to improve the photocatalytic activity of the strontium germanate under visible light irradiation for the degradation of organic pollutants.

To date, photocatalysts have been doped by transition metal elements via chemical vapor deposition,

ion implantation, electrochemcial deposition, sol-gel method and hydrothermal method.[13,16] Hydrothermal method takes the advantages of low cost, simple appratus and doping process.[17,18] In the paper, vanadium doped strontium germanate with rod-shaped morphology and different vanadium contents has been synthesized by a facile hydrothermal process. The structure, morphology, size and optical properties of the vanadium doped strontium germanate have been analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-vis diffuse reflectance spectra. The photocatalytic activity of the undoped and vanadium doped strontium germanate with various vanadium doping levels for the photocatalytic degradation of MB under sun light irradiation are studied in detail. The vanadium doped strontium germanate exhibits good photocatalytic degradation activity for MB under sun light irradiation.

Results and discussion

XRD

Fig. 1 shows the XRD patterns of the vanadium doped strontium germanate synthesized from 180 ℃ for 24 h. It can be seen that the XRD patterns of the vanadium doped strontium germanate with the vanadium content of 1wt.% and 3wt.% (Fig. 1a and 1b) are same. All diffraction peaks are assigned to be orthorhombic $SrGeO_3$ phase (JCPDS card No. 27-0845). The $SrGeO_3$ phase is same to that of the undoped strontium germanate nanowires synthesized under same hydrothermal conditions.[3] For vanadium mass percentage low than 3wt.%, no other phases, such as vanadium or vanadium oxide are detected besides orthorhombic $SrGeO_3$ phase. The result demonstrates that vanadium ions may enter into the $SrGeO_3$ lattices. With the vanadium mass percentage increasing to 5% and 10% (Fig. 1c and 1d), a secondary phase is observed corresponding to orthorhombic $SrV_{11}O_5$ phase (JCPDS card No. 30-1314). Besides orthorhombic $SrGeO_3$ and $SrV_{11}O_5$ phases, no other phases are observed. Some diffraction peaks loacted at $2\theta=41.8°$, 66.5° and 74.8° of the orthorhombic $SrGeO_3$ phase disappear when vanadium content is more than 5wt.%.

The intensities of the diffraction peaks of the orthorhombic $SrV_{11}O_5$ phase increase greatly with the vanadium content increasing to 10wt.%.

SEM

Fig. 2 shows the general morphology and size of the vanadium doped strontium germanate. It is observed that the 1wt.% vanadium doped strontium germanate is mainly composed of free-standing nanowires besides some rod-shaped structure with the diameter of about 1 μm (Fig. 2a). The average diameter of the nanowires is about 60 nm and the length is in the range of several tens to several hundreds of micrometers. The morphology and size of the 1wt.% vanadium doped strontium germanate are very similar to those of the undoped strontium germanate nanowires synthesized under same hydrothermal conditions.[3] Very different from the morphology and size of 1wt.% vanadium doped strontium germanate, the doped strontium germanate with the vanadium content of more than 3wt.% mainly consists of rod-shaped structures with microscale size. The diameter of the rod-shaped structures is in the range of 600 nm-2 μm and length is longer than 10 μm when the vanadium mass percentage is 3% (Fig. 2b). However, some nanowires also exist in the products. The amount of the nanowires further decreases with the increase of the vanadium doping mass percentage to 5% (Fig. 2c). The diameter of the microrods is in the range of 1-2 μm and length is longer than 10 μm. Only a very small amount of nanowires exist in the products. Increasing the vanadium mass percentage to 10%, no nanowires are observed (Fig. 2d). Some microrods with the diameter of about 2 μm and irregular particles with the microscale size are observed besides some nanorods.

UV-VIS diffuse reflectance spectra

The UV-vis diffuse reflectance spectra of the undoped strontium germanate nanowires and vanadium doped strontium germanate are shown in Fig. 3. The band gap (E_g) can be determined by the UV-vis diffuse reflectance spectra. The wavelength at the absorption edge (λ) is determined as the intercept on the wavelength axis for a tangent line drawn on the absorption spectrum. The band gap is determined using the Kubelka Munck function. The band gap of the undoped strontium germanate nanowires and vanadium doped strontium germanate with different vanadium mass percentage is listed in Table 1. It is observed that the absorption of vanadium doped strontium germanate is higher than that of the undoped strontium germanate nanowires. The band gap decreases from 3.67 eV (undoped strontium germanate nanowires) to 2.74 eV (1wt.% vanadium doped strontium germanate). The band gap of the 1wt.% and 3wt.% vanadium doped strontium germanate is similar with the value of 2.74 eV and 2.77 eV, respectively. The band gap increases from 2.88 eV to 3.02 eV with the vanadium mass percentage increasing from 5% to 10%. The band gap of the strontium germanate can be decreased by vanadium doping. However, the band gap of the vanadium doped strontium germanate increases with the increase of the vanadium doping mass percentage. Why the higher V doping leads to higher optical band gap? It is still puzzling. Some groups showed that the band gap was closely relative to the specific surface area of the semiconductors. Kočí *et al.*[19] showed that the band gap of the pure crystalline anatase phase increased from 3.00 eV to 3.14 eV with the decrease of the specific surface area from 122 m^2g^{-1} to 38 m^2g^{-1}. The change of the band gap with the specific surface area corresponded well with the results reported by Lin *et al.*[20] The specific surface area of the vanadium doped strontium germanate is measured to be 35.54, 34.76, 32.67 and 31.16 m^2 g^{-1} for the vanadium doping mass percentage of 1%, 3%, 5% and 10%, respectively. The specific surface area decreases with increasing the vanadium doping mass percentage. Therefore, it is considered that the decrease of the specific surface area of the vanadium doped strontium germanate may cause the increase of the band gap in the vanadium doping mass percentage range of 1% to 10%. The vanadium doped strontium germanate exhibits a red-shift of the adsorption edge and a significant enhancement of light absorption in the visible light region. The vanadium doped strontium germanate shows the higher absorption ability in the visible light region. The absorption edge of the undoped strontium germanate nanowires is 338 nm showing that the undoped strontium germanate nanowires have strong light absorption ability in UV light region. However, The aborption edge of the vanadium doped strontium germanate is larger than 410 nm showing that the vanadium doped strontium germanate has strong light absorption ability in visible light region. Therefore, vanadium doped strontium germanate is strong absorbers of photons in the sun light due to their narrow band gap.

Photocatalytic performance of vanadium doped strontium germanate

The photocatalytic activity of the undoped and vanadium doped strontium germanate has been evaluated by monitoring the photocatalytic degradation of MB. The adsorption equilibrium is reached just under 20 min stirring in the dark. The evolution of the adsorption along the total time of the catalytic experiments of 4 h is analyzed so as to considerate this possible adsorption contribution. However, the intensity of the UV-vis absorbance at 665 nm obtained from the time of 20 min and 4 h maintains similar. The result shows that the adsorption has almost no contribution to the decoloration of MB. Figs. S1-S5 display the UV-vis spectra of the MB solution treated after the sun light irradiation using 20 mg undoped and vanadium doped strontium germanate in 20 mgL^{-1} MB solution. MB shows a major absorption band at 665 nm. The intensity of the UV-vis absorbance at 665 nm decreases obviously after the sun light irradiation using vanadium doped strontium germanate. Fig. 4 shows the MB concentration ratio after the sun light irradiation from 0 to 4 h. MB is very difficult to be degraded using undoped strontium germanate nanowires under sun light irradiation owing to the wide band gap of the undoped strontium germanate nanowires which is difficult to basorb visible light. The vanadium doped strontium germanate shows great improved photocatalytic activity than undoped strontitum germanate nanowires under sun light irradiation beccause vanadium doping can reduce the band gap of the undoped strontium germanate nanowires. The MB degradation ratio is similar when the 1wt.% and 3wt.% vanadium doped strontium germanate are used as the photocatalysts under sun light irradiation. MB degradation ratio is 55.49% and 53.48%, respectively for 1wt.% and 3wt.% vanadium doped strontium germanate under the sun light irradiation for 0.5 h. MB can be degraded totally with the sun light irradiation for 4 h. The band gap is 2.74 eV and 2.77 eV, respectively for 1wt.% and 3wt.% vanadium doped strontium germanate showing that 1wt.% and 3wt.% vanadium doped strontium germanate has similar sun light absorbance ability. Vanadium doped strontium germanate belongs to semiconductor which can absorb visible light. Visible light irradiation leads to the transfer of the electrons from the valence band to conductance band of vanadium doped strontium germanate. Therefore, electrons and holes form from the valence bands and conductance bands, respectively. Hydroxyl species originate from the reaction between the holes and adsorbed water. MB can be degraded by the attack of the holes and hydroxyl species.[21]

The photocatalytic activity of the vanadium doped strontium germanate decreases obviously with the vanadium content increasing to 5wt.% and 10wt.%, respectively. The MB degradation ratio is 94.41% and 52.55%, respectively for 5wt.% and 10wt.% vanadium doped strontium germanate under sun light irradiation for 4 h. The band gap increases to 2.88 eV and 3.02 eV, respectively with the vanadium content increasing to 5wt.% and 10wt.%. The increase of the band gap results in the decrease of the photocatalytic activity of the vanadium doped strontium germanate. It can be concluded that the 1wt.% and 3wt.% vanadium doped strontium germanate have high photocatalytic activity under sun light irradiation. The high photocatalytic degradation ability may be contributed to the better performance of the absorption in visible light range and larger content of oxygen vacancies or defects produced by vanadium.[13] The photocatalytic activity decreases obviously with vanadium doping level in the 5-10% range. This fact is quite puzzling. However, It is noted that the average particle size determines the specific surface area and photon conversion efficiency of the photocatalysts which are the essential factors for the photocatalytic performance of the photocatalysts.[19] The smaller particle size increases the specific surface area and number of the active surface sites where the photogenerated charge carriers can react with absorbed molecules. The photocatalytic performance of the photocatalysts can be greatly enhanced by decreasing the particle size. It had been reported that the particle size played an important role in the nanocrystalline TiO_2 based catalysts by influencing the dynamics of e^-/h^+ recombination.[22] The pure TiO_2 with the particle size of about 10 nm was the optimal value in liquid phase for the photocatalytic decomposition of $CHCl_3$. The effect of the TiO_2 particle size on the photocatalytic degradation of MB in a suspended aqueous solution had also been investigated by Xu *et al.*[23] and *Jang et al.* [24] The results showed that the adsorption rate and adsorbed amount of MB to the suspended TiO_2 particles increased with the decrease of the TiO_2 particle size. And the photocatalytic activity of the TiO_2 increased greatly when the TiO_2 particle size was reduced. The strontium germanate nanowires with smaller size and larger specific surface area than bulk strontium germanate exhibited better photocatalytic activity for MB under UV light irradiation.[3] Saha *et al.*[25] also reported that the CdS nanoparticles displayed size dependent photocatalytic activity towards the degradation of nitroaromatics. The photocatalytic efficiency of the CdS nanoparticles was quintupled with the decrease in the particle size from 5.8 to 3.8 nm. The specific surface area of the vanadium doped strontium germanate is 35.54, 34.76, 32.67 and 31.16 $m^2\ g^{-1}$ for the vanadium doping mass percentage of 1%, 3%, 5% and 10%, respectively. The specific surface area decreases with increasing the vanadium doping mass percentage. Therefore, it is considered that the decrease of the photocatalytic activity with vanadium doping level in the 5-10% range may originate from the specific surface area of the vanadium doped strontium germanate. The 1-3% is the optimum range and then results get worse with further increase of the vanadium doping mass percentage.

In order to analyze the role of the content of the vanadium doped strontium germanate on the photocatalytic performance for the MB degradation, the photocatalytic degradation ratio of MB using vanadium doped strontium germanate with different contents has been determined. Figs. S6-S9 show the absorption spectra of the MB solution after the sun light irradiation for 4 h using vanadium doped strontium germanate with different vanadium contents. The content of the vanadium doped strontium germanate is in the range of 0.25 to 2 mg/ml (40 mg vanadium doped strontium germanate in 20 ml MB solution). The intensity of the absorbance peak at 665 nm decreases sharply with the increase of the content of the vanadium doped strontium germanate. Fig. 5 indicates the MB concentration ratio after sun light irradiation for 4 h using vanadium doped strontium germanate with different vanadium contents. The photocatalytic degradation ratio decreases obviously with the decrease of the content of the vanadium doped strontium germanate. The MB degradation ratio decreases from 95.15% to 40.69% with the increase of the vanadium content from 1wt.% to 10wt.% when the content of the vanadium doped strontium germanate is 0.25 mg/ml. MB can not be degraded totally when the vanadium content of the doped strontium germanate exceeds 5wt.% under sun light irradiation. However, the MB degradation ratio decreases obviously from 97.46% to 72.28% with the increase of the vanadium content from 5wt.% to 10wt.% when the content of the vanadium doped strontium germanate is 2 mg/ml. The results indicate that the photocatalytic degradation ratio of the MB strongly depends on the content of the vanadium doped strontium germanate. The content of the vanadium doped strontium germanate plays an important role on the MB degradation. More MB molecules adsorb on the surface of the vanadium doped strontium germanate leading in the increase of the MB degradation ratio with the increase of the content of the vanadium doped strontium germanate.[3,26,27]

Conclusions

In summary, vanadium doped strontium germanate rod-shaped structures with different vanadium contents have been prepared by a facile hydrothermal process. The band gap of the vanadium doped strontium germanate is smaller than that of the undoped strontium germanate increasing from 2.74 eV to 3.02 eV with the increase of the vanadium content from 1wt.% to 10wt.%. The vanadium doped strontium germanate exhibits higher photocatalytic activity for the photocatalytic degradation of MB than that of the undoped strontium germanate under sun light irradiation. The photocatalytic activity of the vanadium doped strontium germanate depends on the vanadium content. 1wt.% and 3wt.% vanadium doped strontium germanate have high photocatalytic activity under sun light irradiation. The vanadium doped strontium germanate may be considered as good condidates for the photocatalytic degradation of MB under sun light irradiation.

Experimental section

Materials

High pure GeO_2 powders (purity: ⩾99.99%), $Sr(CH_3COO)_2{\cdot}1/2H_2O$ (AR grade) and sodium vanadate (AR grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. of P. R. China. For photocatalytic activity tests, MB was purchased from Sinopharm Chemical Reagent Co., Ltd. of P. R. China. All raw materials were used as received without further purification.

Synthesis of vanadium doped strontium germanate

In a typical procedure, 0.16 g GeO_2, 0.66 g $Sr(CH_3COO)_2{\cdot}1/2H_2O$ and sodium vanadate were dissolved in 60 mL deionized water. The mass ratio of vanadium and strontium germanate is determined to be 1:99, 3:97, 5:95 and 10:90, respectively. The $Sr(CH_3COO)_2{\cdot}1/2H_2O$ and sodium vanadate solution were added to GeO_2 solution under vigorous stirring. Then, the mixture was placed in a 100 mL autoclave with a Teflon liner. The autoclave was maintained at 180 ℃ for 24 h. Subsequently the autoclave was cooled naturally in air.

The white precipitates were filtered, washed with deionized water for several times and dried at 60 ℃ in air. Finally, white vanadium doped strontium germanate products were obtained.

Characterization

The obtained products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-vis diffuse reflectance spectra. XRD pattern was carried out on a Bruker AXS D8 X-ray diffractometer equipped with a graphite monochromatized Cu-Kα radiation (λ=1.5406 Å). The samples were scanned at a scanning rate of 0.05 °/s in the 2θ range of 20-80°. SEM observation was performed using nova nanoSEM FEI 430 SEM with a 15 KV accelerating voltage. The UV-vis diffuse reflectance spectrum was obtained using a UV3600 UV-vis spectrometer (Shimadzu International Co., Ltd. of Japan) and a thermo Electron Corporation with a reflectance diffuse accessory. The specific surface area of the samples was analyzed by Brunau-Emmet-Teller (BET) method using a Micromeritics Gemini VII2390 apparatus (Micromeritics, Norcross, GA) with nitrogen adsorption at 77 K. Prior to adsorption, the samples were purged in He gas atmosphere at 473 K for 1 h.

Photocatalytic tests

Photocatalytic activity of the vanadium doped strontium germanate were tested for the photocatalytic degradation of MB in a quartz reactor (OCRS-IV photocatalytic system, Kaifeng Hongxing Technology Co., Ltd. of Henan province of P. R. China). The photocatalytic experiments were performed under real sun light irradiation at open air using 5-40 mg vanadium doped strontium germanate suspended in 20 ml MB solution with the MB concentration of 2.5-20 mgL^{-1} in a quartz glass cell. Prior to the irradiation, the mixture was maintained in the dark for 20 min under stirring to reach the adsorption equilibrium. All photocatalytic experiments were conducted at room temperature in air. The MB solution was separated from vanadium doped strontium germanate by filter unit. The obtained solution was analyzed by UV756

UV-vis spectrometer (Shanghai Youke Instrument Co., Ltd. of P. R. China). The initial MB concentration (C_0) and MB concentration (C) after a certain reaction time (t) were determined by measuring the absorbance of the reactant solution at its maximum wavelength (665 nm) during the photocatalytic degradation process. The C/C_0 ratio was used to analyze the photocatalytic performance of the vanadium doped strontium germanate.

Acknowledgments

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Table

Table 1 The band gap of vanadium doped strontium germanate with different vanadium mass percentage

Vanadium mass percentage (%)	Absorption edge (λ, nm)	Band gap (E_g, eV)
0	338	3.67
1	453	2.74
3	447	2.77
5	431	2.88
10	410	3.02

Figure captions:

Fig. 1 XRD patterns of the vanadium doped strontium germanate with different vanadium contents. (a) 1wt.%, (b) 3wt.%, (c) 5wt.%, (d) 10wt.%.

Fig. 2 SEM images of the vanadium doped strontium germanate with different vanadium contents. (a) 1wt.%, (b) 3wt.%, (c) 5wt.%, (d) 10wt.%.

Fig. 3 UV-vis diffuse reflectance spectra of the vanadium doped strontium germanate with different vanadium contents. (a) Without vanadium, (b) 1wt.%, (c) 3wt.%, (d) 5wt.%, (e) 10wt.%.

Fig. 4 MB concentration ratio after different irradiation times treated by vanadium doped strontium germanate with different vanadium contents in 20 ml MB solution. Vanadium doped strontium germanate, 20 mg; MB, 10 mgL^{-1}.

Fig. 5 MB concentration ratio treated using vanadium doped strontium germanate with different vanadium contents in 20 ml MB solution. Irradiation time, 4 h; MB, 10 mgL^{-1}.

Figures

Fig. 1

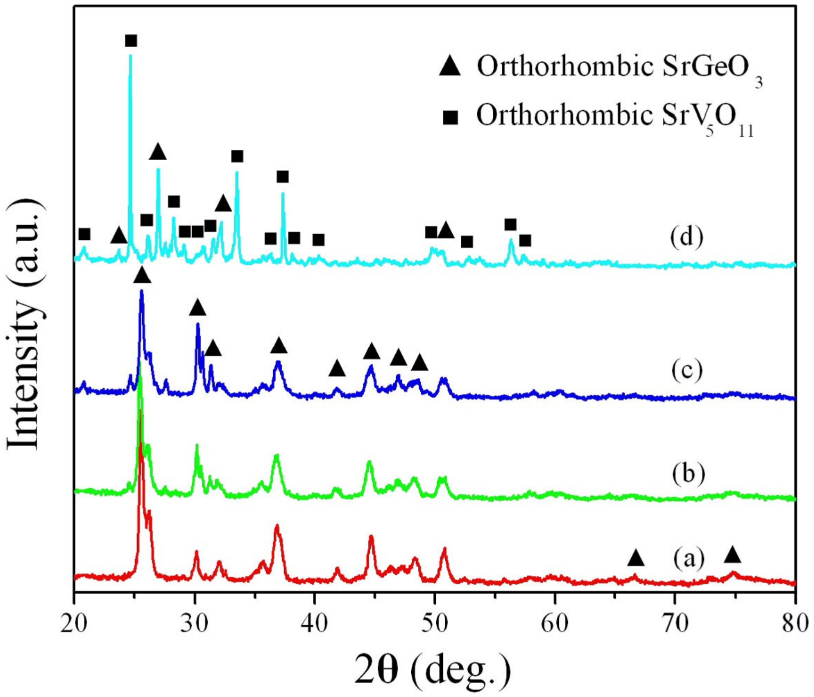


Fig. 2

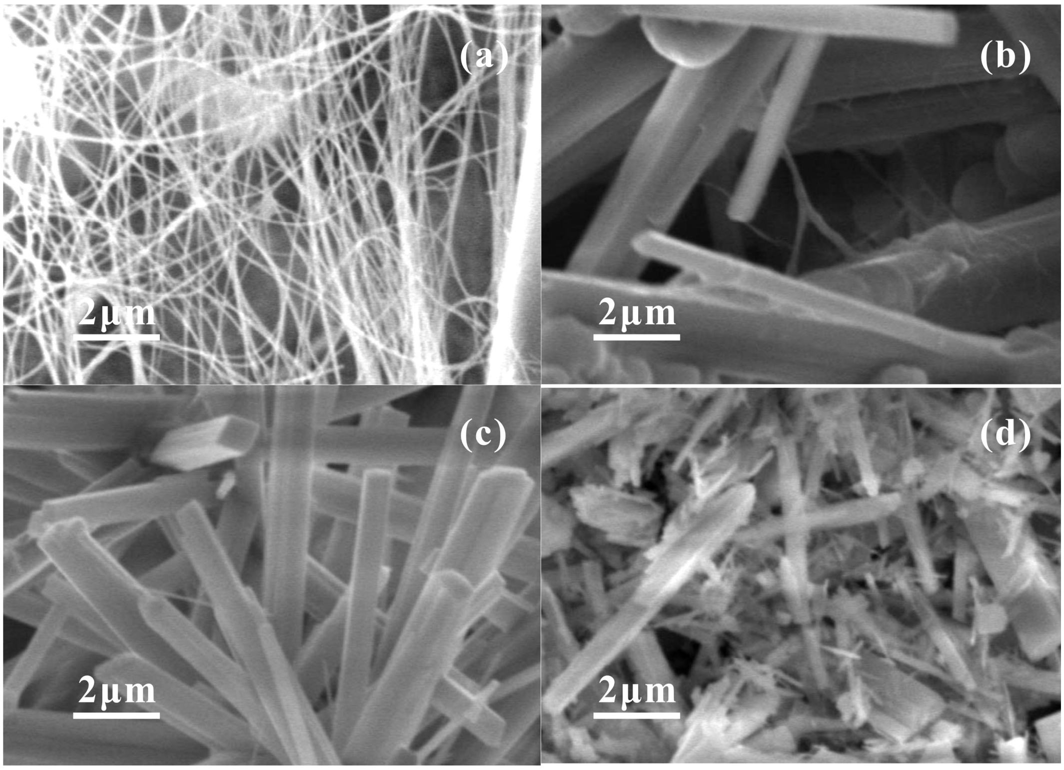
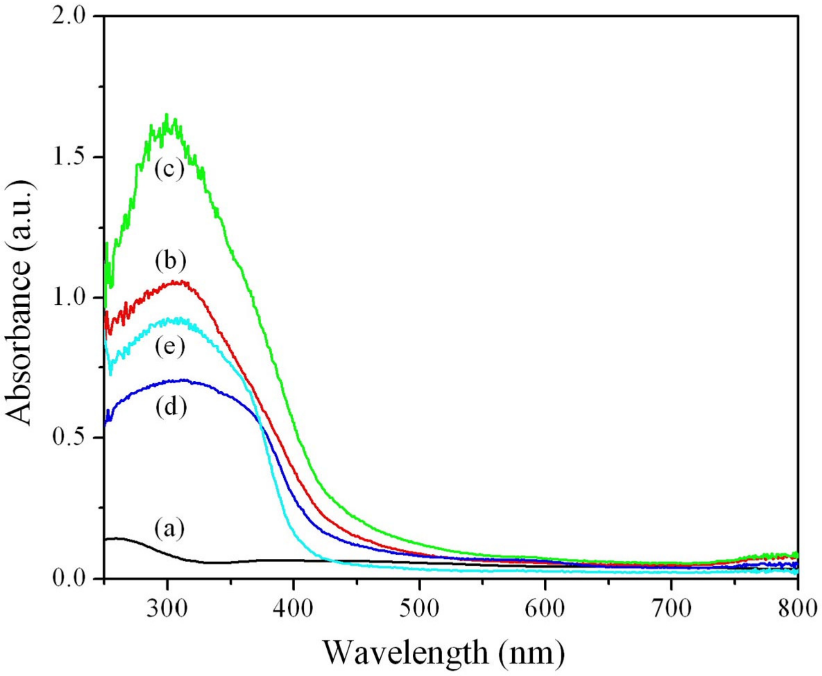


Fig. 3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1.0
0.5
0.0
Absorbance (a.u.)
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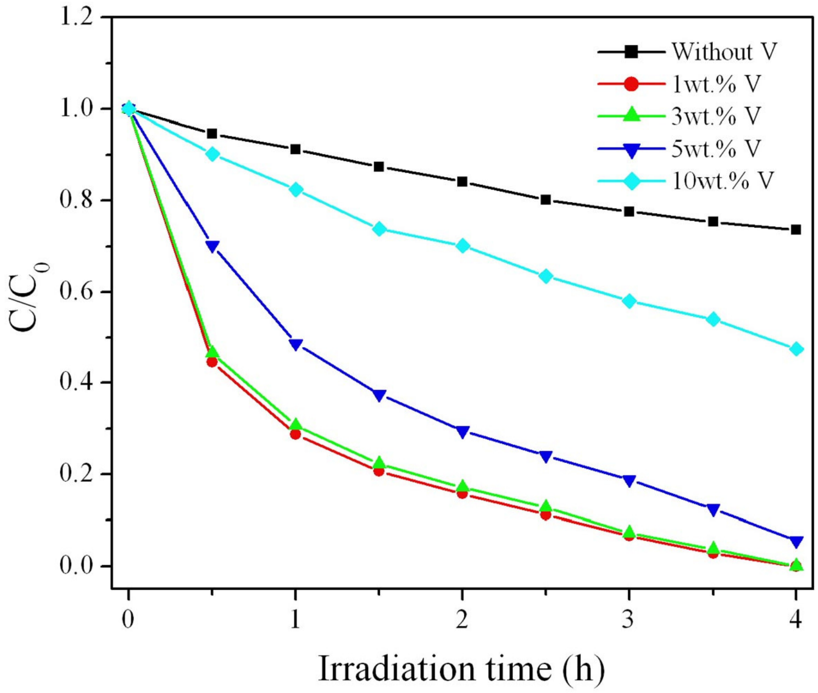
400
500
600
700
800
Wavelength (nm)
(c)
(b)
(e)
(d)
(a)

Fig. 4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1.0
0.8
0.6
0.4
0.2
0.0
C/C_0
0
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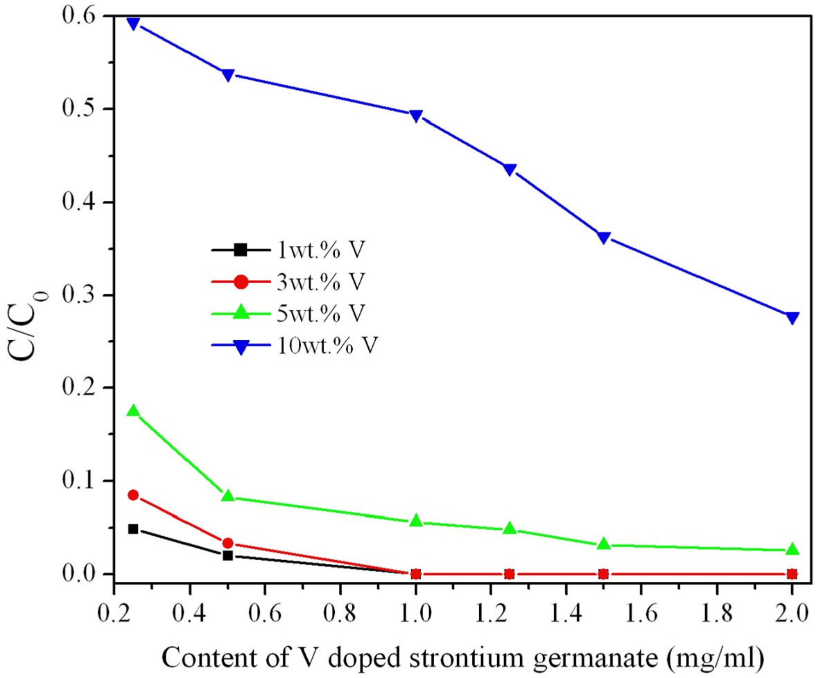
3
4
Irradiation time (h)
Without V
1wt.% V
3wt.% V
5wt.% V
10wt.% V

Fig. 5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0.2
0.1
0.0
C/C_0
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0.4
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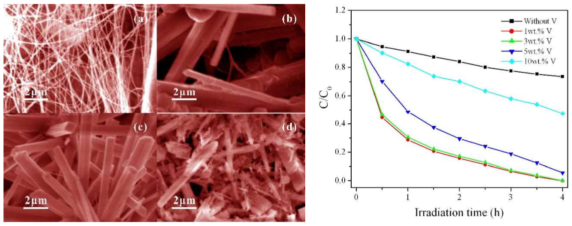
1.0
1.2
1.4
1.6
1.8
2.0
Content of V doped strontium germanate (mg/ml)
1wt.% V
3wt.% V
5wt.% V
10wt.% V



Strontium germanate microrods have been doped by vanadium exhibiting good photocatalytic degradation of methyl blue under sun light irradiation.