Investigation of the use of TiO$_2$ doped with metal ions in water disinfection

M. A. Khraisheh, L. Wu and B. Antizar-Ladislao

ABSTRACT

This research was conducted to improve titanium dioxide by transition metal doping using cooper. Sol gel method was used to prepare metal doped TiO$_2$. Titanium isopropoxide and commercial TiO$_2$ P25 were employed as catalyst precursor. The role played by the varied preparation parameters such as doping level and pH of solution discussed with respect to the final photoreactivity. Photoreactivity was carried out in a solar box with two UVA lamps. The photodisinfection of E. coli in aquatic solution were selected as probe to measure the photoreactivity. It is found that Cu doped TiO$_2$ exhibited enhanced results from E. coli photodisinfection.

Key words | disinfection, E. coli, photocatalyst, TiO$_2$, water treatment

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INTRODUCTION

In early 2000, one sixth of the world's population (which equates to approximately 1.1 billion people) was without access to clean water supply (World Health Organization and UNICEF 2000). No access to good quality drinking water increases the risk of waterborne diseases such as cholera, typhoid fever and other diarrhoeal diseases. This represents a significant global problem, and a number of options available today for disinfection include chlorination, iodine treatment, UV treatment, and boiling.

The last 20 years saw the development of two of the most interesting disinfection alternatives which are solar disinfection and TiO$_2$ photodisinfection under UV illumination. The combination of the two methods would result in a much greener, cheaper, more efficient and less energy consuming solution which could be produced and widely applied whilst causing no harm to human health. Considering the fact that the areas of the world that lack access to safe drinking water are also the world's poorest nations that have an abundance of sunlight irradiation, the provision of

this new technique can alleviate the current burden on the global water supply and improve sanitation (World Health Organization and UNICEF 2000). TiO$_2$, a cheap, non toxic and inert semiconductor photocatalyst is used in many applications in foods, paints and as an antimicrobial material. Recently, it has been used in water disinfection. TiO$_2$ can be photoactivated by the UV spectrum of irradiation. The combination of TiO$_2$ and ultraviolet irradiation is a proven advanced oxidation process and the alteration of ultraviolet irradiation with sunlight or sunlight simulator is therefore promising.

However, the band-gap, as explained in the paragraph below, of TiO$_2$ is large (Eg $=$ 3.2 eV compared to less than 2.5% of the solar photon flux has energy greater than 3.0 eV). Thus, TiO$_2$ is only active in the ultraviolet region ($<$ 400 nm) which is $<$ 10% of the overall solar intensity so that the light harvesting ability of TiO$_2$ is very limited (Linsebigler et al. 1995). In a single free-standing atom or molecule, electrons are accommodated in their electron

orbital (s, p, d etc.), which imply a discrete set of energy levels. When a great number of atoms are brought together to form a solid, the number of orbitals increases dramatically. Orbitals with similar energy levels join to form bands of energy which are separated by void regions where there are no energy levels or orbitals. The empty region is also referred to as band gap. To narrow this band gap, doping with metals is sometimes used. Doping is the process of intentionally introducing impurities into an extremely pure semiconductor to change its electrical properties. Dopants could alter lattice thermal dynamics, electronic structures and furthermore photocatalytic efficiency.

The aim of this paper is to investigate the effect of doping Cu metal on TiO$_2$ and to test its potential effect using organic pollutant degradation and bacteria disinfection in water for various dopent levels and the pH environments.

EXPERIMENTAL MATERIALS AND METHODS

Undoped and Cu/TiO$_2$ catalysts were prepared via a sol gel method described by Ding & Liu (1997). Titanium (IV) isopropoxide (TTIP) and alcohol (ethanol, 2(2-ethoxy-ethoxy) ethanol or isoproponal) were vigorously stirred in a beaker. A mixture of fixed amount of deionised water (DI water), acid (HCl or H$_2$SO$_4$) and alcohol was added drop-wise into the previous TTIP/alcohol solution and magnetically stirred. After gelation, it was dried at 60°C in an oven overnight. The powder was then annealed at a specific temperature for 2 h in furnace. Finally, the catalysts was pulverized through 75ìm sieves and kept in a sealed jar for further use.

For Cu doped TiO$_2$, a given amount of cooper precursor (1 to 10 mol % to TiO$_2$) was mixed with DI water, acid and alcohol solution before the mixture was added into a TTIP/alcohol solution. The rest of the preparation procedure was the same as with undoped TiO$_2$. In our work, a system for naming the resultant catalyst was developed to distinguish between the vast types prepared (Table 1). Only a small number is used and are presented in this research paper. The names given depended on some of synthesis variables, including preparation method, undoped or doped, difference in starting solution composition and annealing temperature. The name of a catalyst can be seen in the format of ATBC. Here "A" stands for the preparation method, it can be sol-gel method (SG) or Wet-impregnation method (IM). "T" is short for TiO$_2$ and means it is a TiO$_2$ based photocatalyst. "B" stands for a dopant which (Cu). "C" is always a number that stands for different conditions in starting solution composition and annealing temperature, a detailed lists corresponding to that information can be found in the list of synthesised materials.

SGTCu43, for example, is a TiO$_2$ based photocatalyst which was prepared from sol-gel method. In the standard sol-gel procedure, the starting solution is composed of TTIP, isopropanol, H$_2$SO$_4$ and H$_2$O at a molar ratio of 1:80:0.06:14. It is doped by Cu at a level of 0.1 mol% towards TiO$_2$ and the final annealing condition is 600°C for 2 hours. Table 2 contains the list of the catalysts synthesised and used in this paper.

Experimental setup

The heart of photocatalytic experimental system is the design of the photoreactor (see Photo 1). The solar box system consists of two chambers: the lamp and reactor chamber. The lamp chamber was installed on top of the reactor chamber. Two UVA lamps were located in the lamp chamber: (i) A commercial ruptile fluorescent tube lamp and (ii) A fluorescent Blacklight Blue tube lamp (18W, Silva) which transmit ultraviolet radiation peaking at 365 nm. In the reactor chamber, Pyrex glass flasks were employed as

Table 1 │ List of synthesised photocatalysts

Sample	Sol	Acid	Molar ratio			Cooper dopant	Doping level (mol%)	Calcination temperature (°C)	BET surface area (m^2 g^{-1})
SGTCu43	Iso	H$_2$SO$_4$	80	14	0.06	CuCl$_2$	0.1%	600	30.91
SGTCu44	Iso	H$_2$SO$_4$	80	14	0.06	CuCl$_2$	0.5%	600	83.16
SGTCu45	Iso	H$_2$SO$_4$	80	14	0.06	CuCl$_2$	1.0%	600	53.37
SGTCu46	Iso	H$_2$SO$_4$	80	14	0.06	CuCl$_2$	10.0%	600	27.09

Table 2 │ Summary of sol-gel prepared photocatalysts used in studying the influence of dopant type

| Material	Sample	Treatment
Cu doped TiO$_2$ from sol-gel method	SGTCu43	Hydrolysis and condensation of sol mixture (TTIP: Isopropanol: H$_2$SO$_4$: H$_2$O: CuCl$_2$ = 1:80:0.06:14:0.001) at room temperature and followed by drying at 600°C for 2 h
Cu doped TiO$_2$ from sol-gel method	SGTCu44	Hydrolysis and condensation of sol mixture (TTIP: Isopropanol: H$_2$SO$_4$: H$_2$O: CuCl$_2$ = 1:80:0.06:14:0.005) at room temperature and followed by drying at 600°C for 2 h
Cu doped TiO$_2$ from sol-gel method	SGTCu45	Hydrolysis and condensation of sol mixture (TTIP: Isopropanol: H$_2$SO$_4$: H$_2$O: CuCl$_2$ = 1:80:0.06:14:0.01) at room temperature and followed by drying at 600°C for 2 h
Cu doped TiO$_2$ from sol-gel method	SGTCu46	Hydrolysis and condensation of sol mixture (TTIP: Isopropanol: H$_2$SO$_4$: H$_2$O: CuCl$_2$ = 1:80:0.06:14:0.1) at room temperature and followed by drying at 600°C for 2 h

batch reactors. Water samples taken from the solar box system at a certain time interval were inoculated in petri dish before incubation for *E. coli* disinfection experiment.

Preparation of test solution

On the day of the experiment, certain amount of *E. coli* stock solution was transferred to centrifuge tubes and centrifuged at 3,650 rpm for 10 min. This formed a tight pellet in each tube. The broth of one centrifuge tube was poured off and the pellet was re-suspended in the same amount of DI water. The samples of DI water suspension were taken every hour for 4 hours while the concentration of viable *E. coli* was enumerated using the Miles & Misra method (1938).

BET characterizations

The surface area of the catalyst samples were obtained from nitrogen adsorption/desorption isotherms at 77 K. Surface area data were calculated by applying the BET method. (Sing *et al.* 1985).
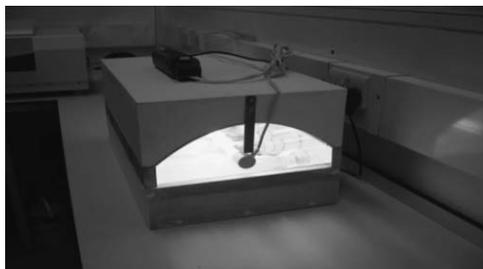
Photo 1 │ Experimental setup.

Point of zero charge determination

In the experiment procedure described by Reymond and Kolenda (Reymond & Kolenda 1999): oxide suspensions with the catalysts solid contents (weight percentage) as 0.01%, 0.1%, 1%, 5%, 10% are introduced in glass beakers (capacity: 10 mL). The beakers were filled with catalysts oxide suspensions in DI water before sealed in order to minimize the residual air volume above suspension. The beakers were then kept in air and shaken at 200 rpm at room temperature for 24 hours. The pH was measured after 24 h of contact time, time for which pH equilibrium was reached in all the cases. For each oxide, curves giving the suspension pH value as a function of solid content were plotted. It is considered that the PZC value of the oxide is the pH value of the suspension having the higher solid content when pH evolution with solid concentration is low.

RESULTS AND DISCUSSION

Overnight grown *E. coli* stock culture was used to investigate the effect of light exposure as well as the existence of catalysts on the *E. coli* inactivation process. TiO$_2$ P25 was used as undoped TiO$_2$ as it is commonly used standard TiO$_2$ in the literature.

As it can be seen from Figure 1 that the presence of TiO$_2$ in dark conditions can hardly affect the viable cell number of *E. coli* culture in the water. A significant increase in the cell number after 2 hours indicates TiO$_2$ did not exhibit any antibacterial effect in the dark. The other two tests were carried out in the solar box with weak UVA exposure. However, the difference of absence and presence of TiO$_2$
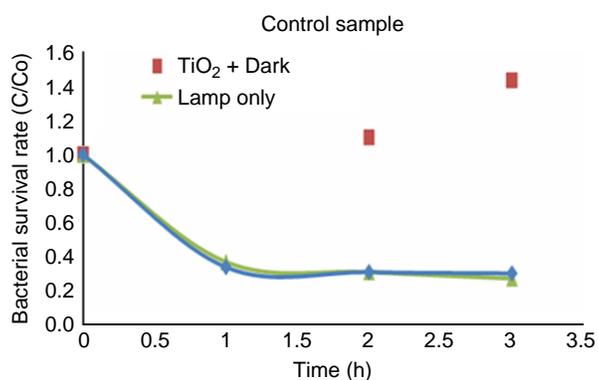
Figure 1 | The decline of *E. coli* on TiO₂ P25 in different irradiation conditions: dark (TiO₂ + Dark) and solar box irradiation (TiO₂ + lamp). Container size = 100 ml, Catalysts dose = 1 g/L, initial *E. coli* concentration = ~10^8 CFU/ml, pH = 6.3, T = 25°C. Control was used in solar box without the addition of TiO₂.

P25 is marginal. In both cases, there is a 60% decrease in viable *E. coli* cell number within the first hour and greater resistance to the UVA damage was found later and the cell number remains at a steady level at least for 2 more hours. The inefficacy of P25 to kill bacteria in the dark can be also found in open literature (Lonnen *et al.* 2005), but the rate of *E. coli* decline in the absence of P25 is much slower than the reference due to the difference of light input. The solar box system in this experiment has an irradiation range in the UVA with low intensity. Such low intensity light input may delay the production of reactive radicals for the attack of bacterial while the presence of catalyst particles in the water suspension may eliminate the penetration of light and protect the bacteria from direct exposure to harmful UV irradiation. Therefore, the use of TiO₂ P25 in water disinfection under weak UV intensity would not be necessary practical. This conclusion is comparable with that of Hu *et al.* (2007), who discovered that the presence of TiO₂ P25 film killed 1.8 log *E. coli* from an initial concentration of 6 log CFU/ml after 3 hours in weak UVA irradiation. No significant decline of *E. coli* can be observed in the same system without the addition of catalyst. This result reveals that TiO₂ P25 is inadequate activated under current weak irradiation conditions and modification on the photocatalysts is needed. Therefore, the following sections will be focussed on Cu doped TiO₂. TiO₂ films deposited with antibacterial metals such as Cu and silver have been developed. Examining the survival rate of *E. coli*

on Cu/TiO₂ thin film under a weak $1 \, \text{uW cm}^{-2}$ UV illumination which intensity similar to the indoor solar UV, Sunada *et al.* (2003) speculated the process was a combination of TiO₂ photocatalysis and Cu antibacterial properties.

As can be seen from Figure 2, the first step is postulated to be the partial decomposition of the outer membrane in the cell envelope by a photocatalytic process, followed by permeation of the Cu ions into the cytoplasmic membrane. In the second step is a disorder of the cytoplasmic membrane caused by the Cu ions, which results in a loss of the cell's integrity. After the outer membrane has been disordered and partially decomposed, the reactive species penetrate to the cytoplasmic membrane, causing the cell to die (Sunada *et al.* 2003).

The influence of doping level

Compared with wet impregnated Cu/TiO₂, the doped catalyst from sol gel method may have a more homogenous distribution of dopant. The investigation into the relation between doping level and disinfection capability may give some clue in explaining its enhanced performance. The series of various Cu doped TiO₂ selected are shown in Table 2.

As Figure 3 illustrates, the 0.5 M% Cu doped TiO₂ has apparently outperformed than other three levels of dopant 0.1 M, 1.0 M and 10.0 M%. Roughly, the low efficiency associated with 0.1 M 1.0 M and 10.0 M% is comparable with that of control without any catalysts addition which all stopped near 20% survival rate after three hours. In contrast, one hour was required for 0.5 M% Cu doped TiO₂ to achieve a more than 80% bacterial disinfection. It must be noted that most photocatalytically active SGTCu44 also has the largest surface area as shown in Table 1. On one hand, low doping level catalyst SGTCu43 has a better anatase crystalline phase than 0.5 M% Cu doped TiO₂. However, due to the lack of Cu ions in the catalysts, the advantage in anatase crystalline phase structure of SGTCu43 is compensated by a weaker Cu ions synthetic effect as was evident in the XRD tests (these are not included in the context of this paper). On the other hand, higher doping level catalyst SGTCu45 and SGTCu46 can provide enough Cu ions but the disadvantages in crystalline
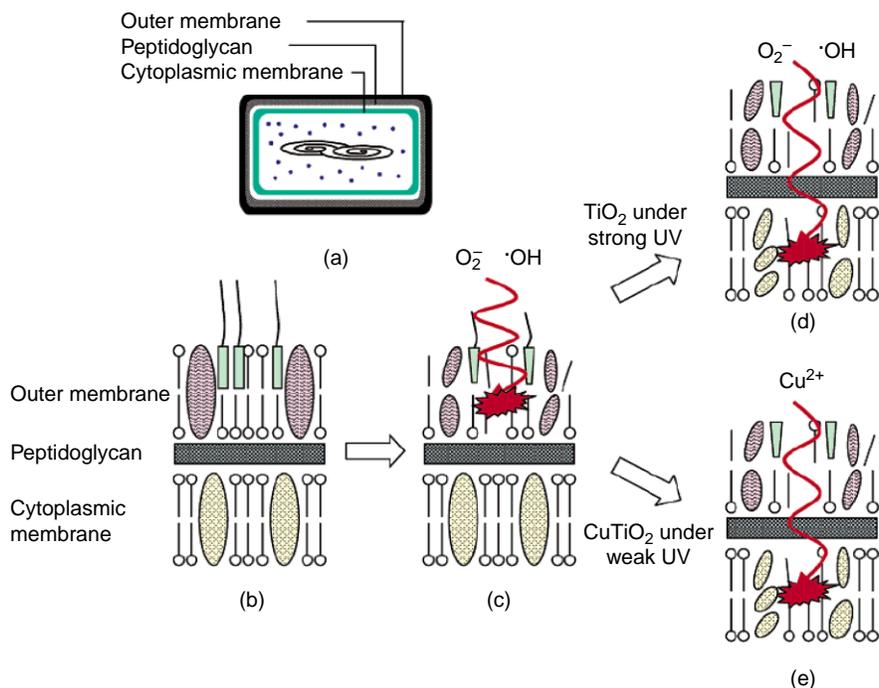
Figure 2 │ A schematic illustration of the bactericidal process for the Cu-resistant *E. coli* cell on a normal TiO₂ film and on a Cu/TiO₂ film: (a) illustration of *E. coli* cell and (b)–(e) enlarged illustration of cell envelope parts.

structure also lead to the degradation of catalysts activity. Hence, there seems to be a balance between doping level and TiO₂ photoreactivity. The optimum doping level suggested in this experiment seems to be in the range of 0.1 M and 1.0 M%.

Synthetic effect of Cu ions with TiO₂ toward E. coli disinfection was also found (Sato & Taya 2006) under white fluorescent lamp irradiation. To understand the mechanism, Sato & Taya (2006) introduced Cu ions differently. In the

first scenario, $Cu^{2+}(10\,mmol/m^3)$ was added to liquid phase on TiO₂ film. The apparent deactivation rate constant was about 5 times as large as that on TiO₂ film in the absence of Cu^{2+}. In another case, the deactivation tests were also examined using a modified film preparation made from Cu-incorporated TiO₂ (1.8 M%). The apparent deactivation rate constant was about nine times larger than those on the original TiO₂ film without Cu^{2+} addition $(10\,mmol/m^3)$. The ICP-AES analysis revealed that the
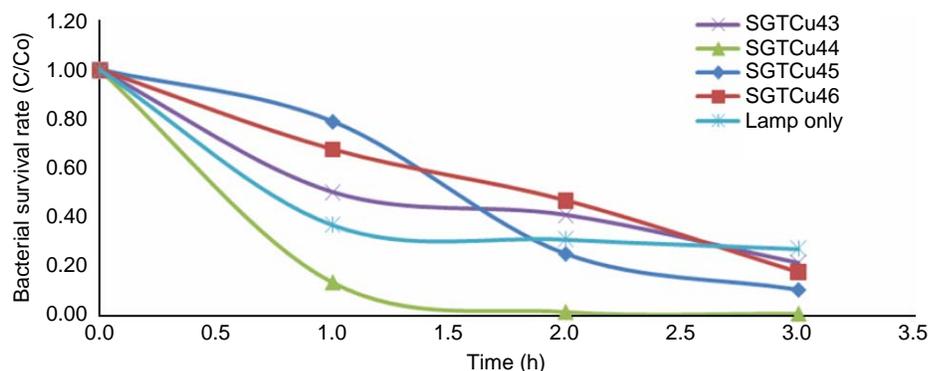

Figure 3 │ The decline of *E. coli* on irradiated Cu doped TiO₂ with different doping levels: 0.1 M% (SGTCu43), 0.5 M% (SGTCu44), 1.0 M% (SGTCu45) and 10.0 M% (SGTCu46). Container size = 100 ml, Catalysts dose = 1 g/L, initial *E. coli* concentration = ~10⁸ CFU/ml, pH = 6.3, T = 25°C. Control was used in solar box without the addition of catalyst.

Cu^{2+} concentration that leached into the bacteria solution was 9 mmol/m³. Apparently, both the Cu ions presence in the solution and on the surface of TiO_2 contributed to the synthetic effect. To explain the synthetic effect of TiO_2 with the Cu^{2+} ions in the aqueous solution, they proposed that reactive radicals such as $\cdot OH$, $\cdot O^{2-}$ and H_2O_2 are generated on photo-excited TiO_2. Because H_2O_2 is more stable than $\cdot OH$ and $\cdot O^{2-}$, it can diffuse from the catalysts surface into bulk liquid. Cu^{2+} ions presented in aqueous solution can receive electron from photo-excited TiO_2 particles and turn into Cu^+. Photo-reduced Cu^+ in bulk liquid can turn back into Cu^{2+} by reacting with H_2O_2 to produce $\cdot OH$ which attacks microbial cells in bulk liquid. In this manner, Cu^{2+} aids in the trapping and delivery of electrons from TiO_2 indicating electron-hole recombination on/in photocatalysts were inhabited. Another explanation provided by Sunada et al. (2003) is different but not in contradiction with this of Sato & Taya (2006). Sunada et al. (2003) argued that Cu^{2+} can intrude into cells where the outer membrane has been injured by $\cdot OH$ attack, and raise a direct disturbance in intracellular metabolic systems. For the Cu^{2+} confined in solid phase (Cu/TiO₂ film), travel into the cell structure is not happening, but its presence on the surface of TiO_2 can also catalyze H_2O_2 into $\cdot OH$.

Application of Cu/TiO₂ in different pH environment

The growth and survival of microorganisms is greatly influenced by the pH of its environment. The microorganism has the ability to grow within a specific pH range reflecting the organism's adaptation to their natural environment. A neutral or nearly neutral environment is generally advantageous to the growth of bacteria. In the present work, the pH was adjusted at the beginning of the illumination by addition of NaOH or HCl (0.1 M) to bacterial suspension. The initial pH value was set at 4, 6 and 9 according to previous report (Rincon & Pulgarin 2004) that the TiO₂ P25 photocatalytic E. coli inactivation rate was independent of the initial pH between 4.0 and 9.0 because of acid tolerance response involves acid-induced proteins that protect the cells from an acid shock (pH 3.0) (Heyde & Portalier 1990).

As shown in Figure 4, in the first hour an increase in the disinfection rate was observed in the both the acidic or base
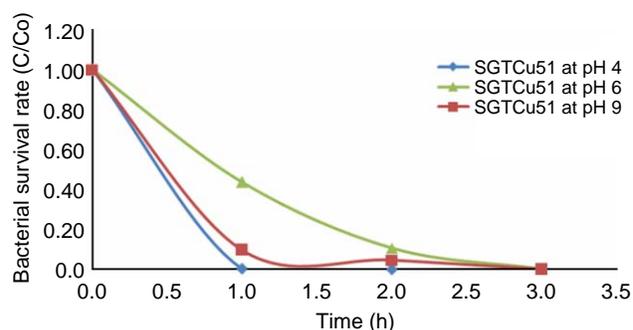

Figure 4 | The decline of E. coli on irradiated Cu doped TiO₂ (SGTCu51) at different water pH value (4, 6 and 9). Container size = 100 ml, Catalysts dose = 1 g/L, initial E. coli concentration = ~10⁸ CFU/ml, pH = 6.3, T = 25°C.

compared with neutral solution. E. coli is a representative of the large neutrophilic bacteria groups which grows optimally between pH 6.0 and 8.0. At pH values of a unit or so beyond these limits, E. coli will grow slowly (Heyde & Portalier 1990). In our experiment, a neutral environment has the least pressure on the E. coli viable number in the presence of Cu-doped TiO₂ because E. coli is more sensitive to both acid and base environment.

The acid shock on E. coli is the most significant, partly due to the increasing acidity pressure along with time and partly due to the fact that pH has an effect on the electrostatic charge of the TiO₂ surface, which determines the adsorption on TiO₂ of both organic substances and bacteria as well as the photocatalytic reactivity of TiO₂ (Rincon & Pulgarin 2004).

For pH values higher than the PZC (point of zero charge, 6.5) of titanium, the surface becomes negatively charged and it is the opposite for pH < PZC, according to the following equilibrium:

$$pH < PZC : TiOH + H^+ \leftrightarrow TiOH_2^+ \tag{1}$$

$$pH > PZC : TiOH + OH^- \leftrightarrow TiO^- + H_2O \tag{2}$$
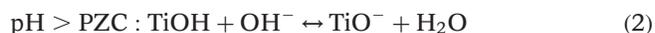
In our experiment, the PZC of Cu-TiO₂ sample SGTCu51 has a PZC around 5.0, which means a positive charge at pH = 4. The positive charged surface is more advantageous for the adsorption of E. coli which has a net negative electrostatic charge by virtue of ionized phosphoryl and carboxylate substituents on outer cell envelope macromolecules (Wilson et al. 2001).

CONCLUSIONS

- Photocatalyst from sol gel method was employed for water disinfection with P25 as reference. P25 shows little sign of photocatalytic activity in *E. coli* disinfection in weak UV irradiation in solar box system. It is the same case for low level of doped TiO$_2$ except 0.5 M% sol gel prepared Cu/TiO$_2$. The best performance is 10.0 M% wet impregnated Cu/TiO$_2$.

- A synthetic effect of doped Cu and TiO$_2$ is discovered. In the mechanism proposed, Cu ions were involved in the production of reactive radicals either in the bulk of solution or on the surface of TiO$_2$ leading to the destruction of *E. coli*. A synthetic effect can occur with a certain amount of doping level as well as good anatase crystalline phase of TiO$_2$.

- The photocatalytic activity of doped TiO$_2$ powder was tested in different water pH conditions. An acid or basic environment both enhanced the disinfection of *E. coli*.

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