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*Research Article*

# Photocatalytic Inactivation Effect of Gold-Doped $TiO_2$ ($Au/TiO_2$) Nanocomposites on Human Colon Carcinoma LoVo Cells

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The photocatalytic inactivation effecting of gold-doped $TiO_2$ ($Au/TiO_2$) nanocomposites on human colon carcinoma LoVo cells was investigated for the first time. The $Au/TiO_2$ samples containing different amounts of Au (1–4 wt%) were prepared by deposition-precipitation (DP) method. These synthesized $Au/TiO_2$ nanocomposites were characterized by transmission electron microscopy (TEM) and inductively coupled plasma atomic emission spectroscopy. It was found that the photocatalytic inactivation effect of $TiO_2$ nanoparticles on LoVo cancer cells could be greatly improved by the surface modification of Au nanoparticles. Furthermore, the loading amount of Au on the surface of $TiO_2$ nanoparticles affects the photocatalytic inactivation efficiency strongly, and it was found that the most efficient nanocomposites were $TiO_2$ nanoparticles doped with 2 wt% Au. When 50 $\mu$g/mL 2 wt% $Au/TiO_2$ nanocomposites were used, all of the LoVo cancer cells were killed under the irradiation of UV light ($\lambda_{max}$ = 365 nm, Intensity = 1.8 mW/cm$^2$) within 100 minutes. But for 50 $\mu$g/mL $TiO_2$ nanoparticles, only 40% cancer cells were killed under the same condition.



## 1. INTRODUCTION

The rising incidence of cancer in the world demands an increase in effort towards the development of novel and effective photocatalysts for killing cancer cells in photodynamic therapy (PDT). $TiO_2$ nanoparticles have been proved to be an important photocatalyst because of their good photocatalytic properties [1–9]. When $TiO_2$ nanoparticles were illuminated by UV light with wavelength of less than 385 nm, photo-induced electrons and holes could be created [10]. Moreover, these photo-induced electrons and holes could further react with hydroxyl ions or water to form powerful oxidative radicals (e.g., $OH^{\cdot}$, $HO_2^{\cdot}$) [11], which are capable of destroying the structure and the component of tumor cells [6]. Therefore, $TiO_2$ nanoparticles exhibited good antitumor activity for cancer cells as well as for animal autochthonous tumor models under the irradiation of UV light. For clinical application, the UV light could be specifically delivered to the photocatalyst in contact with tumor directly through UV light fibers as described by Fujishima [6]. However, the photo-generated holes are easy to recombine with the photo-induced electrons, which greatly reduced the photocatalytic inactivation efficiency of $TiO_2$ [12–14]. We aim to enhance the photocatalytic inactivation efficiency of $TiO_2$ on tumor cells by the surface modification of Au nanoparticles.

In recent years, gold-doped $TiO_2$ ($Au/TiO_2$) nanocomposites have been investigated to enhance the photocatalytic efficiency of $TiO_2$ in decomposing organic compounds and photokilling bacteria [15–18]. In addition, $Au/TiO_2$ nanocomposites have also attracted great interest for their applications in solar energy conversion [19, 20].

In this paper, $Au/TiO_2$ nanocomposites were prepared by deposition-precipitation method, and then used as photocatalysts to kill human colon cancer LoVo cells. It was the first time to investigate the photocatalytic inactivation effect of $Au/TiO_2$ on cancer cells. The experimental results show that the photocatalytic inactivation efficiency on human colon LoVo cancer cells could be greatly increased by the modification of Au on $TiO_2$ nanoparticles.

## 2. MATERIALS AND METHODS

### 2.1. Materials

The materials used in this research were hydrogen tetrachloroaurate(III) trihydrate [$HAuCl_4 \cdot 3H_2O$] (Aldrich Chemical Co., Germany), Degussa P25 $TiO_2$ (BET surface area = 45 $m^2g^{-1,}$ nonporous, 75% anatase and 25% rutile; Degussa, Germany), MTT [3-(4, 5-dimethylthiazol-2-yl)-2, 5-diphenyltetrazolium bromide] kits (Beyotime Co. Ltd., Nantong, China), trypsin-EDTA (Invitrogen Co., USA), polyethylene glycol (PEG, 20.000, Sigma Chemical Co., Germany), human colon carcinoma LoVo cells (American Type Culture Collection, USA) (ATCC), and Ham's F12 medium (PAA laboratories, Australia) supplemented with 2.0 mM L-glutamine, 1.5 g/L sodium bicarbonate ($NaHCO_3$), 50 $\mu$g/ml penicillin, and 15% fetal calf serum (FCS). All other chemical reagents were of analytical grade. The water employed in all preparations was purified by a Milli-Q system (Millipore).

### 2.2. Preparation of Au/$TiO_2$ nanocomposites suspension

The Au/$TiO_2$ nanocomposites were synthesized in the dark using the deposition-precipitation method [21]. Before the preparation, P25 $TiO_2$ was dried in the air at 100°C for 24 hours Then one g of $TiO_2$ powder was added into 100 mL aqueous solution containing 0.42 M of urea and certain amount of $HAuCl_4$. The amount of $HAuCl_4$ we added was calculated according to the designed loading amount of gold in the Au/$TiO_2$ nanocomposites. For example, to prepare 2 wt% Au/$TiO_2$ nanocomposites, 0.04 g $HAuCl_4 \cdot 3H_2O$ was used. It was proposed that urea ($CO(NH_2)_2$) could react with water and gently produce hydroxide ions ($OH^-$), and could avoid the violent increase of pH value in a local solution [21]. Therefore, the gold hydroxide could be homogeneously and equably precipitated. Afterwards, the suspension was kept at constant 80°C for four hour under vigorous stirring. Then the suspension was centrifuged at 12.000 rpm for 10 minutes, washed with deionized water, and centrifuged again. These washing and centrifuging procedures were repeated four times in order to remove residual $Cl^-$ thoroughly. The yellow sediment was dried under vacuum at 100°C for two hours and ground into yellow powder in an agate mortar, and finally became the precursor. The fabrication of Au/$TiO_2$ nanocomposites was carried out via a heat treatment of the precursor under a flowing mixture atmosphere consisted of 95% Ar and 5% $H_2$. The precursors were heated from room temperature to 300°C at a rate of 1°C·$min^{-1}$, and then maintained at 300°C for four hours This calcination treatment leads to the reduction of adsorbed Au (III) complexes into gold nanoparticles. The Au/$TiO_2$ nanocomposites were stored in the dark under vacuum in a desiccator at room temperature.

Various Au/$TiO_2$ samples with different Au ratio were milled in a rotating agate mortar with 2 mL ethanol at 450 r/min for ten hours, and then dried at 70°C. Then they were ultra-sonically dispersed in the phosphate buffer solution (PBS, pH 7.4) to produce the Au/$TiO_2$ suspensions. Afterwards, polyethylene glycol (PEG, 1 mg/mL) was added into the Au/$TiO_2$ suspensions in order to prevent the precipitation of Au/$TiO_2$ nanoparticles. Finally, the Au/$TiO_2$ suspensions were sterilized using an autoclave. The pure P25 $TiO_2$ suspension was prepared through a similar procedure.

### 2.3. Characterization of nanoparticles/nanocomposites

The chemical quantitative analysis of Au in the samples was performed by using an IRIS Intrepid inductively coupled plasma atomic emission spectroscopy (ICP-AES, USA). The concentration of Au in the samples is expressed as the weight of Au in per gram of sample (Au wt%), which equals $[m_{Au}/(m_{Au} + m_{TiO_2})] \times 100\%$, where $m_{Au}$ and $m_{TiO_2}$ are the weight of Au and $TiO_2$, respectively. The morphology and size of the Au/$TiO_2$ nanocomposites and $TiO_2$ nanoparticles were studied with a JEOL 2011 transmission electron microscope (TEM, Japan).

### 2.4. Cell culture and pretreatment

Human colon carcinoma LoVo cells were cultured in vitro in Ham's F12 culture medium in a humidified incubator with 5% $CO_2$ at 37°C. LoVo cells were subcultured with a mixture of ethylenedinitrile tetraacetic acid (EDTA) and trypsin. All experiments were performed using cells during the exponential growth phase. The cell concentration was measured by using a hemocytometer and the cell density was adjusted to the required final concentration.

### 2.5. Photokilling LoVo cells using Au/$TiO_2$ nanocomposites or $TiO_2$ nanoparticles as photocatalysts

The photocatalytic inactivation effects of Au/$TiO_2$ and pure $TiO_2$ on LoVo cells were evaluated according to [1, 6] with a slight modification. The experimental processes were as follows. Firstly, LoVo cells in the exponential growth phase were trypsinized and suspended in the F12 culture medium at a concentration of $5 \times 10^4$ cells/mL. Secondly, 2 mL LoVo cell suspension was added into a sterile dish (Diameter = 35 mm) and incubated for 24 hours. It is very important to disperse the cells as evenly as possible at this step. Thirdly, the culture medium in the sterile dish was replaced by a mixture of 1 mL Au/$TiO_2$ (or $TiO_2$) suspension and 1 mL fresh F12 medium. LoVo cells were incubated continuously for another 24 hours and then the incubation solution was removed. Finally, 1 mL fresh F12 medium was added into the sterile dish, and then the UV-light irradiation process was performed. Four parallel tests were performed for each sample to ensure accuracy, and each experiment was repeated three times. The variation region and the mean value of the experimental data are presented in each resulting diagram.

In the UV-light irradiation process, a 20-W (G20T10, USA) and a 40-W (G40T10, USA) UV light lamps (the light peak wavelength was $\lambda_{max}$ = 365 nm) were used as the light source, and the light intensity on the samples was measured by using a power meter (Thermo Oriel 70260, USA ). The

Table 1: The contents of gold in $Au/TiO_2$ composites prepared by DP methods.

| Designed Au loading amount (wt%) | Actual Au loading amount (wt%) |
|---|---|
| 1 | $0.7 \pm 0.02$ |
| 2 | $1.8 \pm 0.01$ |
| 4 | $3.6 \pm 0.04$ |

choice of UV light with wavelength of 365 nm is very important, because it has much lower influence on the living cell than that of UV light with much shorter wavelength.

### 2.6. Measurement of the viability of LoVo cells

The viability of the LoVo cells in the experiments was detected by a MTT staining method [1, 22–24]. In the MTT assay, the number of living cells was proportional to the absorbance of formazan at 570 nm, which was produced in the cleavage process of MTT. In addition, only the living cells can react with MTT and produce the formazan. Briefly, after LoVo cells were treated with different condition, 250 $\mu$L MTT solution from the MTT kit was added into each 35-mm culture dish and incubated with cells for 4 hours at 37°C until purple formazan crystals appeared. Then, two mL formazan-dissolving solution from the MTT kit was added into each dish and mixed thoroughly to dissolve these purple crystals. After continuing incubation for several hours at 37°C to ensure that all purple crystals were dissolved, the purple solution was dispensed into wells of 96-well plates. The 96-well plates were evaluated spectrophotometrically at 570 nm with a BIO-RAD M-450 microplate reader, and the optical absorptions $[A]_t$ was measured. The survival fraction could be calculated according to $[A]_t/[A]_i$, where $[A]_i$ is the optical absorption of the untreated cells.

## 3. RESULTS AND DISCUSSION

### 3.1. Characteristic of $TiO_2$ nanoparticles and $Au/TiO_2$ nanocomposites

There are several ways to deposit noble metal nanoparticles on the surface of $TiO_2$ nanoparticles, such as chemical reduction, deposition-precipitation, electrochemical deposition, photodeposition, sol-gel, and self-assembly methods [18, 21, 25, 26]. In this work, the deposition-precipitation method was chosen to prepare $Au/TiO_2$ nanocomposites with different Au ratio (1–4 wt%). The representative samples were characterized by TEM and ICP methods.

The TEM images of pure $TiO_2$ particles and 2 wt% gold-doped $Au/TiO_2$ particles are presented in Figure 1. As can be seen, most of the $TiO_2$ particles are spherical or square-shaped with a particle size of 15–35 nm (Figure 1(a)). The gold nanoparticles (dark spots with diameter of 2–5 nm) were uniformly deposited on the surface of $TiO_2$ supports (Figure 1(b) and (c)).

The elemental composition of these samples was analyzed by IRIS Intrepid inductively coupled plasma atomic emission spectroscopy. Table 1 presents the contents of gold in the $Au/TiO_2$ nanocomposites, and indicates that in the preparing process, most of the gold from the raw material $HAuCl_4$ is deposited on the surface of $TiO_2$ nanoparticles.

### 3.2. Photocatalytic killing effect of $TiO_2$ nanoparticles and $Au/TiO_2$ nanocomposites

#### 3.2.1. Cytotoxicity of $TiO_2$ nanoparticles or $Au/TiO_2$ nanocomposites in the dark

It is required that the photosensitive antitumor drugs used in PDT not only have high photocatalytic inactivation capability under irradiation, but also have no toxicity in the dark. So it is very important to investigate the self-engendered cytotoxicity of $TiO_2$ nanoparticles or $Au/TiO_2$ nanocomposites. The cytotoxicity of $TiO_2$ or $Au/TiO_2$ was measured by exposing LoVo cells in the F12 medium containing various concentrations of $TiO_2$ or $Au/TiO_2$ for 24 hours in the dark, respectively. The results showed that when the concentrations of $TiO_2$ nanoparticles or $Au/TiO_2$ nanocomposites were in the range of 0–400 $\mu$g/mL, the surviving fraction of LoVo cells was always greater than 90% (Figure 2). According to the suggestion in [6], in this case, the $TiO_2$ nanoparticles and $Au/TiO_2$ nanocomposites could be considered as non-toxic materials for cancer cells in the dark. This conclusion was consistent with those in [1, 6].

#### 3.2.2. Influence of the gold loading amount on the photocatalytic inactivation effect

Figure 3 shows the photocatalytic inactivation effect of 50 $\mu$g/mL $Au/TiO_2$ nanocomposites with different Au loading amount under the UV light irradiation. The intensity of UV light is 1.8 mW/cm$^2$. It can be seen that the highest photocatalytic inactivation efficiency could be obtained when 2 wt% $Au/TiO_2$ nanocomposites were added. Within a 100-minute irradiation, 100% LoVo cancer cells were photokilled when 2 wt% $Au/TiO_2$ nanocomposites were used, but only 66% and 75% cells were killed in the cases using 1 wt% $Au/TiO_2$ and 4 wt% $Au/TiO_2$ nanocomposites, respectively. Moreover, it should be noted that the photocatalytic killing effect of 4 wt% $Au/TiO_2$ is lower than that of 2 wt% $Au/TiO_2$. It may be due to light shadowing by the deposits when too much noble metal nanoparticles covered the surface of $TiO_2$ particles [27]. Similar results were observed when a UV light with intensity of 4.0 mW/cm$^2$ was used, as shown in Figure 4. The 2 wt% $Au/TiO_2$ nanocomposites also presented the highest photocatalytic inactivation efficiency under the irradiation of UV light.

#### 3.2.3. Influence of the concentration of $TiO_2$ nanoparticles or $Au/TiO_2$ nanocomposites on the efficiency of photocatalytic inactivation LoVo cancer cells

Figure 5 presents the photocatalytic inactivation effect of various concentrations of $TiO_2$ nanoparticles or $Au/TiO_2$

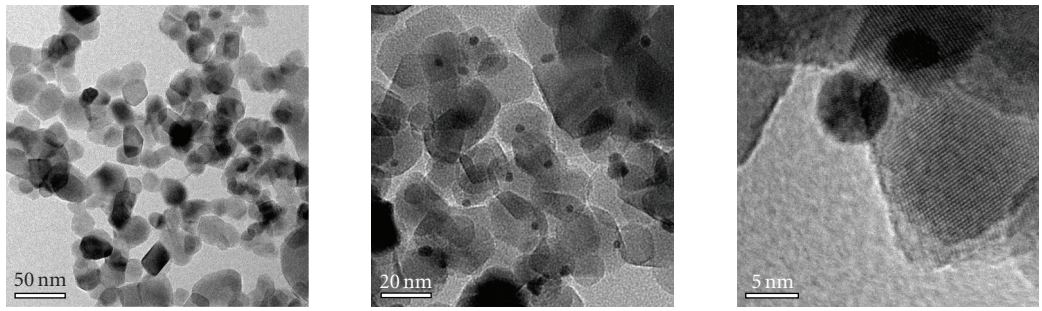



Figure 1: TEM images of $TiO_2$ nanoparticles (a), and 2 wt% $Au/TiO_2$ prepared by deposition-precipitation method with different magnification (b, c). The magnifications of (a), (b), and (c) are 150.000, 40.0000, and 150.0000, respectively.

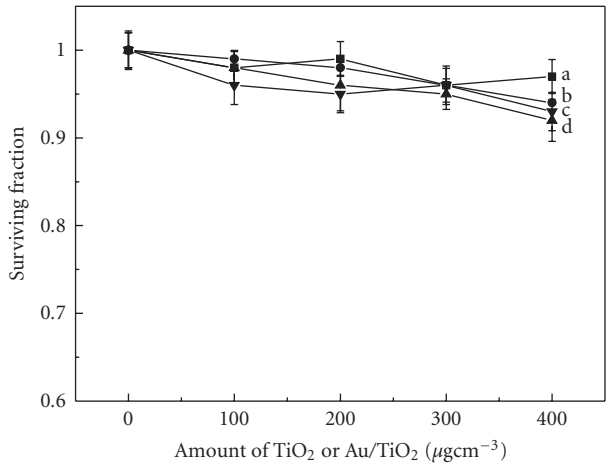



Figure 2: Surviving fraction of LoVo cells after being incubated in culture medium containing different amounts of (a) $TiO_2$, (b) 1 wt% $Au/TiO_2$, (c) 2 wt% $Au/TiO_2$, and (d) 4 wt% $Au/TiO_2$ in the dark for 24 hours. Bars represent the region of measured data and the points represent the mean value from three measurements.

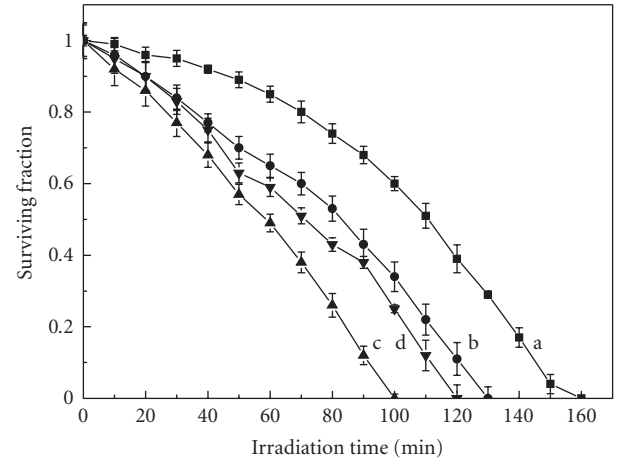



Figure 3: Surviving fraction of LoVo cells as a function of irradiation time after being incubated in culture medium containing 50 $\mu$g/mL $Au/TiO_2$ nanocomposites with different Au ratio: (a) 0 wt%, (b) 1 wt%, (c) 2 wt%, and (d) 4 wt%. The wavelength of UV light is 365 nm, and the intensity is 1.8 mW/cm$^2$. Bars represent the region of measured data and the points represent the mean value from three measurements.

nanocomposites on LoVo cancer cells. LoVo cells were cultured in the culture medium containing various concentrations of $TiO_2$ nanoparticles or $Au/TiO_2$ nanocomposites for 24 hours, and then exposed under the UV light irradiation for 60 minutes. As can be seen, the photocatalytic inactivation effect of $TiO_2$ nanoparticles or $Au/TiO_2$ nanocomposites on LoVo cancer cells enhanced with the increase of their concentration in the culture mediums. In addition, $Au/TiO_2$ nanocomposites presented much higher efficiency in photokilling LoVo cancer cells than $TiO_2$ nanoparticles. For example, in the presence of 100 $\mu$g/mL 2 wt% $Au/TiO_2$ nanocomposites, all the LoVo cancer cells could be photokilled within 60 minutes. But for $TiO_2$ nanoparticles, only 38% LoVo cancer cells could be killed under the same condition.

Although a higher concentration of $Au/TiO_2$ nanocomposites could achieve a higher-photocatalytic killing effect, but it is not preferable to use a very high concentration of photocatalyst for practical consideration because it might block the blood vessel [1]. Thus herein, the concentration of $TiO_2$ and $Au/TiO_2$ was recommended as $< 100\,\mu$g/mL, with which the cytotoxicity of $Au/TiO_2$ nanocomposites in the dark could be neglected (see Figure 2).

#### 3.2.4. *Photocatalytic inactivation effect of $Au/TiO_2$ nanocomposites on LoVo cancer cells*

Figure 6 presents the photocatalytic inactivation efficiency of $TiO_2$ nanoparticles or $Au/TiO_2$ nanocomposites on LoVo cells under the UV light irradiation. The wavelength of UV light is 365 nm and the intensity is 1.8 mW/cm$^2$. In the control experiment without adding $TiO_2$, about 18% LoVo cells were killed within a 100-minute irradiation (curve a). When 50 $\mu$g/mL $TiO_2$ nanoparticles were added, the LoVo cells were killed at a higher rate. After a 100-minute irradiation, 40% of the LoVo cells were killed as shown in curve b.

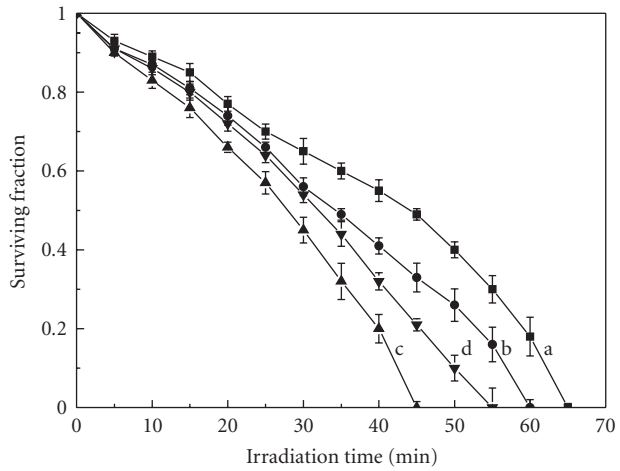



Figure 4: Surviving fraction of LoVo cells incubated in the medium containing 50 $\mu$g/mL Au/$TiO_2$ nanocomposites with different Au ratio: (a) 0 wt%, (b) 1 wt%, (c) 2 wt%, and (d) 4 wt%. The wavelength of UV light is 365 nm, and the intensity is 4.0 mW/cm$^2$. Bars represent the region of measured data and the points represent the mean value from three measurements.

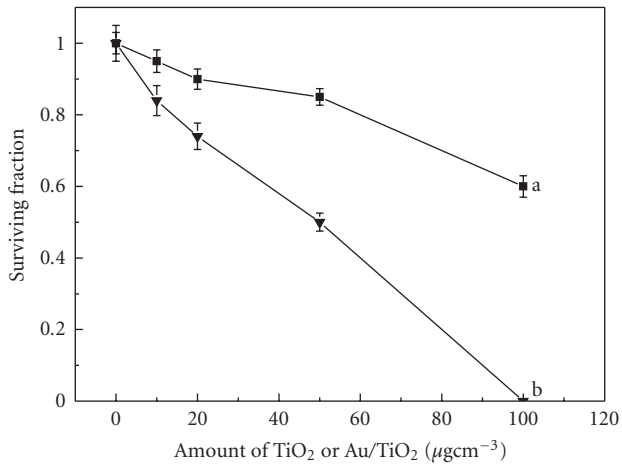



Figure 5: Surviving fraction of LoVo cells measured after the irradiation of UV light for 60 min as a function of concentration of (a) $TiO_2$ nanoparticles and (b) 2 wt% Au/$TiO_2$ nanocomposites. The wavelength of UV light is 365 nm, and the intensity is 1.8 mW/cm$^2$. Bars represent the region of measured data and the points represent the mean value from three measurements.

Once 50 $\mu$g/mL 2 wt% Au/$TiO_2$ nanocomposites were added, the photocatalytic inactivation effect increased dramatically as shown in curve c. After a 100-minute irradiation, all the LoVo cells were photokilled. These results reflected that the modification of gold on the surface of $TiO_2$ nanoparticles greatly enhanced the photocatalytic inactivation effect of $TiO_2$ on LoVo cells. The photocatalytic mechanism of Au/$TiO_2$ nanocomposite is shown in Scheme 1. When Au nanoparticles were modified on the surface of $TiO_2$, the photo-induced electrons can transfer to the surface of gold

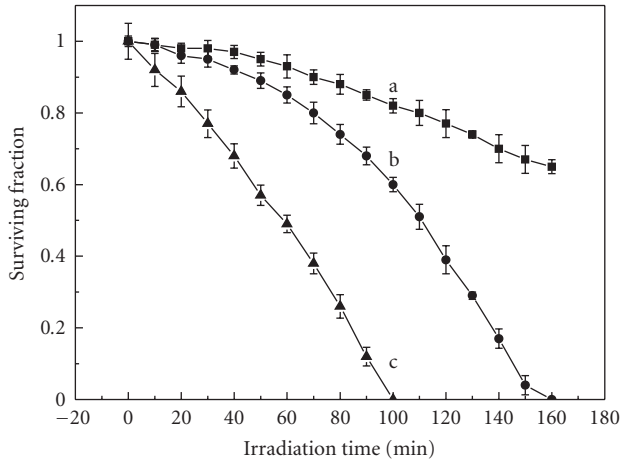
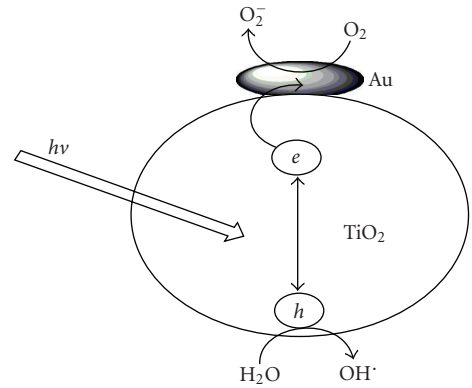



Figure 6: Surviving fraction of LoVo cells under the irradiation of UV light after being incubated in culture mediums: (a) with no $TiO_2$, (b) containing 50 $\mu$g/mL $TiO_2$, and (c) containing 50 $\mu$g/mL 2 wt% Au/$TiO_2$. The wavelength of UV light is 365 nm, and the intensity is 1.8 mW/cm$^2$. Bars represent the region of measured data and the points represent the mean value.




Scheme 1: Interfacial charge transfer process of gold-doped $TiO_2$ nanocomposites under the irradiation of UV light.

nanoparticles and reduce the dissolved $O_2$ easily. In the mean time, the photo-generated holes on the $TiO_2$ surface can react with water to produce powerful oxidative radicals $OH^{\cdot}$ and $HO_2^{\cdot}$. This process inhibited the recombination rate of the photo-produced electrons and holes, so the photocatalytic activity of $TiO_2$ nanoparticles was increased obviously by the modification of Au, as suggested in references [28, 29].

## 4. CONCLUSION

Au/$TiO_2$ nanocomposites were prepared using the deposition-precipitation method, and were firstly applied to photokill human colon LoVo cancer cells in vitro. The experimental results show that the deposition of gold on $TiO_2$ nanoparticles greatly increased the photocatalytic inactivation effect of $TiO_2$ on tumor cells, and the optimum content

of Au in the $Au/TiO_2$ nanocomposites was about 2 wt%. On the other hand, the photocatalytic inactivation effect on LoVo cancer cells increased monotonically as the concentration of the $TiO_2$ nanoparticles or $Au/TiO_2$ nanocomposites increased. The high photocatalytic inactivation effect of $Au/TiO_2$ nanocomposites on human colon LoVo cancer cells suggests that it may have a promising future for cancer treatment.

## ACKNOWLEDGMENT

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