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# Enhancement of photocatalytic disinfection of surface modified rutile $TiO_2$ nanocatalyst

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**Abstract**−We demonstrate a facile modification of rutile $TiO_2$ and its anti-bacterial activity under solar irradiation. The modification of rutile $TiO_2$ was done by microwave-assisted hydrothermal process with hydrogen peroxide ($H_2O_2$) as a solvent. The structural properties were analyzed by using XRD and Raman studies. The modified rutile $TiO_2$ shows no change either crystalline phase or crystalline size. The formation of Ti-OH was observed in Raman study. The TEM analysis shows modification on the surface of rutile $TiO_2$. The photocatalytic disinfection of *Escherichia coli* (*E. coli*) under solar irradiation shows double-times better performance by modified rutile $TiO_2$ compared to rutile $TiO_2$. The enhancement of anti-bacterial activity was attributed surface modification and Ti-OH.

Keywords: Rutile $TiO_2$, *E. coli*, Photocatalyst, Disinfection, Antibacterial

## INTRODUCTION

The harmful microorganisms present around human living areas are the causes for several health issues. The photocatalytic coating of nanoparticles with good disinfection properties has been desired to limit the activities of such harmful microorganism. Metal oxide like $TiO_2$, ZnO, Ag doped ZnO, Ag and CuO have been studied for their unique photo-killing process [1-4]. Among various metal oxide nanoparticles, except $TiO_2$, others are easily corroded and they generate hazards output which are undesirable for human and other useful organisms in the environment. $TiO_2$ has been highlighted for anti-bacterial activity due to its non-toxicity, environmental friendly and high abundance along with low cost of manufacturing. $TiO_2$ exists in three main polymorphism: anatase, brookite, and rutile. The anatase and brookite phases possess unstable property, and at high temperature and pressure they are transformed to rutile phase [5]. All the phase of $TiO_2$ was explored well for photocatalytic degradation of dye and waste materials [6-8]. The sol-gel synthesized $TiO_2$ either in pure form or doped with noble metal like gold and silver was studied for photocatalytic disinfection (PCD) [9-11]. Further, anatase phase or mixed phase $TiO_2$ in the form of thin films was often used for PCD purpose. On other hand, there are few reports on modification of commercially available $TiO_2$ powders to enhance the photocatalytic properties [12]. Recently, we also studied modification of Degussa P25 $TiO_2$ using ultrasonication and reported enhancement in photocatalytic degradation of methyl blue dye [13]. Similarly, a few other researchers also used ultrasonication to treat nano-sized rutile powder for enhancing its sonocatalytic properties [14] and low frequency modification of P25 to enable visible light absorption by creating oxygen vacancies [15].

The aim of the present study is to explore the photocatalytic disinfection properties commercially available rutile powder and method to improve its disinfection performance. The rutile powder was facially modified by microwave-assisted hydrothermal method. The crystalline and surface property was analyzed by using x-ray diffraction (XRD), Raman spectroscopy and transmission electron microscopy (TEM). Finally, the PCD performance was reported by studying the disinfection of *E. coli* under solar irradiation using both pure phase rutile $TiO_2$ and modified rutile $TiO_2$.

## EXPERIMENTAL METHODS

### 1. Modification of Rutile $TiO_2$ Powder

Pure phase Rutile $TiO_2$ nanopowder (99.5% pure, Sigma-Aldrich) with surface area of 50 $m^2/g$ and crystalline size around 50 nm as received was used as starting material. In typical synthesis method, 15 mg of rutile $TiO_2$ was dissolved in 15 ml of hydrogen peroxide (30%) to form a milky white solution. Then, the mixture was sealed in a Teflon-lined stainless steel autoclave. The microwave assistant hydrothermal treatment was done by maintaining temperature of autoclave at 125 °C for 1 hour using industrial grade microwave oven operated at 1.2 kW. After irradiation, the autoclave was cooled naturally to room temperature. The product was rinsed and centrifuged with deionized water for several times before the product was dried at 100 °C.

### 2. Characterization of $TiO_2$ Samples

The XRD patterns were measured by D/MAX 2500 diffractometer (Rigaku Co., Japan) using Cu K-alpha radiation with a scan rate of 1° per minute. Raman spectra were recorded using X-plora spectrometer (Horiba Jobin-Yvon, France) equipped with 532 nm solid-state laser as a source and a holographic grating of 2400 grooves/

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mm. A 50x objective with numerical aperture value 0.5 was used for collecting signal in back scattering mode. The Raman spectra were recoded using low laser power to avoid heating effect by laser irradiation. TEM images were recorded using JEM-2100 (Jeol, Japan) operated at 200 kV. The samples for TEM images were prepared by dispersing the powders in DI water using ultrasonication and drop casted onto carbon coated TEM grids. The TEM grids were dried under vacuum for 24 h prior to TEM analysis.

**3. Antibacterial Activity**

The photocatalytic antibacterial activity of rutile $TiO_2$ and modified rutile $TiO_2$ was tested through the disinfection of bacteria. *Escherichia coli* (*E. coli*) was purchased from Korean Culture Center of Microorganisms (KCCM 40271). *E. coli* was grown in a nutrient agar containing 10 g/L tryptone, 5 g/L yeast extract, 8 g/L NaCl, and 15 g/L micro agar in distilled water. *E. coli* cells incubated overnight in Lysogeny broth plate were condensed by centrifugation for 3 min at 13,000 rpm and were grown to an optical density of 0.8 at 600 nm at pH 7.0. A concentration of $10^5$ colony forming units per ml (CFU/ml) was used to evaluate of antibacterial performance. For antibacterial testing, 1 ml of *E. coli* solution was dispersed in 50 ml of distilled water to prohibit multiplying cells, and then the original and modified rutile powder $TiO_2$ (5 mg) was stirred with the dispersed solution. The disinfection of *E. coli* was tested for different reaction time from 0 min to 120 min under solar irradiation. The solution was collected after every 30 min. The withdrawn solution was spread onto a nutrient agar plate. After spreading, all Petri-dishes were cultured overnight at 30 °C and the number of colonies were counted with CFU/ml unit.

## RESULTS AND DISCUSSION

The initial white color of rutile $TiO_2$ changed to yellow after modification as shown in Fig. 1. The structural properties were studied by XRD. Fig. 2 shows the XRD pattern of rutile $TiO_2$ (R-$TiO_2$) and modified rutile $TiO_2$ (MR-$TiO_2$) powders. All the observed diffraction patterns in both rutile $TiO_2$ and modified rutile $TiO_2$ powders matched well with rutile phase of $TiO_2$ (JCPDS, NO. 76-1940) both

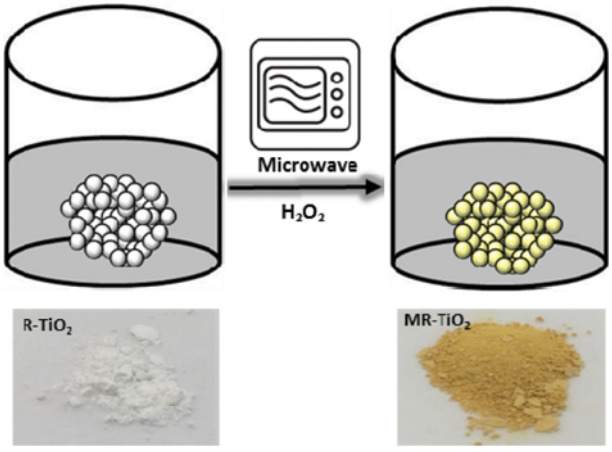


**Fig. 1. Schematic diagram illustrating the method of preparation and photography of rutile $TiO_2$ powder before and after modification.**

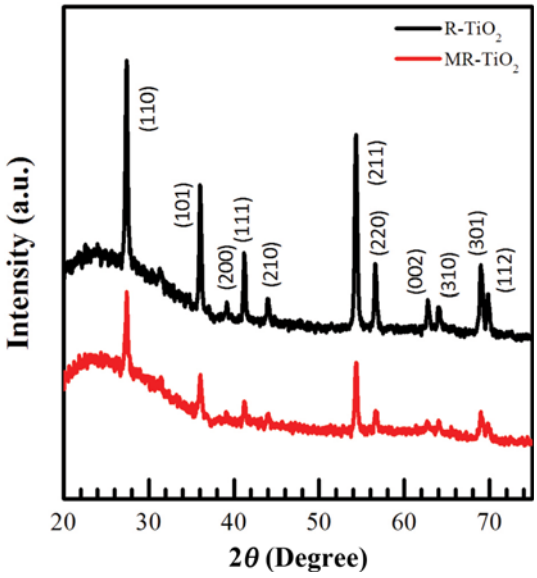


**Fig. 2. XRD pattern of rutile $TiO_2$ (R-$TiO_2$) and modified rutile $TiO_2$ (MR-$TiO_2$) powders.**

in position and in relative intensity. The pattern observed at 27.4°, 36.0°, 39.2°, 41.1°, 43.9°, 54.1°, 56.7°, 62.8°, 64°, 69.1° and 69.7°, corresponded to reflection from the (110), (101), (200), (111), (210), (211), (220), (002), (310), (301), and (112) planes of rutile $TiO_2$, respectively. After modification, there was no noticeable change in the peak position; this indicates there was no phase change due to modification. However, the modified rutile $TiO_2$ pattern shows reduced intensity due to formation of surface defects. To monitor change in the crystalline size before and after modification we used Scherrer's formula $D=(0.9\ \lambda)/(\beta \cos\theta)$, where D is the crystalline size, $\lambda$ is the wavelength of Cu $K_\alpha$ x-ray source (1.54 Å) and $\beta$ is the full width half maximum of the diffraction pattern. The average crystalline size of the original and modified rutile $TiO_2$ was cal-

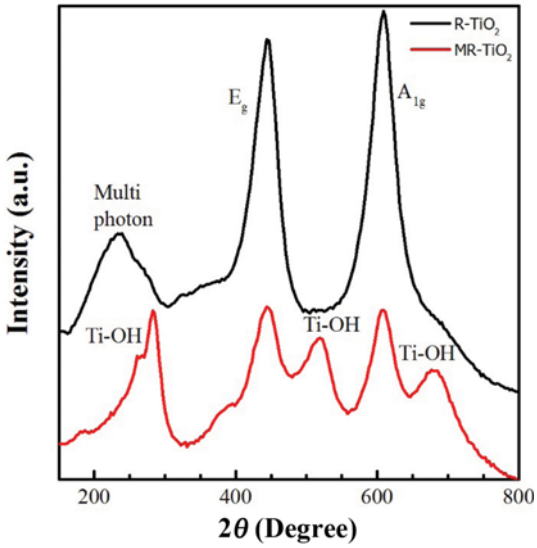


**Fig. 3. Raman spectra of rutile $TiO_2$ (R-$TiO_2$) and modified rutile $TiO_2$ (MR-$TiO_2$) powders.**

culated to be 47 and 45 nm, respectively. Thus, the XRD results of rutile $TiO_2$ and modified rutile $TiO_2$ confirm no changes in crystalline phase as well as in crystalline size after modification.

Fig. 3 shows micro Raman spectra of rutile $TiO_2$ and modified rutile $TiO_2$ powders in the region of 100-800 $cm^{-1}$ recorded with 532 nm laser source. The Raman spectra of both rutile $TiO_2$ and modified rutile $TiO_2$ powders show the dominant modes at 140, 442 and 610 $cm^{-1}$, which correspond to classical $B_{1g}$, $E_g$ and $A_{1g}$ Raman active modes of rutile phase $TiO_2$, respectively [16,17]. The broad mode at 238 $cm^{-1}$ in rutile $TiO_2$ powder arises due to multi-photon process [18,19]. Apart from the classical modes, the modified rutile $TiO_2$ powder shows extra modes, which are not related to other crystalline phases of $TiO_2$. The modes at 266, 284, 518, and 680 $cm^{-1}$ were identified to be surface hydroxyl related modes [20]. However, the Raman mode at 284 $cm^{-1}$ showed peak broadening due to oxygen deficiency. Similar hydroxyl modes were reported for other metal oxides such as $SnO_2$ and ZnO [21-23] with an inner crystalline core surrounded by an outer hydroxyl shell due to surface modification. Therefore, in the present scenario we also propose a similar kind of Ti-OH formation around the crystalline $TiO_2$ particles due to microwave irradiation in the presence of $H_2O_2$. Thus, the Raman spectra also confirm that there is no phase change and formation of surface hydroxyl group on the surface of rutile particles.

The TEM images were analyzed to study the surface property of rutile $TiO_2$ samples before and after microwave treatment. Fig. 4 shows the TEM and high-resolution TEM (HR-TEM) images of rutile $TiO_2$ sample. The inset TEM image shows the agglomeration of tetragonal shaped nanoparticles with size around 50 nm. The interplaner distance in HR-TEM image was calculated to be around 0.318 nm, which corresponds to the (110) plane of tetragonal rutile crystalline $TiO_2$ [24]. Fig. 5 shows the TEM and HRTEM images of modified rutile $TiO_2$ sample. The TEM image of modified rutile $TiO_2$ also appears tetragonal with a size under 50 nm The HRTEM image shows clear lattice fringes with an interplaner distance of 0.322 nm, which also corresponds to (110) plane of rutile

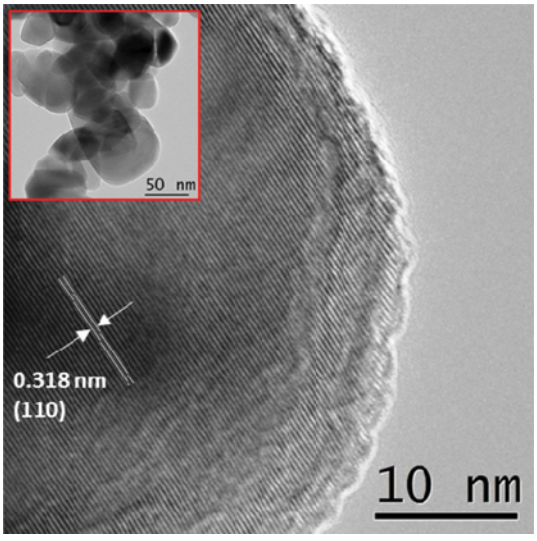


**Fig. 4. HR-TEM and TEM images of rutile $TiO_2$ sample.**

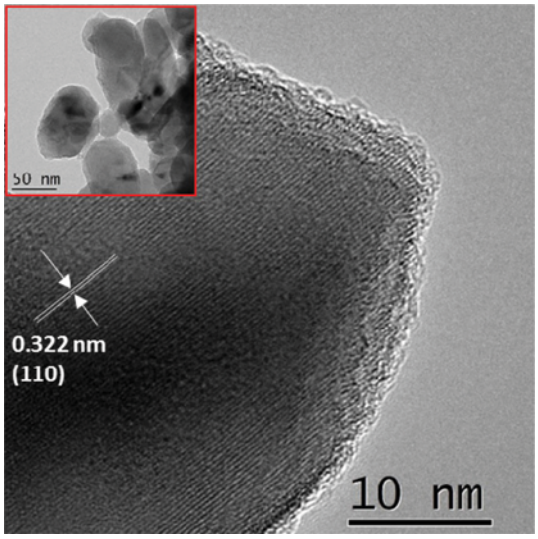


**Fig. 5. HR-TEM and TEM images of modified rutile $TiO_2$ sample.**

$TiO_2$. The close observation of HRTEM image of modified rutile $TiO_2$ sample clearly shows the presence of disordered on the surface.

Finally, the antibacterial activity of the rutile $TiO_2$ and modified rutile $TiO_2$ powders was investigated by measuring the disinfection of *E. coli* at the interval of 30 min. Fig. 6 displays *E. coli* bacterial colony growth at 0 and after 120 min exposure to solar irradiation. The photocatalytic disinfection efficiency was estimated by counting the *E. coli* bacterial cell using CFU unit with individual agar plates. Fig. 6(a) and 6(c) show image of *E. coli* bacterial colony for rutile $TiO_2$ and modified rutile $TiO_2$ at 0 min (initial stage). Fig. 6(b) and 6(d) display photocatalytic bacterial disinfection results after treating *E. coli* with catalyst for 120 min under solar irradia-

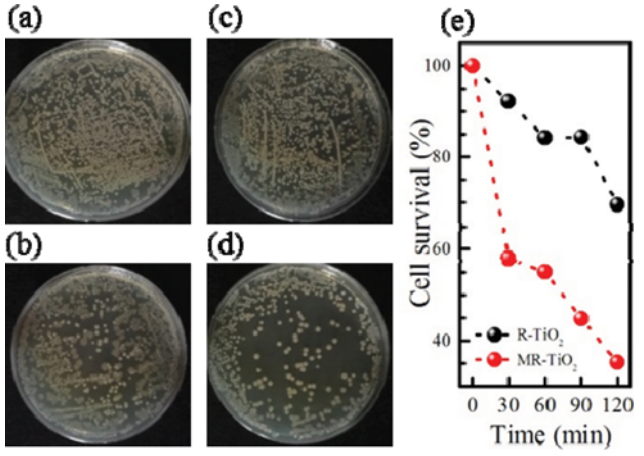


**Fig. 6. Photocatalytic disinfection activity of rutile (R-$TiO_2$) and modified rutile $TiO_2$ (MR-$TiO_2$) powders under solar irradiation. (a) and (b) images of *E. coli* colonies on an agar plate before and after 120 min photocatalytic treatment with original rutile $TiO_2$, respectively, (c) and (d) images of *E. coli* colonies on an agar plate before and after 120 min photocatalytic treatment with modified rutile $TiO_2$ respectively, and (e) Inactivation of *E. coli* by original and modified rutile $TiO_2$ for various photocatalytic treatment time.**

tion. Fig. 6(e) indicates the survival rate for rutile $TiO_2$ and modified rutile $TiO_2$ samples as a function of irradiation time. The results indicate that 30% of *E. coli* was disinfected with rutile $TiO_2$ and 64% with modified rutile $TiO_2$ for 120 min solar irradiation with catalyst. It shows that the modified rutile $TiO_2$ shows double times better performance as compared to original rutile $TiO_2$ under solar irradiation. The enhancement in disinfection property can be correlated to the bacterial adhesion to hydroxyl group present on the surface of modified rutile $TiO_2$ [25], and the bacteria attached to $TiO_2$ will be destroyed by oxidative destruction of cell walls caused by hydroxyl group [11,26].

## CONCLUSION

We have successfully synthesized modified rutile $TiO_2$ via microwave-assisted hydrothermal method in presence of hydrogen peroxide solvent. The modified rutile $TiO_2$ exhibits high photocatalytic bacterial disinfection under solar irradiation due to surface disorder and Ti-OH groups present at the surface. The presence of hydroxyl group was supported by Raman spectra of modified rutile $TiO_2$ sample. Further, XRD and Raman studies showed no phase change after modification. Thus, this study provides a simple method of modification using microwave to enhance the photocatalytic disinfection of rutile $TiO_2$ by two fold.

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