

Synthesis and characterization of TiO₂/BaF₂/ceramic radio-sensitive photocatalyst

C.F. Wang^a, C.T. Yu^{a,b,*}, B.H. Lin^a, J.H. Lee^{a,c}

^a Department of Atomic Science, National Tsing Hua University, Hsinchu 300, Taiwan

^b Chemical Analysis Division, Institute of Nuclear Energy Research, P.O. Box 3-19, Longtan 325, Taiwan

^c National Radiation Standard Laboratory, Institute of Nuclear Energy Research, P.O. Box 3-10, Longtan 325, Taiwan

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Abstract

Nanophase TiO₂/BaF₂ immobilized on micron size ceramic powder was prepared using the TiCl₄ hydrolysis and EDTA chelating agent method. The photo-catalytic degradation effects for MB dye using UV and γ -radiations were investigated. The prepared nanocomposites were characterized using Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis. It is shown that MB can be effectively photodecomposed using prepared composites under UV or γ -radiation. Experimental results indicated that the existence of BaF₂ enhances the photoactivity of TiO₂ and becomes a light source around TiO₂ by converting the γ -radiation. A relevant photo-catalytic mechanism induced using ionization radiation is proposed.

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1. Introduction

TiO₂-based nanocomposites are of considerable interest in environmental protection technology for applications as photo-catalytical materials. In addition to their higher thermal stability in the atmosphere, non-toxic nature, low price, easy fabrication and good physical–chemical behavior, TiO₂ is also a material that possess a direct band-gap (3.2 eV at room temperature), a large band strength with large excitation binding energy ($E_b = 60$ meV) and a high melting temperature of 2248 K [1–3].

The TiO₂ based photocatalyst has been proven effective in UV–vis radiation. Many researchers reported that titania particles loaded with Pt, Ag, Fe, ZnO and CdS show improved photoactivity in the visible range [4–6]. Some multicomponent or mixed oxides such as SrTiO₃, BaTiO₃, titania/zirconia, K₂La₂TiO₃ and silica–titania also have good photoactivity [7–12]. However, weak penetration ability and low light source intensity that has limited their applications in many industrial or environmental fields.

For light amplification purposes, materials doped with transition metals or rare earth element in the form of fluorite crystals have been developed [13]. Among these, BaF₂ has been considered as an intrinsic scintillation material with transparency in the visible and near IR spectra regions, fast decay time (sub-nanosecond), high density and non-hygroscopic properties. Most of all, it has an excellent emission yield with photo-peaks at 220 and 310 nm after excited by higher radiation. It is expected that TiO₂ based photo-catalytic reactions can be significantly triggered using the γ -radiation because of the co-existence of scintillation crystals in the composite.

Not many references discussed using γ -radiation to induce the TiO₂ photo-catalytic reaction. Seino et al. discussed phenol photo-degradation effects for TiO₂ and Al₂O₃ nanoparticle excited using γ -radiation [14]. DOE explored the feasibility if ionization radiation used to catalytically destroy EDTA organics in the high level radwaste over semiconducting metal oxide particles [15]. Both need a very high radiation dose to facilitate the experiment.

The major benefit of using γ -radiation as a light source is attributed to its deep penetrating ability into most materials. The existence of BaF₂ enhances the photoactivity of TiO₂ and becomes a light source around TiO₂ by converting the γ -

* Corresponding author. Tel.: +886 3 471 1400; fax: +886 3 471 1410.
E-mail address: ctyu@iner.gov.tw (C.T. Yu).

radiation. As a result, nanophase BaF₂/TiO₂ composites can be prepared on porous substrates, and applied in various industrial and environmental applications as a real three-dimensional technology.

Several preparation methods, like sol–gel [16–18], impregnation [19,20] and molecular capping [21,22], have been proposed for TiO₂ nanoparticles dispersion in silica [16–20] or polymeric [21,22] matrices to avoid the nanoparticle aggregation tendency. The TiCl₄ hydrolysis method is also a versatile and easy method that allows a homogeneous TiO₂ nanophase deposition onto different supporting materials. TiO₂ based nanocomposites preparations have been widely investigated [23–27]. However, the co-precipitation of BaF₂ with TiO₂ may significantly influence the photo-catalytic properties of TiO₂.

This work explores preparing a nanophase TiO₂/BaF₂ composite while keeping the TiO₂ phase as anatase by co-precipitating both of them onto commercial mesoporous materials, such as ceramic powder. The structural and crystal evolution of these samples after thermal treatment and elemental concentrations deposited onto the ceramic powder are studied using BET, XRD and ICP-AES, respectively. The effect of the TiO₂ and BaF₂ content on the photoactivity for MB decomposition is also investigated with both UV and γ -radiation. A relevant photo-catalytic mechanism induced by ionization radiation is proposed to illuminate this novel phenomenon.

2. Materials and methods

To overcome the immobilization and dispersion problem of nano-photocatalysts in these experiments, a state-of-the-art composite was synthesized first. BaF₂ and TiO₂ nanoparticles are immobilized onto ceramic powder synthesized using the TiCl₄ hydrolysis and EDTA chelating method. BET is used to analyze the porous characteristic surface area of the produced composite. XRD is used to examine the crystalline of TiO₂ and BaF₂ on ceramic. The Ba and Ti concentrations determination on each sample are performed using an acid mixture digestion and ICP-AES method. The photo-catalytic degradation effects of MB using UV and ⁶⁰Co irradiation are studied to examine the feasibility of the addressed radio-catalytic mechanism.

2.1. Synthesis

Two kinds of samples were prepared in the experiment to compare the role of nanophase TiO₂ and BaF₂ on the photo-catalytic process. Type A samples contain only nano-TiO₂ on the ceramic powders. The type B samples contain both TiO₂ and BaF₂. Table 2 lists the amount of reactants added and the ICP results for each sample.

During synthesis, an EDTA chelating agent was chosen to functionally link the Ba compounds with the ceramic substrate using electrostatic attraction. The composite samples were prepared using the following method: the chelating solution was first made by dissolving an appropriate amount of EDTA and ammonia in pH 10 borate buffer. The mixture was stirred magnetically for 30 min and then both Ba(NO₃)₂ and NaF solutions were separately poured in slowly to obtain a suspended

nanoparticle BaF₂ solution. The solution was then mixed with 5 g ceramic powder and stirred for 2 h to deposit BaF₂ onto the substrate.

Referring to Yu et al. [28,29], the deposition of TiO₂ was performed by dissolving 1 g citric acid in 20 ml 0.5 M HCl and stirring to produce clear solution. Ceramic powder substrate was mixed with solution stirred in ice water and then dropped TiCl₄ into the solution slowly for 2 h. The suspended solution was shaken sonically for 30 min and dried using hot plate. The residue was calcinated in 450 °C to obtain the composite sample.

A sample that contains only BaF₂ on the ceramic was prepared by 5.1 g Ba(NO₃)₂, 1.8 g NaF and 5 g ceramic. The BaF₂/ceramic was used to evaluate the photo-catalytic activity for MB degradation under the gamma radiation.

All solutions were adjusted to pH 10 using a borate buffer solution during the experiment. TiCl₄, Ba(NO₃)₂, NaF, MB, EDTA and all other chemicals were of AnalaR grade and commercially available.

2.2. Photocatalyst characterization

The porous specific surface area and composite adsorbed volume were determined using a Quantachrome NOVA 2000 BET facility.

The overall crystalline of sample were examined by XRD measurements performed on an American Scintag XDS-2000 Diffractometer using Cu K α radiation ($\lambda = 0.1541$ nm) at 30 kV and 30 mA. The XRD data for index and cell parameter calculations were collected using a scanning mode with a step of 0.02° in 2θ range from 10° to 70° and scanning rate of 4° min⁻¹.

To determine the Ba and Ti content deposited on ceramic substrates, the sample was digested in a high-pressure bomb system (Berghof, Germany). A 10 mg sample was digested with 8 ml acid mixture of HNO₃ + HClO₄ + HF (5:3:2, v/v/v) in a 25 ml polytetrafluoroethylene (PTFE) vessel. After digestion, the sample solution was transferred into a PTFE beaker and heated gently (<90 °C) on a hot plate to allow the residual acid to evaporate. The residue was then diluted to 50 ml for ICP-AES analysis. A PE-Optima 3000DV ICP-AES instrument was employed for both Ti and Ba determination.

2.3. Photo-catalytic experiment

The prepared composite exhibits both photo- and radio-catalytic behavior. Two kinds of light sources were used to examine the photo-degradation experiment of MB dye. The photo-catalytic experiment was performed by 70 ml slurry solution made of 10 ppm MB and approximately 0.2 g composite. A 125 W medium pressure Hg lamp (UVP Co.) with 50 mW/cm² UV intensity was employed. The irradiations distance between the UV source and the center of the reaction bottle was 20 cm.

A 1400 Ci ⁶⁰Co irradiation facility (Canada AECL Co.) was used to irradiate the slurry from the topside of the bottle. The air kerma rate for the ⁶⁰Co irradiation field was measured using a standard ionization chamber constructed at the Institute of Nuclear Energy Research [30]. The distance between the

Table 1
BET results for ceramic and photocatalyst

Product	Pure ceramic (<i>n</i> = 5)	Composite A (<i>n</i> = 5)	Composite B (<i>n</i> = 6)
Specific surface area (m ² /g)	4.10 ± 0.21	4.05 ± 0.18	3.81 ± 0.20
Specific adsorbed volume (cm ³ /g)	1.21 ± 0.05	1.13 ± 0.05	0.92 ± 0.04

irradiated slurry and topside ⁶⁰Co was 100 cm. The maximum air kerma used for excitation is about 25 Gy.

The photo-catalytic degradation MB effect was investigated using a Shimadzu pharmaSpec UV-1601 spectrometer.

3. Results and discussion

3.1. Characterization of prepared composite samples

The mesoporous ceramic powder was chosen as a host for solving the immobilization problem of nanophase TiO₂ and BaF₂, and providing a site for the photo-catalytic reaction. A particle size of 3–5 μm composite was prepared to facilitate the material recovery during the consecutive use.

It is doubtful that the synthesis may alter the surface area and/or pore size of the prepared composites. Table 1 lists the results of BET and adsorbed specific volume for pure ceramic, composite A and composite B, respectively. It is shown that TiO₂ and BaF₂ on ceramic would not significantly change the surface area characteristics and adsorbed volume for the prepared composite.

It is important to examine the structure of TiO₂ nanoparticles by using XRD, in order to confirm the formation of pure anatase TiO₂ phase separated from BaF₂. However, it is difficult to simultaneously show the structure of TiO₂ and BaF₂ on the ceramic. The difficult is mainly due to the complex peak of ceramic on XRD spectrum. These mixed metal oxides of ceramic were belonging to a kind of gahnite (JCPDS 05-0669), which inherently interfere with the TiO₂ and BaF₂ signals.

Nevertheless, the crystalline of pure anatase TiO₂ phase (JCPDS 21-1272) and frankdicksonite BaF₂ (JCPDS 04-0452) phase can be shown on simple graphite substrate (JCPDS 41-1487). It is worthy to emphasize that the same preparation procedure can be applied to various substrates such as ceramic and graphite; it is possible to confirm the co-formation of pure anatase TiO₂ phase separated from BaF₂ on the ceramic.

Because the TiO₂ and BaF₂ formation was inhomogeneous during the synthetic procedure, and the Ti and Ba content within the original ceramic powder was significant. To quantify the Ti and Ba concentrations prepared on the ceramic powder, an acid mixture digestion method with ICP-AES measurement was performed during the experiment. Literature revealed that only superficial nano-anatased TiO₂ has the capability for photo-degrading organic substance [31]. It is thus important to determine the actual Ti and Ba compound concentrations immobilized onto the substrate surface to evaluate the photo-catalytic efficiency of the prepared composite samples.

Table 2
Amount of reactant added and ICP results (*n* = 5)

Product	Amount of reactant added			ICP results (mg/g)	
	TiCl ₄ (g)	Ba(NO ₃) ₂ (g)	NaF (g)	Ti	Ba
A1	0.4	–	–	15.3 ± 1.0	–
A2	0.8	–	–	26.4 ± 2.1	–
A3	1.2	–	–	35.4 ± 2.6	–
A4	1.6	–	–	41.2 ± 2.5	–
A5	2.0	–	–	46.4 ± 2.1	–
B1	0.4	1.0	0.7	15.3 ± 1.5	43.2 ± 2.6
B2	0.4	3.1	1.1	16.2 ± 1.6	105 ± 5
B3	0.4	5.1	1.8	18.1 ± 1.4	156 ± 5
B4	2.0	1.0	0.7	45.2 ± 2.5	38.1 ± 2.1
B5	2.0	3.1	1.1	44.5 ± 2.6	102 ± 4
B6	2.0	5.1	1.8	41.1 ± 2.3	140 ± 5

Table 2 shows the reactant ratio and the Ti/Ba elemental concentrations from ICP analyzed result of prepared photocatalyst. The Ti and Ba content of the pure ceramic substrates were 8.50 ± 0.24 and 0.50 ± 0.01 mg/g, respectively (*n* = 5), which should be corrected from the ICP data of samples.

An experiment to investigate the immobilized stability of TiO₂ and BaF₂ on the ceramic powder was performed by observing the variation in MB degradation ability after at least four-repeated 60 min UV irradiations and catalyst recovery. *A_t* and *A₀*, the measured MB solution absorbance activity after and before the irradiation, respectively. It was found that the MB photo-degradation ratio (*A_t/A₀*) catalyzed by A4 and B6 composite were still maintained at 0.20 ± 0.01 and 0.51 ± 0.03, respectively (*n* = 4). The ICP result of Ba content at prepared BaF₂/ceramic was 138 ± 5 mg/g (*n* = 3).

3.2. Photo-catalytic decomposition of MB

The photo-degradation effects of prepared composite samples induced by various radiation sources, including UV and γ, were studied by choosing the MB as target component. We expected that factors such as pH, concentration and pile-up effect, etc., might affect the decomposition efficiency of the organic substance.

An important issue of most concern in the photo-catalytic mineralization of organic substrates is whether the initial oxidation of the organic substrates occurs on the photo-catalyst surface or in solution. It is believed that the pH effect on the photo-catalytic degradation rate of MB may provide the information we need. Our result showed that the MB absorbance decreased with increasing pH, exhibiting a minimum of around pH 9–10. The observed trend is more or less like the result of Lakshmi et al. The pH effect on the photo-catalytic degradation of MB⁺ can be rationalized on the basis of the positive charge cations are more readily accommodated at the negative sites on TiO₂ [32].

Fig. 1 presents the decomposition rates of 10 ppm MB solution with 0.2 g composite A4 and B6 under the UV irradiation, respectively. Both A4 and B6 contain the similar concentrations

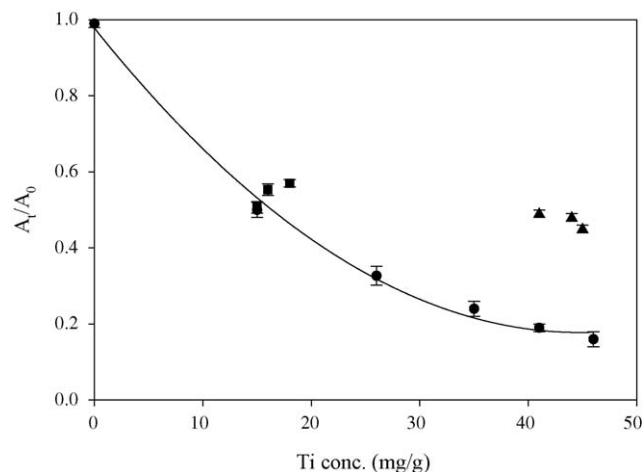


Fig. 1. Dependence of photo-catalytic degradation rate on the 0.2 g composite A and composite B. UV irradiated time: 60 min, MB conc.: 10 ppm. (●) A1–A5, (■) B1–B3 and (▲) B4–B6.

of Ti. A_t and A_0 , the measured MB solution absorbance activity after and before the irradiation, respectively, the A_0 was corrected to avoid ceramic substrate absorption interference. As the curves show in the figure, the MB concentration decreases rapidly at first and then levels off gradually after a period of irradiation time. It was inferred that a heterogeneous photo-catalytic reaction occurs on/or near the surface of TiO_2 and is strongly dependent on the concentration of MB in the solution. Composite B6 revealed a worsen decomposition efficiency than A4, which may be attributed to the effect of BaF_2 pile-up on the surface of TiO_2 .

Fig. 2 also exhibits a similar pile-up phenomenon when the Ti concentration increases. This indicates that increasing the amounts of TiO_2 in the sample results in a decrease in the decomposition efficiency. The observed increase in the rate of MB^+ photo-catalytic decomposition with an increase in pH, also seems to support the process surface location. Owing to the weak penetrating ability of UV light, only the outer core of TiO_2 layer on the ceramic powder can be excited and used as the MB

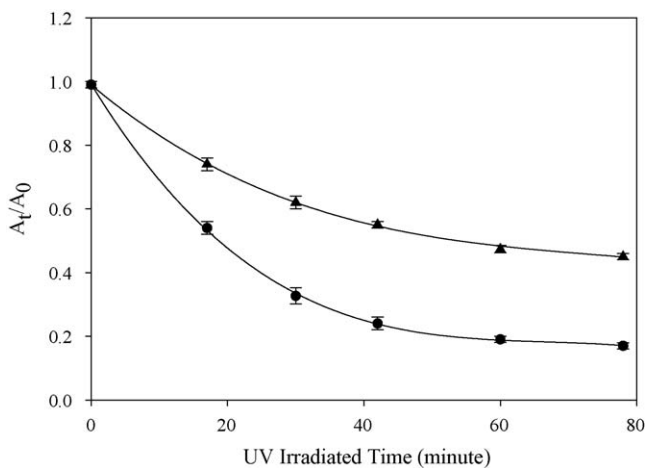


Fig. 2. Dependence of UV irradiating time on photo-degradation effects of MB. Composite weight: 0.2 g A4, 0.2 g B6, MB conc.: 10 ppm. (●) A4 and (▲) B6.

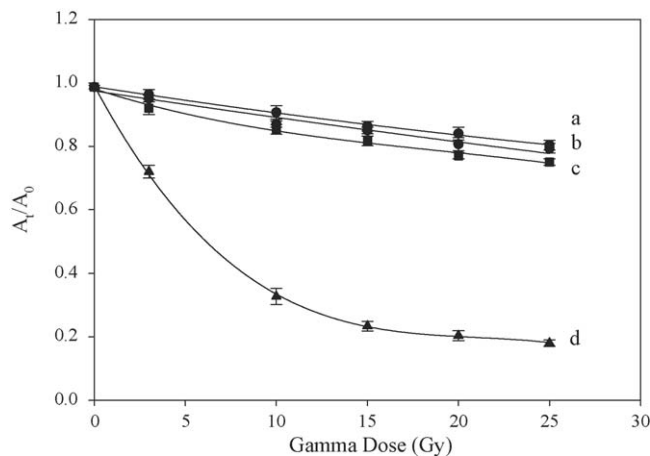


Fig. 3. Dependence of γ dose (Gy) on photo-degradation effects of 10 ppm MB. (a) Blank without composite added (radiolysis), (b) 0.2 g BaF_2 /ceramic, (c) 0.2 g A4 and (d) 0.2 g B6.

photo-catalytic degradation site. Nevertheless, we have proven that the prepared composite samples possess a reasonable photo-catalytic ability with the nanosized TiO_2 on the ceramic powder.

The sole existence of BaF_2 has no effect on the MB decomposition under UV irradiation. However, BaF_2 plays an important role in converting high-energy radiation into the UV light that the catalyst requires. Fig. 3 displays the decomposition of 10 ppm MB solution with 0.2 g composite A4, 0.2 g B6, 0.2 g

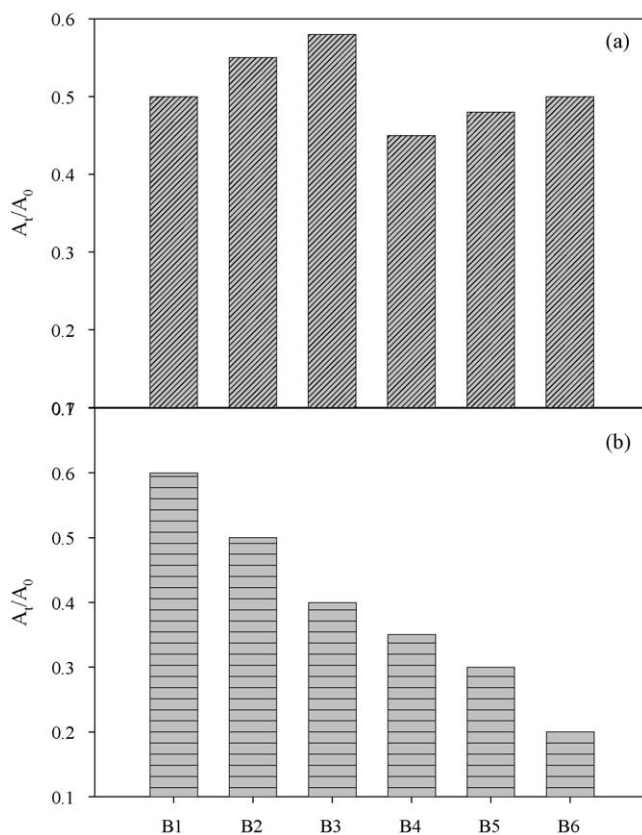


Fig. 4. Photo-decomposition effect of MB irradiated by various sources. Composite weight: 0.2 g B1–B6, MB concentration: 10 ppm. (a) UV source irradiating 60 min and (b) 25 Gy ^{60}Co irradiation dose.

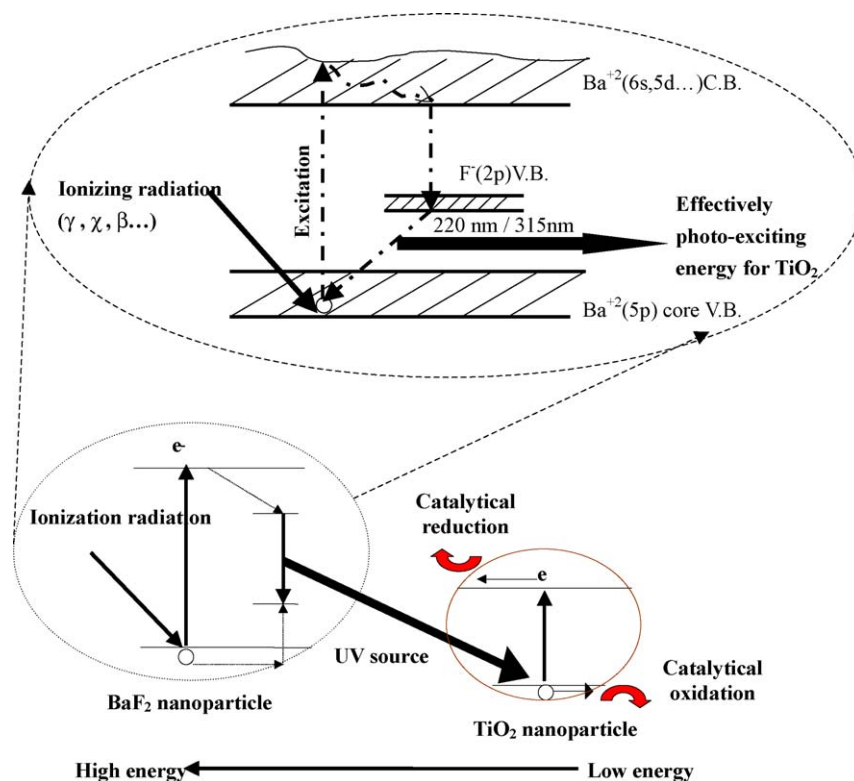


Fig. 5. Diagram of proposed photo-catalytic reaction induced by ionizing radiation. (Upper figure presents more detail diagram of radiation induced photocatalytic inorganic scintillator BaF_2 .)

BaF_2 /ceramic and a blank (radiolysis) under the ^{60}Co irradiation, respectively. As shown in the figure, both MB on the blank and A4 samples decompose slightly and linearly with increasing radiation dose. The sample that contains only BaF_2 on the ceramic has the similar MB photo-catalytic activity variation as radiolysis and A4. It was excluded the possibility of MB dye might be decomposed by the direct absorption of UV light at 220 or 310 nm emitted from BaF_2 under the gamma radiation.

On the other hand, a significant MB decomposition phenomenon was observed for B6 samples that cannot be simply explained by the radiolysis. It is believed that, in the dark condition, BaF_2 crystal can absorb the γ -radiation and emit lower energy UV photons to excite the TiO_2 in the surrounding area.

Fig. 4 further reveals the combined effect of photo-catalyst (TiO_2) and scintillator (BaF_2) by comparing the irradiated results of different composite samples. As listed in Table 2, six B type samples can be classified into two groups. For example, the first group including B1, B2 and B3 samples have similar TiO_2 content but varied significantly in the BaF_2 content for each sample. The second group including B4, B5 and B6 have also similar BaF_2 content distributions with group one but a much higher TiO_2 content. It was observed that samples with higher TiO_2 content exhibited a better decomposition efficiency with both UV and γ -irradiation. On the other hand, higher BaF_2 content may deteriorate the decomposition efficiency of UV light but enhances that of γ -radiation.

As a result, the photo-catalytic behavior of A type composite is generally superior to that of the B type composite if a UV

source is applied. Opposite results will be obtained if ionization radiation is used as the source. Therefore, Fig. 5 proposes a multi-step photo-catalytic reaction mechanism. As described in the figure, γ -radiation is absorbed by the BaF_2 crystal. The excited Ba core valence band electrons may jump into the conducting band area, travel around the crystal and gradually lose its energy. These electrons are finally relaxed and captured by fluorine ions. After that transition, a 220 or 315 nm UV light will be emitted and absorbed by the surrounding TiO_2 for further MB photo-oxidation. A photo-catalytic γ -induced organic substance degradation can be triggered using the prepared composite even without a UV source.

4. Conclusions

$\text{TiO}_2/\text{BaF}_2$ nanoparticles immobilized onto ceramic powder were successfully prepared using the proposed TiCl_4 and EDTA chelating method. The specific surface area and Ba, Ti concentration were characterized using BET and ICP-AES, respectively. The photo-catalytic mechanism induced by TiO_2 or BaF_2 was proven using an MB degradation experiment. The results showed that with the strong penetrating ability of γ -radiation, $\text{TiO}_2/\text{BaF}_2$ based photocatalyst can function well in great depth or darkness. As a result, the technology is no longer considered two-dimensional surface technology only. Further studies will prove that the proposed method is a promising candidate for number of environmental applications.

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