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# Photocatalytic degradation of Rhodamine B and Ibuprofen with upconversion luminescence in Ag-BaMoO<sub>4</sub>: Er<sup>3+</sup>/Yb<sup>3+</sup>/K<sup>+</sup> microcrystals



Schindra Kumar Ray<sup>a</sup>, Yuwaraj K. Kshetri<sup>b</sup>, Dipesh Dhakal<sup>c</sup>, Chhabilal Regmi<sup>a</sup>, Soo Wohn Lee<sup>a,\*</sup>

<sup>a</sup> Department of Environmental and Bio-Chemical Engineering, Sun Moon University, Chungnam, 31460, Republic of Korea

<sup>b</sup> Department of Advanced Materials Engineering, Sun Moon University, Chungnam, 31460, Republic of Korea

<sup>c</sup> Department of Life Science and Bio-Chemical Engineering, Sun Moon University, Chungnam 31460, Republic of Korea

#### ARTICLE INFO

Article history: Received 7 November 2016 Received in revised form 11 February 2017 Accepted 16 February 2017 Available online 22 February 2017

Keywords: Microwave hydrothermal Upconversion luminescence Photons Rhodamine B Ibuprofen

#### ABSTRACTS

Silver dispersed BaMoO<sub>4</sub> octahedron microcrystals doped with  $Er^{3+}$ ,  $Yb^{3+}$ , and  $K^+$  were synthesized by microwave hydrothermal process. The photocatalytic activity of different samples toward the degradation of Rhodamine B (Rh B) dye and Ibuprofen (IBP) drug were carried in solar light and visible light irradiation, respectively. The sample, Ag-BaMoO<sub>4</sub>: Er<sup>3+</sup>/Yb<sup>3+</sup>, degraded the Rh B within 90 min about 99.60%, which is nearly 30 times as compared to the host material BaMoO<sub>4</sub> Similarly, Ag-BaMoO<sub>4</sub>: Er<sup>3+</sup>/Yb<sup>3+</sup>, degraded the IBP within 90 min about 41.49%, which is nearly 31 times as compared to the host in visible light. IBP photodegradation intermediates were identified by highresolution quadrupole-time of flight-electrospray ionization-mass spectrometry (HR-QTOF ESI/MS) in negative ion mode and detailed degradation pathway mechanism was proposed. Under 980 nm excitation, two strong green emission peaks (526 nm and 555 nm) and a less intense red emission peak (661 nm) were observed, which are assigned to the  ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ ,  ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ , and  ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transitions of the Er<sup>3+</sup> ions, respectively. Two photons upconversion process for green emission was observed. The upconversion luminescence intensity was increased by two-fold in magnitude by the addition of  $K^+$  ion in  $Er^{3+}/Yb^{3+}$  doped BaMoO<sub>4</sub>. Moreover, silver particles were found to favor the photocatalytic activity while K<sup>+</sup> ions significantly enhanced upconversion. The photocatalytic as well as upconversion mechanism was explained. The combination of efficient photocatalytic activity and upconversion emission of the Ag-BaMoO<sub>4</sub>:  $Er^{3+}/Yb^{3+}/K^+$  make the material suitable for the multifunctional application.

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# 1. Introduction

Textile and dyeing industries have a major contribution of nearly 17–20% to water pollution [1,2]. The majority of dyes applied in different industries are toxic and carcinogenic that causes a serious hazard to humans as well as to freshwater and marine ecosystem [3,4]. Various pharmaceutical wastes are also serious factors of water pollution. For example, the Non-Steroidal Anti-Inflammatory Drugs (NSAIDs), Ibuprofen is extensively used to treat various health problems such as headaches, muscular aches, rheumatoid arthritis, toothache and fever [5–7]. However, the release of such drugs in water may cause human health hazards and toxic effect to the aquatic ecosystem [8]. To solve the water

\* Corresponding author. E-mail address: swlee@sunmoon.ac.kr (S.W. Lee).

http://dx.doi.org/10.1016/j.jphotochem.2017.02.014 1010-6030/© 2017 Elsevier B.V. All rights reserved. pollution that arises from the dyes and pharmaceutical pollutants, semiconductor photocatalyst can be employed to degrade the organic dyes and drugs by utilizing the natural energy of sunlight. [9,10].

In past decades, the reports of the photocatalytic activity of BaMoO<sub>4</sub> were rarely found, mainly because of its large band gap with rapid recombination of electron and hole [11]. The Scheelite structures of BaMoO<sub>4</sub> photocatalyst have  ${}^{6}C_{4h}$  space group with 4.2 eV energy band gap [12]. The wide band gap makes it active only under UV-light spectral range. To overcome this frustration of poor photocatalytic activity of BaMoO<sub>4</sub>, the plasmonic photocatalyst is designed that composed mainly of noble metals (silver/gold) and semiconductors. The plasmonic behavior induces strong visible light absorption based on localized surface plasmon resonance (LSPR) [13,14]. An internal electric field and Schottky junction are produced in the region near the metal–semiconductor interface, which causes the migration of photogenerated electrons



and holes in different directions to promote the charge-separation efficiency for enhancement of photocatalytic activity [13–15].

In addition, the doping of rare earth ions  $(Er^{3+}/Yb^{3+})$  in BaMoO<sub>4</sub> host enhances the photocatalytic activity due to the increase in the optical absorption and increase of surface barrier by 4f electron transition of the rare earth [16]. The  $Er^{3+}$  and  $Yb^{3+}$  ions have suitable energy level with equally spatial long-lived metastable 4f states [17]. Under 980 nm NIR excitation, the  $Yb^{3+}$  has very large absorption and it transfers energy to  $Er^{3+}$  ions that produce NIR to visible upconversion. The  $Er^{3+}$  ions transfer the energy to the host material and make efficient charge separation for dye degradation [16–18].

The  $Er^{3+}/Yb^{3+}$  doped BaMoO<sub>4</sub> is good upconverting material due to its moderately low phonon energy [19,20]. The molybdate structure supports the reduction of the excitation energy and its low phonon energy improves luminescence efficiency [21]. The  $Er^{3}$ <sup>+</sup> ion produces upconversion by sequential absorption of multiple photons by long-lived ladder like 4f energy levels [22]. In addition to sensitized luminescence by Yb<sup>3+</sup>, other strategies such as SPR has been used for improving upconversion from  $Er^{3+}$  [22,23]. The SPR of silver nanoparticles has already been utilized in many applications, which modifies absorption, emission and decay rate by changing the electric and magnetic fields at the location of an upconverting emitter [24]. In past decades, a plethora of research papers has been published in plasmon related upconversion and it is still challenging field from the view of scientific perspective and technological stand point [23,24].

The doping of non-lanthanides ion like potassium ion ( $K^+$ ) also provides an alternative approach to enhance the upconversion luminescence [25]. The aim of  $K^+$  ion doping in BaMoO<sub>4</sub> crystal lattice is to alter the Yb-Er distance that strongly enhances the intensity of upconversion luminescence [25,26]. The introduction of  $K^+$  also decreases the intrinsic symmetry around  $Er^{3+}$  ions which increases the electric dipole transition probability leading to enhanced upconversion [27]. The doping system modifies the free energy of materials and stabilizes a certain crystal phase and particular morphology [28]. Moreover, the introduction of  $K^+$  in host lattice can create oxygen vacancies for enhancing the energy transfer system with better luminescence [29].

Herein, we have synthesized octahedron microcrystals of Ag-BaMoO<sub>4</sub> co-doped with  $\mathrm{Er}^{3+}$ , Yb<sup>3+</sup> and K<sup>+</sup> ions by the microwave hydrothermal process. The photocatalytic degradation of Rh B and IBP were investigated in detail. HR-QTOF ESI/MS analysis was carried out for determining the IBP intermediate products to find out detailed reaction pathway mechanism. The effect of K<sup>+</sup> ions and silver particles on upconversion luminescence intensity was described.

# 2. Experimental details

#### 2.1. Preparation of samples

The chemicals were of analytical grade and purchased from Sigma Aldrich. Ag-BaMoO<sub>4</sub>:  $Er^{3+}/Yb^{3+}/K^+$  samples were synthesized by the microwave hydrothermal system. In typical experimental procedure, aqueous solution (40 mL) of the calculated amount of Barium nitrate (0.005 mol), Erbium chloride (2 mol%) hexahydrate, Potassium chloride (10 mol%) and Ytterbium chloride hexahydrate (12 mol%) were prepared in one beakers. Another beaker contained Molybdic acid (0.005 mol) with Polyethylene Glycol (PEG). PEG was used as surfactant, which is about 0.1 g. The mole percentage of Erbium chloride hexahydrate, Potassium chloride and Ytterbium chloride hexahydrate were taken with respect to mole of Barium nitrate and Molybdic acid. The different solutions were mixed each other dropwise by continuous magnetic stirring for 120 min until the white precipitate was obtained. The pH of the solution was maintained to 9 by using the aqueous ammonia (30%). The resulting precursor suspension was placed in a microwave reactor (Eyla MWO-1000 wave Magic) for the microwave hydrothermal treatment at 150 °C, for 50 min under 200 W microwave power. The obtained precipitate was washed with deionized water and ethanol several times. Then, it was dried at 70 °C. It was further calcined at 400 °C for 5 h. The silver nitrate solutions (1 mol%) were dispersed in the above synthesized-samples and reduced under UV light. For convenience, samples were identified hereafter as B (BaMoO<sub>4</sub>), B1 (BaMoO<sub>4</sub>:  $Er^{3+}/Yb^{3+}$ ), BS (Ag-BaMoO<sub>4</sub>:  $Er^{3+}/Yb^{3+}$ ), BK (BaMoO<sub>4</sub>:  $Er^{3+}/Yb^{3+}/K^+$ ).

# 2.2. Characterization

The samples were characterized by powder X-ray diffraction (XRD) using X-ray diffractometer (Rigaku, D/Max 2200HR diffractometer, Japan). Diffuse reflectance spectra (DRS) were measured by UV–vis DRS spectrophotometer (V 570, Jasco International Co. LTD., Japan). Raman spectra were obtained by the Raman spectrometer (LabRam, Horiba, Scientific Research System, France). XPS measurement was taken from the Multilab system with Al K $\alpha$  source at 15 kV and 200 W. The upconversion spectra were measured by photoluminescence spectrometer (Shamrock 303i, Andor technology LTD., UK) at 980 nm excitation wavelength. The morphologies of different samples were analyzed by the field emission scanning electron microscope (FESEM, JSM-6700F). The Portable solar simulator (PEC-L01, Pecell, Am 1.5G, 150 mW/cm<sup>2</sup>) was used for the photocatalytic performance of the as-synthesized samples.

# 2.3. Photocatalytic activity

In our photocatalytic experimental procedure, 0.1 g of powder sample was placed in a Pyrex glass, and 70 mL of aqueous solution of Rh B dye (20 ppm) was poured into it. The mixture was then placed in dark for 30 min with constant stirring for obtaining the absorption-desorption equilibrium. After this procedure, sample dye suspension was constantly stirred by magnetic stirrer under the simulated solar light irradiation. The distance between lamp and Pyrex glass cell containing dye suspension was nearly 12 cm. The photocatalytic degradation rates of Rh B and IBP were obtained by using UV–vis spectrophotometer (MECASYS, Optizen2120) at every 30 min. An ultraviolet cutoff ( $\lambda < 420$  nm) filter in solar simulator was applied for visible light source for degradation of IBP and clear liquid after 90 min irradiation with sample BS was used to identify the degradation product.

# 2.4. Analytical procedure for IBP degradation

The reverse-phase HPLC-PDA (high performance liquid chromatography- photodiode array detector) analysis was performed with a C18 column (YMC-Pack ODS-AQ; 4.6 mm internal diameter, 150 mm long, and 5 m particle size) connected to a PDA (220 nm) using isocratic condition of solvent A (acetonitrile:methanol: phosphate buffer (50:20:30, v/v/v) (pH: 5.6) for 20 min. The sample irradiated by visible light for 90 min with reasonable amount of depletion of ibuprofen was used for analysis of transformation products. The HRQTOF-ESI-MS was used for analysis of the degradation products. The binary mobile phases were composed of the solvent A (HPLC-grade water with 0.05% formic acid) and solvent B (acetonitrile with 0.05% formic acid). Total flow was maintained at  $0.3 \,\mu$ L/min for the 15 min program. The flow of acetonitrile was 0-100% from 0 to 9 min and maintained at 100% until 9-12 min, followed by 100-0% in 12-15 min, and then stopped at 15 min. For exact mass analysis, HR-QTOF ESI/MS analysis was performed in negative ion mode using an ACQUITY (Billerica, United States of America) column coupled with a SYNAPT G2-S (Water Corp) column.

### 3. Results and discussion

#### 3.1. Structural and morphological analysis

XRD patterns of Ag-BaMoO<sub>4</sub>: Er<sup>3+</sup>/Yb<sup>3+</sup>/K<sup>+</sup> microcrystals are shown in Fig. 1. In these XRD patterns, all the diffraction peaks were well-indexed to the Scheelite tetragonal structure of BaMoO<sub>4</sub> (JCPDS card no. 29-0193). No additional peaks for associated impurities were detected in the Ag-BaMoO<sub>4</sub>:  $Er^{3+}/Yb^{3+}/K^+$  samples. The silver peak was not detected in XRD because of the small quantity of dispersed Ag that might be below the detection limit of the instrument. The peak intensities of the doped samples were found to be decreased in comparison with the undoped sample which indicates decrease in the degree of cationic ordering [30]. As shown in Fig. 1, the doping of  $Er^{3+}/Yb^{3+}/K^+$  in BaMoO<sub>4</sub> causes decrease in crystallinity as well as the broadening of the (112) diffraction peak due to lattice shrinkage and steric effect that is supported by value of full width at half maximum (FWHM) and crystallite size of Scherrer's equation in Table 1 [16,26]. According to the Scherrer's equation,

$$D = K\lambda/\beta \cos\theta \tag{1}$$

where, *D* is the size of crystals,  $\lambda$  is X-ray wavelength, *K* is dimensionless shape factor (0.9),  $\beta$  is broadening at half the

Table 1

Crystallite size of different samples on the basis of Scherrer's equation.

Samples	Crystallite size (nm)	FWHM (β) (rad)			
В	125.6	0.1550			
B1	118.3	0.1587			
BS	76.3	0.1973			
BK	80	0.1913			
BSK	92.8	0.1779			

maximum intensity (FWHM) and  $\theta$  is the scattering angle in radian [31].

Fig. 2 shows the FESEM images of as-prepared samples. Well defined octahedron-like morphology is evident. The formation mechanism of micro-octahedron is aggregation and ripening of small octahedrons [12]. Due to the high surface energy of particles after doping in the host, the particles are agglomerated [30]. The particle size ranges from 0.5 to 3.0 µm. Due to the aggregating nature of octahedron crystals, silver particles could not be observed on the surface of BaMoO<sub>4</sub>. Surface defects appear in the faces of the crystals, which can be explained by the following reasons: (i) Rapid hydrolysis might occur during addition of aqueous ammonia into the solution mixture during the synthesis process, (ii) Formation of supersaturated solution takes place due to the high concentration of salts and acids dissolved in the aqueous solution, and (iii) Polvethylene Glycol (PEG), polymeric surfactant might have been highly adsorbed on the surface of octahedron due to high collision rate and heating, regulated by microwave radiation during the microwave hydrothermal process.



**Fig. 1.** XRD patterns of  $Er^{3+}/Yb^{3+}/K^+$  co-doped Ag-BaMoO<sub>4</sub> samples annealed at 400 °C for 5 h. Inset shows broadening of diffraction peak (112).



Fig. 2. FESEM images of Ag-BaMoO<sub>4</sub>: Er<sup>3+</sup>/Yb<sup>3+</sup>/K<sup>+</sup> microcrystals. (a) B; (b) B1; (c) BS; (d) BK; (e) BSK.



 $\textbf{Fig. 3.} \ XPS \ spectra \ of \ Ag-BaMoO_4: \ er^{3+}/Yb^{3+}/K^+ \ sample. \ (a) \ Ba \ 3d; \ (b) \ Mo \ 3d; \ (c) \ O \ 1s; \ (d) \ Ag \ 3d; \ (e) \ Er \ 4d; \ (f) \ Yb \ 4d; \ (g) \ Survey \ spectrum. \ (a) \ Ba \ 3d; \ (b) \ Mo \ 3d; \ (c) \ O \ 1s; \ (d) \ Ag \ 3d; \ (e) \ Er \ 4d; \ (f) \ Yb \ 4d; \ (g) \ Survey \ spectrum. \ (a) \ Survey \ spectrum.$ 

The effective collision and coalescence between the octahedrons drive the growth process of microcrystals with a new crystallographic plane. Actually, the growth rate of crystal face is associated with the surface energy of each crystal face. Due to the  $\text{Er}^{3+}$ ,  $\text{Yb}^{3+}$ , and K<sup>+</sup> dopant ions, faces of octahedrons were found to be slightly distorted. The possible reasons may be associated with the insertion of dopant ions into the BaMoO<sub>4</sub> host matrix and new equilibrium positions of surface atoms to balance free energy [32]. The particle size decreased after doping the ions, which is also evidenced by the results from Scherrer's equation.

Because each element has a unique set of binding energies, Xray photoelectron spectroscopy (XPS) was applied to determine the presence of specific elements in the sample. Fig. 3 shows the XPS spectra of BSK (Ag-BaMoO<sub>4</sub>:  $Er^{3+}/Yb^{3+}/K^+$ ) sample. From the XPS spectra, it is observed that sample consists of Ba, Mo, O, K, Cl, Er and Yb element without any impurity peaks. The Ba 3d signal consists two peaks, Ba 3d<sub>3/2</sub> and 3d<sub>5/2</sub> at 798.5 eV and 783.2 eV, respectively [21]. The peaks noted at 370.2 eV and 376.2 eV can be ascribed to Ag  $3d_{3/2}$  and Ag  $3d_{5/2}$  of metallic silver [19]. The difference (6.0 eV) of binding energy between Ag  $3d_{3/2}$  and Ag  $3d_{5/2}$ suggests that the silver is found in metallic form in BSK sample. The value of binding energy at 235.2 eV, and 238.6 eV is assigned to  $3d_{5/}$ 2 and 3d<sub>3/2</sub> of Mo, respectively, originated from Mo<sup>+6</sup> oxidation state [21]. The peak at 533.5 eV is ascribed to O 1s. The binding energies for Er 4d, Yb  $4d_{3/2}$ , and Yb  $4d_{5/2}$  are observed at 168.4 eV, 188.1 eV and 180.4 eV respectively [19]. In addition, the peak for K 2p is observed at 286 eV [21]. From the XPS measurements, it was confirmed that  $Er^{3+}$ ,  $Yb^{3+}$  and  $K^+$  ions have been successfully incorporated in the BaMoO<sub>4</sub> host lattice.

Raman spectra of different samples are shown in Fig. 4.  $BaMoO_4$ shows 26 different vibrations in which all the even vibrations ( $A_g$ ,  $B_g$  and  $E_g$ ) are Raman active modes and odd vibrations ( $4A_u$  and  $4E_u$ ) are infrared active [33]. The vibrational motion in molecular

**Fig. 4.** Raman spectra of Ag-BaMoO<sub>4</sub>: Er<sup>3+</sup>/Yb<sup>3+</sup>/K<sup>+</sup> samples.

crystals, external modes and internal modes arise due to the motion of  $Ba^{2+}$  cation with the rigid molecular unit and vibrations inside the  $[MoO_4]^{2-}$  [34]. Table 2 reveals the Raman active modes of different samples. The different position of Raman active modes may be related to defects, the degree of structural order-disorder into the lattice as well as the interaction force between the clusters. Sharp and intense Raman active modes inform the presence of a strong interaction between the ions, which originate from the stretching and bending vibrations of the metal-oxygen bonds within the anionic groups. The appearance of additional Raman peaks at 442.82 cm<sup>-1</sup> and 629.24 cm<sup>-1</sup> in B1 sample and 433.81 cm<sup>-1</sup>, 474.52 cm<sup>-1</sup> and 620.95 cm<sup>-1</sup> in the BK sample, as shown in Fig. 4, are due to the dopant ions and the bulk vibration modes [19].

UV-vis diffuse reflectance spectra of different samples are shown in Fig. 5a. The absorption band ranging from 200 to 320 nm represents the O-Mo charge transfer transitions of MoO<sub>4</sub><sup>2-</sup> groups [35]. It is seen that Ag containing samples (BS and BSK) show a strong absorption band around 325-600 nm which is attributed to the surface plasmon resonance (SPR) effect caused by the silver particles [31]. The UV-vis spectra of samples BS and BSK also suggest that the surface plasmon resonance frequency of Ag particles overlaps with the green and red emission frequencies of the upconversion; this overlapping allows the coupling the SPR of silver with upconversion emission [24]. The coupling of SPR changes the energy transfer, radiative decay rate, and emission intensity [36]. In the case of B, B1 and BK samples, the steep absorption marked by the Urbach's tail is assigned to the low energy tails of direct absorption band gap [31]. From the absorbance spectrum of BSK sample (in Fig. 5a), the absorption bands at 370 nm, 421 nm, and 520 nm can be assigned to the transition of  $\text{Er}^{3+}$ , from  ${}^{4}\text{I}_{15/2}$  to  ${}^{4}\text{G}_{11/2}$ ,  ${}^{2}\text{H}_{9/2}$  and  ${}^{2}\text{H}_{11/2}$ , respectively [21].

The optical band gap energy is related to the absorbance and electronic transition in the materials [33]. The band gap energies of different samples were calculated by using Kubelka-Munk equation, which is shown in Fig. 5b. The band gap energy of sample B, B1, BK, BS and BSK are 4.34, 4.31, 4.18, 3.95 and 3.71 eV, respectively. It is noted that the band gap is reduced by addition of silver particles. The possible reason for the reduction in band gap is that the metallic clusters of Ag introduces localized energy levels in BaMoO<sub>4</sub> band gap [37]. The small decrease in band gap values for  $Er^{3+}/Yb^{3+}/K^+$  doped BaMoO<sub>4</sub> may be related to the quantum confinement effect [38].

# 3.2. Photocatalytic activity

The photocatalytic activity of various samples was observed by photodegradation of Rh B dye (20 ppm) in aqueous solution dispersions under simulated solar light irradiation. The photocatalytic activities were measured under similar conditions with the help of kinetic plot  $(C/C_0)$ , recycle stability test and degradation percentage. As shown in Fig. 6a, the negligible absorption of Rh B dye under dark condition was noted. The presence of rare earth ions (Er<sup>3+</sup>/Yb<sup>3+</sup>) in BaMoO<sub>4</sub>, sample B1, slightly increases the degradation process which is nearly two times than the BaMoO<sub>4</sub> host. With the silver addition that is for the sample BS the degradation of Rh B was rapidly increased. The highest photocatalytic activity was seen in the sample BS, which degraded the Rh B within 90 min about 99.60% as shown in Fig. 6a and b. It can be concluded that silver and rare earth ions enhanced the photocatalytic activity dramatically by 30 times than that of the BaMoO<sub>4</sub> host. However, the doping of K<sup>+</sup> ions in BaMoO<sub>4</sub> host slightly reduces the photocatalytic activity. To quantify the degradation rate of Rh B, the reaction kinetics was ascribed to a pseudo-firstorder reaction,  $\ln (C_o/C) = k_{app} \cdot t$ , where  $k_{app}$ , is the apparent first-



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Samples	$B_{g}(cm^{-1})$	$E_{g}(cm^{-1})$	$E_{g}(cm^{-1})$	$B_{g}(cm^{-1})$	$A_g (cm^{-1})$	$E_{g}(cm^{-1})$	$B_{g}(cm^{-1})$	$A_g (cm^{-1})$
В	85.74	116.83	147.96	196.44	333.43	800.16	846.72	899.44
B1	85.67	-	-	-	335.79	791.18	839.37	894.23
BS	86.92	-	-	-	326.61	786.89	838.12	889.64
BK	86.92	-	-	-	335.72	779.94	848.72	901.11
BSK	82.83	-	-	-	322.02	782.03	833.55	885.62

 Table 2

 Raman active modes of different samples with extra peaks.



Fig. 5. (a) UV-vis DRS spectra; (b) Kubelka-Munk plot for band gap energy of different samples.

order rate constant while C and C<sub>o</sub> are concentration at time t and 0 respectively [39]. As displayed in Fig. 6c, the degradation rate constant of B, B1, BS, BK and BSK samples are 0.000328, 0.00090, 0.06301, 0.00018 and 0.02977 min<sup>-1</sup> respectively. This result also indicates that the sample BS has the best photocatalytic performance. Furthermore, the stability and reusability of the sample BS were investigated by repeating the Rh B degradation experiment three times. The result presented in Fig. 6d demonstrates the high photocatalytic stability.

The kinetic plot, degradation percentage of IBP (20 ppm) and UV-vis spectra by different samples under visible light irradiation are depicted in Fig. 7. The adsorption of IBP was not seen in dark condition. Initially, the presence of rare earth ions (Er<sup>3+</sup>/Yb<sup>3+</sup>) in BaMoO<sub>4</sub>, sample B1, slightly enhances the degradation process than the BaMoO<sub>4</sub> host. The degradation of IBP was rapidly increased by the addition of silver. The highest photocatalytic performance was seen in the sample BS, which degraded 41.49% of IBP within 90 min as shown in Fig. 7a and b. The combined effect of silver and rare earth ions enhanced the photocatalytic activity dramatically by 31 times than that of the BaMoO<sub>4</sub> host. However, the doping of K<sup>+</sup> ions in BaMoO<sub>4</sub> host slightly reduced the photocatalytic performance. The UV-vis spectra during photodegradation of IBP aqueous solution mediated by the sample BS is depicted in Fig. 7c. The absorption peak of IBP was seen at 221 nm. The new peak appeared at 257 nm after the degradation in 30 min. The appearance of the new peak indicates that some intermediated photoproducts appeared during the degradation process. The absorbance at 257 nm decreased with an increase of the reaction time.

In order to identify the intermediate products of IBP, HR-QTOF ESI/MS (negative ion mode) was used. The total ion chromatogram (TIC) of degradation products of IBP is shown in Fig. S1 (Supporting Information). The degradation product of IBP was confirmed by HR-QTOF ESI/MS analysis in Fig. S2 (Supporting Information). The different IBP fragments were observed on the basis of retention time ( $t_R$ ), observed molecular mass [M–H]<sup>-</sup>, and fragment ions (m/ z) value. Table 3 shows the various degradation products and their skeleton structure, elemental formula, experimental molecular mass  $[M-H]^-$ , observed molecular mass  $[M-H]^-$ , fragments (m/z), and retention time  $(t_R)$ . The mass spectrum of IBP consists the ion of m/z. 205.1238. The fragment in the mass spectrum of the product IBP 1 is the ion of m/z 221.1165, which corresponds to hydroxylation of the IBP molecule in solution by OH<sup>•</sup> radical. The OH<sup>•</sup> radical may attack at one of the two benzyl positions, tertiary carbon atom positions, and aromatic ring. A detail mechanism of the IBP degradation pathway is described in the reaction mechanism (Supplementary Information) and the corresponding photodegradation pathway for the mineralization has been presented in Fig. 8. On the basis of various degradation product of IBP, the degradation pathways followed through the attack by OH• radical with decarboxylation process, and leading subsequently to further mineralization [8,40–42].

The photocatalytic activity of Ag-BaMoO<sub>4</sub>:  $Er^{3+}/Yb^{3+}$  is associated with the closed junctions and the synergistic plasmon response of Ag [3]. Under simulated solar light irradiation, both Ag and BaMoO<sub>4</sub> can be simultaneously excited to generate electronhole pairs. Afterward, the plasmon resonance excites the electron in silver, the photogenerated electrons from the conduction band of BaMoO<sub>4</sub> are transferred to the silver and electrons are trapped by it [37,43]. The silver particles present in the BaMoO<sub>4</sub> surface can also increase the interfaces and heterostructures [44]. Due to these processes, electrons and holes are separated effectively giving rise to enhanced photocatalytic activity. The Rh B and IBP react with the holes in valence band giving rise to the oxidation products whereas



Fig. 6. (a) Kinetic plot for the degradation of Rh B (20 ppm) using solar simulator; (b) degradation percentage; (c) pseudo first order kinetics of different samples; (d) three recycling runs of BS sample.



Fig. 7. (a) Kinetic plot for the degradation of Ibuprofen (20 ppm); (b) degradation percentage; (c) UV-vis spectra during degradation of IBP aqueous solution mediated by the sample BS under visible light irradiation.

the electrons in the conduction band give reduction products [14,45]. However, the doping of  $K^+$  ions in BaMoO<sub>4</sub> host slightly reduces the photocatalytic activity because of fast recombination electron and hole.

The rare earth metals act as stock for photogenerated electrons. Surface oxygen vacancies and defect states may also arise due to the rare earth ion doping. The oxygen vacancies and defect states can capture the photoinduced electrons during photocatalytic process [46,47]. Also, the presence of the  $\text{Er}^{3+}$  ions in the lattice can help in trapping the photoelectrons by reducing itself to  $\text{Er}^{2+}$ , thereby preventing the recombination chance of electrons and holes by reaction between the  $\text{Er}^{2+}$  species and O<sub>2</sub> [48]. The large cross section area of Yb<sup>3+</sup> ions transfers energy to  $\text{Er}^{3+}$  ions and  $\text{Er}^{3+}$  ions transfer the energy to the host material and make efficient

 Table 3
 Identification of IBP degradation products by HR-QTOF ESI/MS analysis.

Name	Structure	Elemental formula	[M–H] <sup>–</sup> Theoretical	[M–H] <sup>–</sup> Observed	Fragment ions ( <i>m</i> / <i>z</i> )	Retention time (t <sub>R</sub> )
Ibuprofen (IBP)	HO	C <sub>13</sub> H <sub>18</sub> O <sub>2</sub>	205.1234	205.1238	161,119	5.715
IBP 1a 2-(4-(1-hydroxy-2-methyl propyl) phenyl) propanoic acid	НО НО	C <sub>13</sub> H <sub>18</sub> O <sub>3</sub>	221.1193	221.1165	177,159	4.417
IBP 1b 2-hydroxy-2-(4-isobutyl phenyl) propanoic acid	Но					
IBP 1c 2-(4-(2-hydroxy-2-methyl propyl) phenyl) propanoic acid	HO HO					
IBP 1d 2-(3-hydroxy-4-isobutyl phenyl) propanoic acid	OH HO					
IBP 2 1-ethyl-4-isobutyl benzene		$C_{18}H_{18}$	161.1335	161.1306	161,119	5.533
IBP 3a 1-(4-ethylphenyl)-2-methyl propan-2-ol	HO	C <sub>12</sub> H <sub>18</sub> O	177.1285	177.1299	177,149	3.538
IBP 3b 1-(4-ethyl phenyl)-2-methyl propan-1-ol	HO					
IBP 3c 1-(4-isobutyl phenyl) ethanol	ОН					
IBP 3d 1-ethyl-4-isobutyl phenol	-(					
IBP 4a 1-isobutyl-4-vinyl benzene		C <sub>12</sub> H <sub>16</sub>	159.1183	159.1183	143,117	5.697
IBP 4b 1-ethyl-4-(2-methyl prop-1-en-1-yl) benzene						

# Table 3 (Continued)

Name	Structure	Elemental formula	[M–H] <sup>–</sup> Theoretical	[M–H] <sup>–</sup> Observed	Fragment ions ( <i>m</i> / <i>z</i> )	Retention time (t <sub>R</sub> )
IBP 4c 1-ethyl-4-(2-methyl allyl) benzene						
IBP 5a 2-methyl-1-phenyl propan-1-ol	OH C	C <sub>10</sub> H <sub>14</sub> O	149.0972	149.0914	133,119	5.153
IBP 5b 2-methyl-1-phenyl propan-2-ol	ОН					



Fig. 8. The proposed degradation pathways for the mineralization of IBP.



Fig. 9. Schematic diagram of photocatalytic mechanism.

charge separation for dye and drug degradation. The model of photocatalytic degradation of Rh B and IBP by Ag-BaMoO<sub>4</sub>:  $\text{Er}^3$  <sup>+</sup>/Yb<sup>3+</sup>/K<sup>+</sup> photocatalyst is shown in Fig. 9.

#### 3.3. Upconversion properties

The upconversion emission spectra of different samples under 980 nm laser excitation are shown in Fig. 10. Intense green and less intense red emissions were observed. The emissions at 526 nm 555 nm, and 661 nm are assigned to the transitions  ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ ,  ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$  and  ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$  respectively [21,49]. The intense green upconversion emission is the result of efficient energy transfer from Yb<sup>3+</sup> to Er<sup>3+</sup> [50]. The green upconversion is also associated with the charge transfer transition with in MoO<sub>4</sub> clusters [34].

The upconversion luminescence intensity of BSK and BK samples (containing K<sup>+</sup> ions) is higher as compared to that of B1 and BS samples (without  $K^+$  ions). It is evident that the upconversion emission has been enhanced by K<sup>+</sup> ions. It is known that the emission in Er<sup>3+</sup> is originated from electric dipole transitions among the 4f subshells. These radiative transitions are in general forbidden by parity considerations [27]. When the non-luminescent K<sup>+</sup> ion occupies the interstitial site in the lattice. it lowers the local symmetry around the Er<sup>3+</sup>/Yb<sup>3+</sup> ions [22]. As a result, the intrinsic wave functions of 4f subshell mix with other wave functions of opposite parity and the parity forbidden nature of the 4f transition is partially broken enhancing the radiative and absorption transition probabilities of Er<sup>3+</sup>/Yb<sup>3+</sup> ions [51]. Moreover, the presence of K<sup>+</sup> in the lattice decreases the effective distance between the Er<sup>3+</sup> and Yb<sup>3+</sup> and hence increases the energy transfer probability between the ions [25,52]. Hence, the lowering of local symmetry around the lanthanide dopants and the effective decrease of the distance between the Er<sup>3+</sup> and Yb<sup>3+</sup> ions due to the presence of K<sup>+</sup> ions in the lattice has favored the efficient upconversion emission [22,25,26].

Although the presence of silver particles enhances the absorption of visible light by surface plasmon resonance phenomenon, a significant reduction in upconversion intensity was observed in B1 and BS samples. The reason for this reduction in emission intensity can be correlated with the local field around the  $\text{Er}^{3+}$  ions induced by the Ag, which redistributes the population level of the emitting excited states of  $\text{Er}^{3+}$  [53]. In addition, plasmon absorption by the aggregation of silver particles, competed absorption among the silver particles and the degree of crystallinity also reduce the upconversion intensity [54,55].



Fig. 10. Upconversion emission spectra upon excitation at 980 nm of Er<sup>3+</sup>/Yb<sup>3+</sup>/K<sup>+</sup> doped Ag-BaMoO<sub>4</sub> samples.



Fig. 11. Dependence of emission intensity on incident laser power for sample BK.



**Fig. 12.** Double logarithmic plot of incident laser power versus emission intensity of different samples at 526 nm. (a) B1; (b) BS; (c) BK; (d) BSK.

Furthermore, silver particles can provide additional nonradiative decay channels, enhancing the nonradiative decay rate, as a result quenching of upconversion luminescence occurs [55].

Pump power dependence of the upconversion emission intensity in the sample BK is shown in Fig. 11. The upconversion photoluminescence intensity has a nonlinear dependence on the excited light density, which is represented by the following equation:

$$I_{UC}=KP^n \tag{2}$$

Where,  $I_{UC}$ , *P*, *K* and *n* are upconversion photoluminescence intensity, power of pump laser, material associated coefficient and the number of the excitation photons participating the upconversion process, respectively [56]. The value of n is given by the slope of the intensity versus pump power in double logarithmic plot. From Fig. 12, the value of n is found to be 2 indicating a two-photon absorption process for the green emission. The slop for the red emission has significant deviation from the two-photon model.

Based on the energy level diagram, as shown in Fig. 13, the following possible upconversion mechanism in Ag-BaMoO<sub>4</sub>:  $Er^3$ 



**Fig. 13.** Simplified energy level diagram and the possible upconversion pathways for Ag-BaMoO<sub>4</sub>:  $Er^{3+}/Yb^{3+}/K^+$  microcrystals. Dashed upward arrows represent absorption. Solid downward arrows represent radiative emission. Short dotted downward arrows represent non radiative relaxation.

<sup>+</sup>/Yb<sup>3+</sup>/K<sup>+</sup> microcrystals has been presented. Under 980 nm laser excitation, Yb<sup>3+</sup> ions are first excited from the ground state  ${}^{2}F_{7/2}$  to the excited state  ${}^{2}F_{5/2}$ . The excited Yb<sup>3+</sup> ion then transfers the energy (ET-1) to the Er<sup>3+</sup> ions exciting it from the  ${}^{4}I_{15/2}$  to the  ${}^{4}F_{7/2}$  level by absorbing another photon via ET-2. The excited population non-radiatively relax to the  ${}^{2}H_{11/2}$ ,  ${}^{4}S_{3/2}$  and  ${}^{4}F_{9/2}$  and subsequently produce green (526 nm and 554 nm) and red (661 nm) emissions by radiative relaxations to the ground state  ${}^{4}I_{15/2}$ . In addition, some Er<sup>3+</sup> ions in the  ${}^{4}I_{11/2}$  level non-radiatively decay to the lower level  ${}^{4}I_{13/2}$  from where they undergo ET-3 process to further contribute to the red emission as shown in the diagram [19].

The CIE (Commission Internationale de L'Eclairage) diagram of all the samples under 980 nm excitation has been shown in Fig. 14. The inset shows the digital photograph of the actual emission from the representative samples BK and BS against the dark background. The CIE coordinates as calculated from corresponding upconversion emission spectra are (0.293, 0.687), (0.397, 0.586), (0.264, 0.712) and (0.280, 0.694) for the samples B1, BS, BK and BSK, respectively. The color coordinates of B1, BS and BK lie in green region. However, the color coordinates shift to the green-yellow region for the sample BSK due to enhancement in red emission and decrease in green emission. This observation shows that the synthesized materials have a potential application as a green upconversion optical material.

#### 4. Conclusions

In summary, the photocatalytic and upconversion luminescence of silver dispersed BaMoO<sub>4</sub> octahedron microcrystals doped with  $\text{Er}^{3+}$ , Yb<sup>3+</sup>, K<sup>+</sup> has been investigated. The individual effect of Ag and K<sup>+</sup> in photocatalysis and upconversion has been evaluated. The photocatalytic efficiency of Ag-BaMoO<sub>4</sub>:  $\text{Er}^{3+}$ /Yb<sup>3+</sup> is nearly 30 and 31 times as compared to that of the pure BaMoO<sub>4</sub> for Rh B (solar light irradiation) and IBP (visible light irradiation), respectively. The HR-QTOF ESI/MS was used to detect IBP photodegradation



Fig. 14. CIE chromaticity diagram of Ag-BaMoO<sub>4</sub>: Er<sup>3+</sup>/Yb<sup>3+</sup>/K<sup>+</sup> samples. The inset shows the luminescent photograph of sample BK and BS under 980 nm excitation.

intermediates for finding out detailed degradation pathway mechanism. The dispersion of silver particles as well as rare earth ions doping in BaMoO<sub>4</sub> played a vital role for photocatalytic enhancement. Although the addition of K<sup>+</sup> reduced the photocatalytic efficiency, a two-fold enhancement in upconversion intensity was observed in BaMoO<sub>4</sub>: Er<sup>3+</sup>/Yb<sup>3+</sup>/K<sup>+</sup> as compared to that of BaMoO<sub>4</sub>:  $Er^{3+}/Yb^{3+}$ . The presence of Ag slightly reduced the upconversion intensity of BaMoO<sub>4</sub>: Er<sup>3+</sup>/Yb<sup>3+</sup>. Very intense green and less intense red emissions were observed in Ag-BaMoO<sub>4</sub>: Er<sup>3</sup> <sup>+</sup>/Yb<sup>3+</sup>/K<sup>+</sup>. Two photon absorption process was responsible for the observed upconversion emission. The presence of Ag and K<sup>+</sup> both in BaMoO<sub>4</sub>: Er<sup>3+</sup>/Yb<sup>3+</sup> results in the combination of enhanced photocatalytic activity for removal of organic contaminants (IBP and Rh B) and efficient upconversion emission which makes the Ag-BaMoO<sub>4</sub>:  $Er^{3+}/Yb^{3+}/K^+$  microcrystal suitable for the multifunctional application.

# Acknowledgments

This Research was supported by the Global Research Laboratory Program of the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (MEST) of Korea (Grant Number: 2010-00339).

# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2017.02.014.

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