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Radical Macro Spatial Separation: a Novel Way to Enhance the Photocatalytic Efficiency

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Radical macro spatial separation can be achieved *via* a new photocatalytic system separating electrons and holes into two reaction chambers which are connected by a salt bridge thereby significantly improved the photocatalytic efficiency of ZnO single crystal.

Heterogeneous photocatalysis has attracted increasing attention because of its applications in removal of pollutants and hydrogen production.[1-7] Undoubtedly, during the process of heterogeneous photocatalysis, a key issue is the separation of photogenerated electrons-holes pairs. However, the process of photogenerated electrons-holes pairs participating in the redox reaction is fraught with possibility of trapping or recombination. Only overcame a series of body and surface recombination could electrons and holes participate in the photocatalysis directly[8-10] or indirectly[11,12]. Both the bulk and surface recombination are directly related to the intrinsic properties of material, therefore large endeavor has been particularly devoted to material modification to improve the separation efficiency of photogenerated electron-hole pairs.[13-20] However, for decades, conventional methods could not achieve the purpose of substantial increase in the quantum efficiency of photocatalytic degradation.

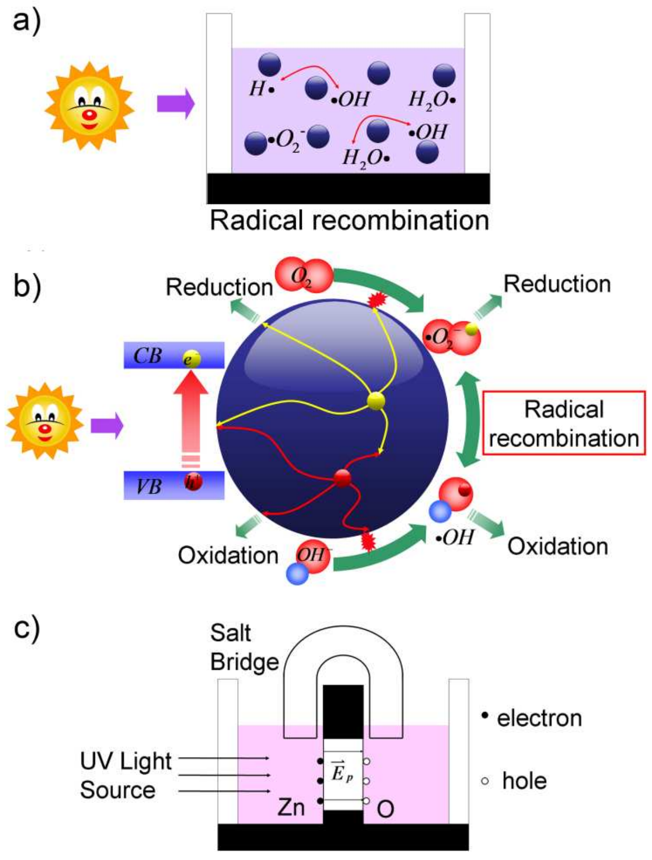

Fig.1 a) Photocatalytic system: a) In conventional photocatalytic system, different kinds of initial radicals and derivatives are coexisting within the same solution; b) Photogenerated electron-hole recombination: recombined before separating in position space, body and surface recombination and recombination of radicals that generated by photogenerated electrons and holes; c) A new type of photocatalytic system: electrons will cumulate on the Zn-polar surface and holes on O polar surface because of the spontaneous polarization electric field that from Zn to O-polar surface, which eventually results in the spatial separation of the electron-generated and hole-generated radicals, and thus decreasing the recombination between radicals.

In the current photocatalytic system, photogenerated holes and electrons seperated on micro scale, as shown in the Fig. 1a), different kinds of initial radicals and derivatives which generated by two kinds of photogenerated carriers are coexisting within the same solution. Except for the bulk and surface recombination, there is still a third recombination which is a material-independent parameter in solution: the radical recombination,[19,21] as shown in Fig.1b). Not all the initial radicals generated by photogenerated electrons and holes are involved in the redox reaction, most of which recombined in solution. Iglev *et al.*[22]found that nearly 50% of $\cdot$OH radical was quenched in 700 fs in KOH aqueous solution after being excited by femtosecond laser. Moreover, the recombination probability will increase with the concentration of initial radicals.[19] However, most of the present research on improving activities of photocatalysts was focused on suppressing the direct recombination of photogenerated electrons and holes.[23-28] The recombination of radicals is not considered as a decisive factor affecting photocatalysis, since the concentration of initial radicals in solution is very low, which is limited by the capacity of charge separation of the common photocatalyst. With the ongoing efforts of researchers, a significant increasing of initial radical concentration in solution can be achieved because of the enhancement of the charge separation capability of photocatalysts. In such case, radical recombination will become an important factor that could not be ignored. Otherwise, even a high charge separation efficiency obtained by material modification, the superior performance of modified materials is still hard to achieve due to the radical recombination in the solution. Lack of understanding this aspect will mislead the direction of material modification, as a consequence constraining the overall development of photocatalytic materials. However, up to now, far from sufficient attention is devoted to studying the impact of radical recombination on photocatalytic efficiency.

In this work, a novel way, radicals macro spatial separation can be achieved *via* a new photocatalytic system separating electrons and holes into two reaction chambers which are connected by a salt bridge. In this system, ZnO single crystal was selected as a photocatalyst and Rhodamine B was employed as model pollutant. As a polarized single crystal with spontaneous polarization electric field (E_p), ZnO can separate photogenerated electrons and holes[29,30], as well the radicals generated by two kinds of photogenerated carriers. As shown in Fig. 1c), RhB solution in a quartz cuvette was separated into two isolated compartments (left and right reaction chamber) by a PTFE sheet where the ZnO single crystal was embedded in. Zn and O-polar surface contact with one of the two parts solution respectively. Twin purposes could be obtained without changing the electrochemical environment of solution by using this system: 1), charges were spatial separated in a macro level. Due to the E_p in ZnO single crystal, photogenerated electrons and holes will move to the Zn and O-polar plane, and then inject into solution respectively. Compare to nanoparticle system, the macro level of charge spatial separation in the new system will suppress the surface recombination. 2), radicals were spatial separated into two isolated reaction chambers. The radical will be spatial isolated so that recombination can be suppressed due to the initial radicals and derivatives derived from electrons and holes existing in different reaction chamber. In order to assure the ongoing reaction of the whole system, a salt bridge was used to connect the two reaction chambers to keep charge and ionic balance. So for this specific device, only a kind of photogenerated carriers takes part in the redox reaction in each part of solution if the E_p in ZnO single crystal is strong enough.

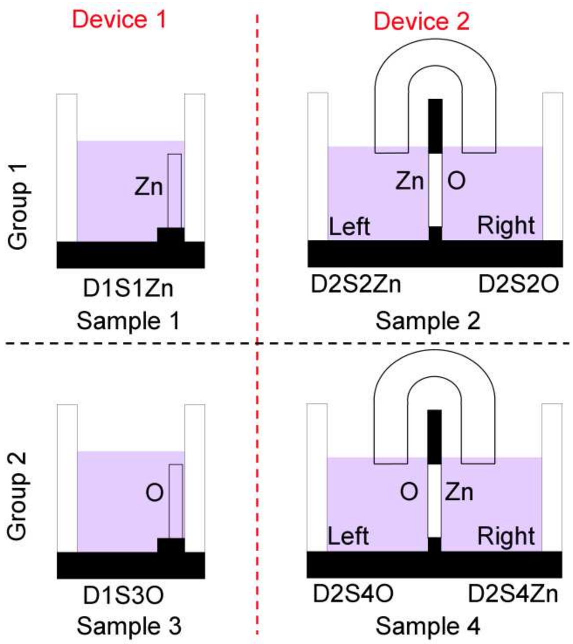

Fig. 2 The schematic of two groups of four samples in device 1 and 2, respectively. The photocatalytic activity of six surface of ZnO sample was studied. Direction of UV irradiation: from left to right and perpendicular to ZnO single crystals. The right reaction chamber of sample 2 and 4 was designed to can not be irradiated by UV light.

Table 1. The degradation percentage of two groups of four samples. Every reaction chamber was charged with 2.5mL RhB solution with a concentration of 10^{-5}M. Sample R (only irradiated with UV) and R' (unirradiated original solution) as reference samples. NH_4Cl was selected as the electrolyte for salt bridge.

Sample	Group one		Group two		Reference	
	1[a]	2	3[a]	4	R	R'
Degradation percentage[b] (%)	D1S1Zn 33.2	D2S2Zn 59.5	D1S3O 22.9	D2S4O 32.0	2.2	//
	//	D2S2O 6.1	//	D2S4Zn 12.8	//	//

[a] To make the solution environment consistent, salt bridge was also immersed in sample 1 and 3. The electrolyte dissolved into RhB solution from the salt bridge was ensured not to

influence the experiment, as shown in Fig. S1. [b] Degradation percentage=(A_0-A_t)×100/A_0, where A_0=absorbance at t=0 min, A_t= absorbance at t minute.

ZnO single crystal were grown by hydrothermal method in our group.[31] Four experiments were carried out in conventional (designated as device 1) and new type of photocatalytic system (designated as Device 2), respectively, as shown in Fig. 2. The photocatalytic activity of six crystal surface, i.e., Zn-polar surface of sample 1 in device 1, O polar surface of sample 3 in device 1, Zn-polar surface of sample 2 in device 2, O polar surface of sample 4 in device 2, O polar surface of sample 2 in device 2 and Zn-polar surface of sample 4 in device 2 (denoted as D1S1Zn, D1S3O, D2S2Zn, D2S4O, D2S2O and D2S4Zn) in four samples were studied. Among the six polar surfaces, D1S1Zn, D1S3O, D2S2Zn and D2S4O were irradiated under UV light source, while D2S2O and D2S4Zn were in the dark. The RhB solution irradiated without ZnO single crystal in the device 1 was designated as R and the original RhB solution was designated as R'. After photodegradation for 2.5 h, the degradation of the RhB solutions in all compartments was detected by UV-2550 spectrometer and the degradation percentage was employed for evaluating photocatalytic activity.[32] As shown in Table 1, for the surfaces under irradiation in group one, the degradation percentage of D1S1Zn is 33.2% and D2S2Zn is 59.5%, while in group two, the degradation percentage of D1S3O is 22.9%, and D2S4O is 32.0%. In the same group, the photocatalytic activity of device 2 is better than device 1, while in the same device, Zn polar surface is better than O polar surface, which is the same to our previous report.[11] The penetration depth of UV light in ZnO single crystal is for only about 100 nm[33,34], therefore D2S2O and D2S4Zn could not be irradiated by UV light. However, as showed in Table 1 and Fig. S2, RhB was photodegraded by D2S2O and D2S4Zn, moreover, the photocatalytic activity of Zn-polar surface was still better than O polar surface.

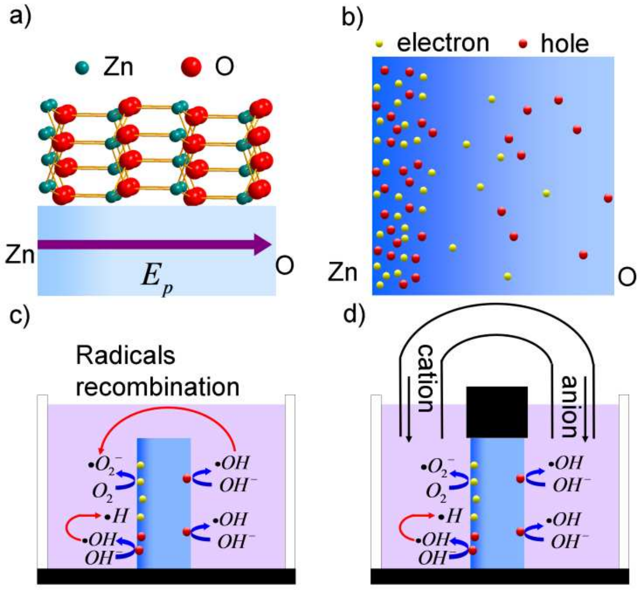

Fig. 3. The migration of photogenerated electrons, holes and radicals in ZnO single crystal photocatalytic system when irradiating to Zn-polar surface. a) Because of the unique structure, an E_p from Zn to O-polar surface existing in ZnO. b) Large amount of photogenerated carrier excited in a depth about 100nm. c) Different kinds of initial radicals and derivatives coexist within the same solution and recombination each other. d) The radical were spatial isolated so that recombination colud be suppressed.

As shown in Fig. 3a), there is an E_p from Zn to O-polar surface in the ZnO single crystal because of noncoincidence of positive and negative charge center induced by the unique structure of ZnO. Fig. 3b) shows the migration of photogenerated electrons and holes in ZnO single crystal under irradiation. A large amount of photogenerated carriers were excited in the effective light-absorbing layer below surface of Zn-polar surface. Under the action of E_p, part of photogenerated electrons was injected into solution in left compartment directly while majority of them recombining before separation; for photogenerated holes, except for recombination, part of them overcame the effect of E_p with larger momentum and injected into solution in left compartment, while a small quantity of them moved to O polar surface, which degraded the RhB in right compartment. Because of huge E_p region which scales with the thickness of the crystal (about 0.5 mm, far more than electron mean free path for 7-30 μm[35,36]), photogenerated electrons cannot reach to O polar surface. As a consequence, there was only one kind of photogenerated carriers, i.e. holes, participating in the redox reaction in D2S2O. The reaction of photogenerated carriers with water can be described as below: [37]

$$h^+ + H_2O \rightarrow \bullet OH + H^+ \qquad (1)$$

$$e^- + H_2O \rightarrow OH^- + \bullet H \qquad (2)$$

$$e^- + O_2 \rightarrow \bullet O_2^- \qquad (3)$$

$$\bullet O_2^- + H^+ \rightarrow HO_2\bullet \qquad (4)$$

$$2HO_2\bullet \rightarrow H_2O_2 + O_2 \qquad (5)$$

$$H_2O_2 + \bullet O_2^- \rightarrow \bullet OH + O_2 + OH^- \qquad (6)$$

$$H_2O_2 + e^- \rightarrow \bullet OH + OH^- \qquad (7)$$

As shown in formula (1) to (7), compared to electron, only one kind of radical was generated by the reaction of hole and water. Therefore the type of carriers could be confirmed through detecting species of radicals. ESR spectra of radical-DMPO (5, 5-dimethyl-1-pyrroline-N-oxide) adducts in water after UV irradiation also confirmed that hole was the sole carrier in D2S2O, as shown in Fig. S3. It also could be deduced that electron was the sole carrier in D2S4Zn.

Because of a small quantity of hole moved to the O polar surface, the total number of the carriers that participating in the reaction in D2S2Zn decreased compared to D1S1Zn, which would reduce the photocatalytic activity. However, as shown in Table 1, instead of reduction as estimating, the degradation percentage of D2S2Zn increases to almost double. We could see in device 1, as shown in Fig. 3c), Zn-polar surface inject holes and electrons into solution to generate large amount of initial radicals and derivatives. The initial radicals and derivatives can either participate in redox reaction, or recombine each other, the relationship of which can be treated as competition. Meanwhile, hydroxyl radical generated by holes from O polar surface also recombined with initial radicals and derivatives from Zn-polar surface. However in device 2, as shown in Fig. 3d), the radical were spatial separated because of isolated solution. Hydroxyl radical generated by holes from D2S2O and initial radicals and derivatives from D2S2Zn involved in photocatalytic degradation respectively. Without this part of recombination, the amount of initial radicals and derivatives that participating in redox reaction would increase naturally. As a consequence, compared to D1S1Zn, the degradation percentage of D2S2Zn increased remarkably although the total number of the carriers decreased. Similarly, we could understand why the degradation percentage of D2S4O was higher than D1S3O. To some extent, the reduction of the radicals recombination would have more positive effects on increasing photocatalysis efficiency than merely modifying material.

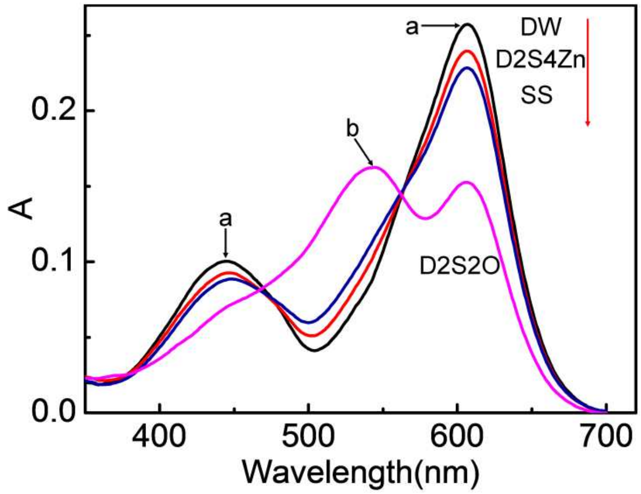

Fig 4. UV-vis spectrum of the complex of dithizone with Zn^{2+} in water in right compartment of device 2. The relative concentration of Zn^{2+} in the solution was calibrated by using the chloroform solution of dithizone as chromogenic reagent. The absorption peaks at 445 and 606 nm were assigned to dithizone, and the absorption peaks at 545 nm was assigned to the Zn^{2+}-dithizone complex. The controlled sample DW represented deionized water and SS represented saturated solution of ZnO.

From Table 1 we also could see that the degradation percentage of Zn-polar surface was larger than O polar surface under the same conditions. In our previous report, it is simply attributed to an electron dominated photocatalytic degradation process without a deeper discussion. Further study found that it was related to photocorrosion. During the photocatalytic degradation process, a part of photogenerated hole was consumed:

$$ZnO + 2h^{+} \rightarrow Zn^{2+} + \frac{1}{2}O_2 \qquad (8)$$

By detecting the concentration of Zn^{2+}, the extent of corrosion of different polar surface could be obtained. 2.5ml deionized water was trickled into four compartments of sample 2 and 4 and irradiated by UV for 2.5h. Chloroform solution of dithizone utilized as chromogenic reagent to calibrate the relative concentration of Zn^{2+}. The UV spectrum of the complex of Zn^{2+} with chromogenic reagent in the solution in D2S2O and D2S4Zn were shown in Fig. 4. Compared to the ZnO saturated solution, the concentration of Zn^{2+} in D2S2O increased while the D2S4Zn decreased. The holes were injected into solution by D2S2O, and therefore, Zn^{2+} came from hydrolysis of ZnO and photocorrosion. However, the electrons were injected into solution by D2S4Zn without any photocorrosion. Moreover, as shown in formula (3-7), the hydrolysis of ZnO was also suppressed by OH- that generated during the process of photocatalytic degradation and therefore the concentration of Zn^{2+} was lower than sample SS. The same result was shown in Fig. S4 . It is obvious that O polar surface was more likely to be photocorroded for abundance of holes under the action of E_p. The photocorrosion of ZnO during the photocatalytic degradation process is not a uniform photocorrosion but a crystal plane selective photocorrosion, which could be observed obviously in Fig. S5. As a consequence, the degradation percentage of Zn-polar surface was larger than O polar surface under the same conditions.

In conclusion, a new type of photocatalytic system was constructed based on the E_p of ZnO single crystal, where not only carriers but also radicals were spatial separated because of isolated solution and therefore suppressed the radical recombination. Utilizing this system, the impact of radical recombination on photocatalytic efficiency was studied for the first time. It is found that the photocatalytic activity of ZnO single crystal could be significantly improved through spatial separation of radicals. Single radical is found in one of isolated solution in the new system, which may give a convenient way to study the mechanism of photocatalytic reaction. Furthermore, a spontaneous polarization electric field induced crystal plane selective photocorrosion in ZnO single crystal was found for the first time. This result will help to design more efficient and more corrosion-resistant ZnO-based photocatalytic materials. On the other hand, the amount of electrons and holes that separated by E_p is very small due to the E_p of ZnO single crystal is small, which induced a very small separation of radicals. However, it was such a small change of radicals that increased the photocatalytic efficiency of ZnO single crystals to almost double. It seems in the conventional photocatalytic degradation system, only a small amount of radicals involved in the redox reaction while most of them recombined. We assume that the further research photocatalytic degradation should focus on how to avoid the radicals recombination.

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Notes and references

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1 Q. R. Zhao, Y. Xie, Z. G. Zhang and X. Bai, *Cryst. Growth Des.*, 2007, **7**, 153.

2 S. K. Joung, T. Amemiya, M. Murabayashi, K. Itoh, *Chem. -Eur. J.*, 2006, **12**, 5526.

3 C. Y. Sun , D. Zhao, C. C. Chen, W. H. Ma, J. C. Zhao, *Environ. Sci. Technol.*, 2009, **43**, 157.

4 I. Tsuji, H. Kato, H. Kobayashi, A. Kudo, *J. Am. Chem. Soc.*, 2004, **126**, 13406.

5 K. Maeda, M. Higashi, D. L. Lu, R. Abe, K. Domen, *J. Am. Chem. Soc.*, 2010, **132**, 5858.

6 R. Abe, M. Higashi, K. Domen, *J. Am. Chem. Soc.*, 2010, 132, 11828.

7 S. Zheng, W. J. Jiang, Y. Cai, D. D. Dionysiou, K. E. O'Shea, *Catal. Today.*, 2014, **224**, 83.

8 W. Kubo, T. Tatsuma, *J. Am. Chem. Soc*., 2006, **128**, 16034.

9 M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.,* 1995, **95**, 69.

10 A. L. Linsebigler, G. Lu, J. T. Yates, *Chem. Rev*., 1995, **95**, 735.

11 Y. H. Wang, F. Huang, D. M. Pan, B. Li, D. G. Chen, W. W. Lin, X. Y. Chen, R. F. Li, Z. Lin, *Chem. Commun*., 2009, **44**, 6783.

12 M. A. Henderson, *Surf. Sci. Rep.*, 2011, **66**, 185.

13 J. W. Tang, Z. G. Zou, J. H. Ye, *Angew. Chem. Int. Ed.*, 2004, **34**, 4463.

14 X. B. Chen, L. Liu, P. Y. Yu, S. S. Mao, *Science*, 2011, **6018**, 746.

15 P. V. Braun, P. Osenar, S. I. Stupp, *Nature*, 1996, **6572**, 325.

16 R. Abe, K. Shinmei, N. Koumura, K. Hara, B. Ohtani, *J. Am. Chem. Soc*., 2013, **45**, 16872.

17 Q. P. Lu, Z. D. Lu, Y. Z. Lu, L. F. Lv, Y. Ning, H. X. Yu, Y. B. Hou, Y. D. Yin, *Nano lett*., 2013, **11**, 5698.

18 Y. S. Jun, J. H. Park, S. U. Lee, A. Thomas, W. H. Hong, G. D. Stucky, *Angew. Chem. Int. Ed.*, 2013, **42**, 11083.

19 H. Kim, S. Shin, S. Lee, K. J. Shin, *J. Chem. Phys.*, 1996, **105**, 7705.

20 W. J. Jiang, J. A. Joens, D. D. Dionysiou, K. E. O'Shea, *J. Photochem. Photobiol. A: Chem.*, 2013, **262**, 7.

21 S. A. Rice, in Comprehensive Chemical Kinetics, Vol. 25. (Eds: C. H. Bamford, C. F. H. Tripper, and R. G. Compton), *Elsevier*, Amsterdam, 1985.

22 H. Iglev, M. K. Fischer, A. Gliserin, A. Laubereau, *J. Am. Chem. Soc.*, 2011, **133**, 790.

23 D. S. Muggli, L. Ding, *Appl. Catal. B: Environ*., 2001, **32**, 181.

24 D. D. Lin, H. Wu, R. Zhang, W. Pan, *Chem. mate*r., 2009, 21, 3479.

25 Y. C. Chen, Y. C. Pu, Y. J. Hsu, *J. Phys. Chem. C*, 2012, 116, 2967.

26 F. P. Yan, Y. H. Wang, J. Y. Zhang, Z. Lin, J. S. Zheng, F. Huang, DOI: 10.1002/cssc.201300818.

27 J. Y. Zhang, Y. H. Wang, J. Zhang, Z. Lin, F. Huang, J. G. Yu, *ACS Appl. Mater. Interfaces*, 2013, **5**, 1031.

28 J. Y. Zhang, Y. H. Wang, J. Zhang, Z. Lin, F. Huang, J. G. Yu, *ACS Appl. Mater. Interfaces*, 2013, **5**, 10317.

29 Y. Chen, H. Zhao, B. Liu, H. Q. Yang, *Appl. Catal. B-Environ*.,2015, **163**, 189

30 S. G. Kumar, K. S. R. K. Rao, *RSC adv.,*2015, **5**, 3306.

31 W. W. Lin, D. G. Chen, J. Y. Zhang, Z. Lin, J. K. Huang, W. Li, Y. H.Wang, F. Huang, *Cryst. Growth Des.,* 2009, **9**, 4378.

32 R. T. Sapkal, S. S. Shinde, T. R. Waghmode, S. P. Govindwar, K. Y. Rajpure, C. H. Bhosale, *J. Photoch. Photobio. B*, 2012, **110**, 15.

33 Z. Zhan, Y. H. Wang, Z. Lin, J. Y. Zhang, F. Huang, *Chem. Commun.*, 2011, **47**, 4517.

34 J. M. Khoshman, M. E. Kordesch, *Thin Solid Films*, 2007, 515, 7393.

35 A. Wander, F. Schedin, P. Steadman, A. Norris, R. McGrath, T. S. Turner, G. Thornton, N. M. Harrison, *Phys. Rev. Lett.*, 2001, **86**, 3811.

36 C. Wöll, *Prog. Surf. Sci.*, 2007, **82**, 55.

37 M. V. Rao, K. Rajeshwar, V. R. P. Verneker, J. D. Bow, *J. Phys. Chem.*, 1980, **84**, 1987.