Accepted Manuscript

Title: Enhanced photocatalytic activity induced by sp^3 to sp^2 transition of carbon dopants in BiOCl crystals

Authors: Jianguo Sun, Sujuan Wu, Shi-Ze Yang, Qi Li, Jiawei Xiong, Zhenzhong Yang, Lin Gu, Xixiang Zhang, Lidong Sun

PII: S0926-3373(17)30876-7
DOI: <http://dx.doi.org/10.1016/j.apcatb.2017.09.037>
Reference: APCATB 16044

To appear in: *Applied Catalysis B: Environmental*

Received date: 10-7-2017
Revised date: 31-8-2017
Accepted date: 16-9-2017

Please cite this article as: {<http://dx.doi.org/>}

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Enhanced photocatalytic activity induced by sp^3 to sp^2 transition of carbon dopants in BiOCl crystals

Jianguo Sun[†], Sujuan Wu^{†,‡,*}, Shi-Ze Yang[‡], Qi Li[†], Jiawei Xiong[†], Zhenzhong Yang[§],
Lin Gu[§], Xixiang Zhang[†], Lidong Sun^{†,*}

[†]Electron Microscopy Center of Chongqing University, College of Materials Science and Engineering, Chongqing 400044, China

[‡]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

[§]Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

[†]King Abdullah University of Science and Technology (KAUST), Division of Physical Science and Engineering, Thuwal 23955-6900, Saudi Arabia

Corresponding Authors

* E-mail: sujuan.wu@cqu.edu.cn, lidong.sun@cqu.edu.cn

Graphical abstract

The transition of carbon dopants from sp^3 to sp^2 hybridization and the enhancement in photocatalytic activity under visible light.

Highlights

- Carbon atoms are doped into BiOCl crystals via glucose treatment.
- The carbon dopants exhibit a transition from sp^3 to sp^2 hybridization at elevated temperature.
- The increased content of sp^2 hybridization facilitates charge separation and hole transport.
- One order of enhancement in photocatalytic activity is achieved upon the transition toward phenol degradation under visible light.

ABSTRACT: The insufficient light absorption and low quantum efficiency limit the photocatalytic performance of wide bandgap semiconductors. Here, we report a facile strategy to engineer the surface disordered defects of BiOCl nanosheets via carbon doping. The surface defects boost the light absorption and also the quantum yields, as the doped carbon atoms exhibit a transition from sp^3 to sp^2 hybridization at elevated temperature, corresponding to a change of assembly state from 3D cluster to 2D graphite-like structure. This transition results in an effective charge separation and thus one order of enhancement in photocatalytic activity toward phenol degradation under visible light. The current study opens an avenue to introduce sp^3 to sp^2 transition of carbon dopants for simultaneous increment of light absorption and quantum efficiency for application in photocatalysis and energy conversion.

KEYWORDS: Photocatalysis, BiOCl, Carbon doping, Surface defects engineering, 2D materials

1. Introduction

An efficient photocatalytic activity is dominated, to a large extent, by the light harvesting ability and charge separation process in a semiconductor [1]. Bismuth oxychloride (BiOCl) nanocrystals with layered structure exhibit impressive photocatalytic performance and hence attract extensive attention in the past decade [2-5]. Nevertheless, the photocatalysis can only be driven by ultraviolet light because of the large bandgap energy ($E_g=3.45$ eV for intrinsic BiOCl [6]). As such, enormous efforts have been devoted to narrowing the bandgap energy by doping metal [7,8] or nonmetal [9,10] impurities for improved light harvesting. This usually extends the light response into the visible region with enhanced photocatalytic activity [11-15]. However, it is on the other hand still limited by the charge separation process. Considering the layered structure of BiOCl crystals and the established electric field within each single layer, doping would be possible to maintain the electric field within

each layer meanwhile enhance the electronic coupling between the layers. This in turn gives rise to narrowed bandgap energy and promoted charge separation simultaneously. Besides, surface defects engineering is an effective strategy to tune the surface states that affect the charge separation during the photocatalysis [1, 16]. The surface states can trap the photogenerated electrons or holes and thus suppress the recombination. This yields intriguing photocatalytic performance [17, 18]. Therefore, engineering the surface disordered defects in a good manner is capable of enhancing the light absorption and meanwhile facilitating the charge separation for efficient photocatalysis.

In this study, surface disorders are introduced into bismuth oxychloride nanosheets by glucose treatment. Both the experimental results and density functional simulations indicate that surficial chlorine atoms are partially replaced by the carbon dopants (C_{Cl}). The resulting $BiOCl$ nanosheets exhibit strong visible light absorption and significantly enhanced photocatalytic activity toward phenol degradation. Moreover, it is found that the transition from sp^3 to sp^2 hybridization of the carbon dopants at elevated temperature, resulting in further improvement of the photocatalytic activity. These findings pave ways for developing efficient photocatalysts by engineering the surface disordered defects.

2. Experimental

2.1 Preparation of $C-BiOCl$ powders

All of the reagents were analytical grade without further purification. 5 g Bi_2O_3 was dissolved in 20 mL 37% hydrochloric acid under vigorous stirring for 5 min. Then, the solution was evaporated at 350 °C, and white precipitates were obtained by adding 200 mL deionized water. Subsequently, the resulting precipitates were annealed at 400 °C for 4 h to acquire pure bismuth oxychloride powders. For carbon doping, the $BiOCl$ powders and glucose were mixed with a mole ratio 7:5, and annealed at 160 °C, 180 °C, 200 °C and 220 °C under Ar (purity, 99.99%) protection. When the annealing temperature exceeded 220 °C, Bi metals were formed. Accordingly, the annealing temperature was controlled under 220 °C in this study. After washing with

deionized water, the carbon-doped BiOCl (C-BiOCl) powders were attained. For comparison, the glucose alone was annealed at 220 °C under Ar protection to get carbon powders. The obtained carbon and BiOCl powders were mixed together with a mole ratio of 1:1, and then dispersed in alcohol by ultrasonication for 30 min. The solution was left for 12 h to attain carbon adsorbed BiOCl (C@BiOCl) powders.

2.2 Characterization

X-ray diffraction (XRD) patterns were recorded by an Empyrean X-ray diffractometer with monochromatic Cu K α radiation ($\lambda=1.5418$ Å). Scanning transmission electron microscopy (STEM) images were collected using an FEI Titan 80-300 Super Twin electron microscope operated at 200 kV and Nion Ultra STEM 200 with sub-Ångstrom resolution at 200 kV. Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) were collected by using a field emission JEOL-SEM (JSM-7800F) equipped with energy spectrometer. X-ray photoelectron spectra (XPS) were carried out with the Thermo ESCALAB 250Xi system with Al K α ($h\nu = 1486.6$ eV) as the excitation source. Raman spectra were recorded in the region of 40-2000 cm $^{-1}$ using a confocal Laser Micro-Raman Spectrometer (LabRAM HR Evolution) with a laser of 532 nm and 10 mW. The optical absorption spectra were measured from 240 to 800 nm using Shimadzu UV-2100 UV-Vis spectrophotometer.

2.3 Photocatalytic Measurements

The visible light driven photocatalytic activity was evaluated by photocatalytic degradation of 15 mg/L Phenol under 500 W Xe lamp with an ultraviolet cutoff filter ($\lambda>420$ nm). In a typical process, 50 mg photocatalysts were dispersed into 100 mL and 15 mg/L phenol solution. Prior to illumination, the solution was continuously stirred for 1 h at 800 rpm in dark to establish the adsorption-desorption equilibrium. Then the concentration of phenol was measured to monitor the photocatalytic degradation by UV-Vis Spectrophotometer (Shimadzu UV-2100).

2.4 Electrochemical Measurements

The electrochemical experiments were carried out with a CHI 660E electrochemical system using a constructed three-electrode system. A Pt plate

(0.5×0.5 cm²) was used as a counter electrode and saturated calomel electrode was used as a reference electrode. As-prepared powders of 0.01 g were uniformly self-deposited onto an ITO glass with an area of 1.1×1.3 cm² and employed as the working electrode. The solution of 0.1 mol/L Na₂SO₄ was used as the electrolyte and a 500 W Xe lamp with a cutoff filter ($\lambda > 420$ nm) was utilized as the visible light source. Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency between 1 Hz and 1 MHz in Na₂SO₄ (0.5 mol/L) solution, which was performed at an open circuit potential with 5 mV amplitude of the sinusoidal wave.

2.5 Computational Methods

Density function theory (DFT) calculations were performed using the projected augmented wave method (PAW) [19, 20] as implemented in Vienna ab initio simulation package (VASP) [21, 22]. For the structural relaxation and electronic structure calculations, generalized gradient approximation (GGA) method was used with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [23]. The wave-plane cutoff energy was 520 eV and a regular Monkhorst-Pack grid of 6×6×4 points were used in all of the calculations. A 2×2×2 supercell was used in the simulation. The convergence criteria for structural optimization and energy on each atom were set to 0.01 eV/Å and 10⁻⁴ eV, respectively. A GGA+U method was adopted in calculation of density of states. The U values were set to 4.8 eV for the p-states of Bi and O, 7 eV for the p-states of Cl.

3 Results And Discussion

3.1 Crystal structure analysis

Figure 1. Detailed XRD patterns of (001), (200) and (104) peaks (a-c) and corresponding Raman spectra (d-e) of pure and carbon-doped BiOCl powders prepared at different temperatures.

BiOCl nanosheets with an average thickness of about 120 nm were prepared via solvothermal method. The nanosheets were subsequently reduced through glucose treatment. Scanning electron microscopy (SEM) images reveal that no obvious morphological changes appear after reduction of BiOCl (see Figure S1 in the Supporting Information). The incorporation of carbon atoms through glucose reduction is confirmed by the energy dispersive X-ray spectroscopy measurement (see Figure S2 and Table S1 in the Supporting Information), where the main compositions are Bi, O and Cl elements. To confirm the carbon doping, X-ray diffraction measurements were performed. Figure S3 shows that the BiOCl nanosheets remain tetragonal structure (JCPDS No.85-0861) after glucose treatment, while no impurity phases (e.g., graphite) are observed. However, detailed observation (Figure 1a-1c) discloses that, upon glucose treatment, the (001) peak shifts to smaller angle, whereas the (200) and (104) peaks shift to larger angle as the annealing temperature increases. The shift of (001), (200), (104) peak is about 0.10° , 0.11° , 0.08° , respectively, which

is much larger than the instrument error of about 0.02° (see Figure S4). This demonstrates that the crystal lattice has an anisotropic distortion along different directions. The magnitude of lattice expansion is determined to be about 1% along the [001] direction. This is much smaller than ~5% for a perfect intercalation of carbon dopants between the [Cl-Bi-O-Bi-Cl] units, as computed by simulations (see Figure S5 in the Supporting Information). Instead, it is consistent with the case that the C dopants substitute the Cl terminals, resulting in a distortion of ~1.3%. This suggests that carbon atoms are doped into the BiOCl lattice by replacing partial of the Cl terminals in the [Cl-Bi-O-Bi-Cl] units.

Raman spectra were employed to further examine the microstructure of the carbon-doped BiOCl (C-BiOCl) crystals. Figure 1d displays three characteristic peaks at 58.3, 142.6 and 199.5 cm^{-1} for each condition, which are assigned to the A_{1g} internal, the E_g external and internal Bi-Cl stretching modes in BiOCl crystals, respectively [24]. As the annealing temperature increases, the intensity of internal Bi-Cl stretching peak decreases and almost disappears at 220°C , indicating the breaking of Bi-Cl bonds. This reveals that partial of the Cl atoms are removed during the reduction reaction, in good agreement with the substitution of Cl terminals with C dopants. More importantly, another four peaks at 1310, 1439, 1560 and 1654 cm^{-1} arise upon glucose treatment, as shown in Figure 1e. The peaks at around 1310 and 1560 cm^{-1} are associated with the disordered (D-band) and graphitic carbon (G-band) [25], respectively. Red shifts up to $\sim 40\text{ cm}^{-1}$ and $\sim 20\text{ cm}^{-1}$ are observed for the D and G bands, as the annealing temperature increases. This can be attributed to the interactions between carbon atoms and BiOCl [26, 27], in line with the lattice distortion observed by the peak shift in the XRD patterns. The band at 1654 cm^{-1} (D' band) originates from the vibrational mode induced by the formation of nano-crystalline or defect graphitic carbon [28, 29]. The band at 1439 cm^{-1} is a special Raman-active phonon mode related to the vibrations of pentagonal rings in fullerenes [30]. In general, the formation of fullerenes requires either high temperature or ultrahigh pressure [31, 32]. These two bands are usually absent in common graphene, graphite, and diamond-like carbon materials, while their presence herein implies the

abnormal environment that the carbon atoms encounter. This could only be achieved by the constraint from the BiOCl lattice, echoing the structure that the carbon dopants replace the Cl terminals in the [Cl-Bi-O-Bi-Cl] unit and are thus confined between neighboring units. Besides, it is also found that the intensity of the peak ratio I_G/I_D exhibits a drastic increment between 180 and 220 °C, as is discussed later.

Figure 2. X-ray photoelectron spectroscopy results of BiOCl and C-BiOCl annealed at 220 °C. (a) C 1s core level, (b) Bi 4f core level, (c) valence band.

Chemical states of the BiOCl before and after glucose treatment were examined with X-ray photoelectron spectroscopy (XPS), as shown in Figure 2. The C1s spectrum can be deconvoluted into three peaks upon glucose treatment. The peak at 284.6 eV can be assigned to -C-C bands, while another two additional peaks at 287.3 eV and 286.1 eV are attributed to -C-O-C and -O-C bands, respectively [33, 34]. The Bi4f spectrum can be deconvoluted into two pairs of doublets, with those at 164.7 eV and 159.4 eV being ascribed to the Bi^{3+} in stoichiometric BiOCl. The emerging pairs at 164.2 eV and 158.9 eV are attributed to a lower chemical state of bismuth ions, which may originate from the bonding between carbon and Bi [4, 35]. This further supports the microstructure that partial of the chlorine terminals are replaced by carbon atoms because of doping. Considering the coordination feature of the Bi ions in a BiOCl bulk, where one Bi^{3+} ion is coordinated to four chlorine elements with a distance of 3.06 Å and four oxygen elements with a distance of 2.32 Å, the longer Bi-Cl bonds tend to break off and are thus replaced by Bi-C bonds. Figure 2c reveals that the valence band maximum shifts from 2.44 eV to 1.75 eV upon doping. This agrees well with the calculated density of states for carbon-doped BiOCl (see Figure

S6 in the Supporting Information). The carbon doping via replacing the chlorine terminals gives rise to defect levels near the valence band maximum, hence facilitating the hole transport in the BiOCl crystals.

Figure 3. Atomic-resolution HAADF-STEM images of the (001) (a, c) and (010) (b, d) facets for pure BiOCl (a, b) and C-BiOCl annealed at 220 °C (c, d).

Atomic-resolution high-angle annular dark field (HAADF) scanning transmission electron microscopy images show that the pure BiOCl nanosheets are well crystallized without any lattice distortion at both (001) and (010) facets, as displayed in Figure 3a and 3b. In contrast, upon glucose treatment, the peripheral region of the (001) facets become disordered (Figure 3c). However, the central region remains unchanged as evidenced by the same lattice spacing of 0.275 nm for both (100) and (010) planes. Obvious distortion occurs at the (010) facets (Figure 3d), where the outmost layers are almost destroyed, as a result of carbon doping. This indicates that surface disorders are introduced into the BiOCl crystals at the (010) facets via carbon doping. The dopants replace partial of the chlorine terminals in the [Cl-Bi-O-Bi-Cl] unit, and are thus confined between neighboring units. This induces the lattice expansion along the [001] direction (see XRD patterns in Figure 1), the emerging

Bi-Cl vibration modes because of lattice confinement (see Raman spectra in Figure 1), and the binding energy shift toward lower end for Bi4f (see XPS spectra in Figure 2). Such a doping incorporates defect levels close to valance band maximum, therefore narrowing the bandgap energy and facilitating charge separation as well as hole transport.

3.2 Visible light Photocatalysis Analysis

Figure 4. UV-Vis diffuse reflection spectra (a), transient photocurrent generation (b), photocatalytic degradation of phenol under visible light (c), and kinetic fit for phenol degradation under visible light illumination (d). Insets in (a) are corresponding photographs of different BiOCl powders.

The photocatalytic property of the carbon-doped BiOCl is evaluated by degradation of colorless phenol under visible light illumination at $\lambda > 420 \text{ nm}$. Figure 4a shows that the pristine BiOCl exhibits negligible absorption in visible light region, because of the large bandgap. In contrast, substantial increment in absorption is achieved upon incorporating the surface disorders and carbon doping, which enhances with the treatment temperature. This is attributed to the narrowed bandgap energy from 2.99 to

2.26 eV (estimated based on Tauc plots in Figure S7). Figure 4b displays that a very small photocurrent of 0.2×10^{-7} A/cm² is produced with the pristine BiOCl, due to the limited absorption in visible region. The photocurrent is substantially enhanced upon carbon doping and increased gradually with elevated temperature. The C-BiOCl annealed at 220 °C exhibits the largest photocurrent of about 2.7×10^{-7} A/cm², an order of enhancement as compared to the pristine BiOCl. As a consequence, the pure BiOCl renders no obvious degradation of phenol under visible light, while all of the carbon-doped BiOCl present impressive degradation rate under the same conditions, as compared in Figure 4c and 4d. For comparison, control samples with carbon adsorbed onto the surface of BiOCl powders (referred to as C@BiOCl) were also prepared and used for degradation of phenol under the same conditions. Although the C@BiOCl exhibits similar absorption as the C-BiOCl annealed at 220 °C, it shows negligible photocatalytic degradation of phenol neither, this further verifies that the excellent visible light photocatalytic activity of C-BiOCl indeed originates from doped carbon atoms. Based on the previous reports, superoxide radicals ($\text{O}_2^{\cdot-}$) and holes (h^+) from carbon doped BiOCl play a key role in such a photocatalytic process [12].

Table 1. Raman peak intensity of D and G bands for C-BiOCl prepared at different temperatures

	I_D	I_G	I_G / I_D
160 °C	1099.11	540.12	0.49
180 °C	1098.59	540.59	0.49
200 °C	212.18	248.93	1.17
220 °C	96.51	179.26	1.86

Very interestingly, about 40% of the phenol is degraded after 120 min using C-BiOCl powders annealed at 160 or 180 °C, whereas approximately 80% is achieved with those annealed at 200 or 220 °C, more than twice enhancement in the

degradation rate. This is closely related to the I_G/I_D ratio, which exhibits a dramatic increase between 180 and 220 °C (See Table 1). In general, the D-band corresponds to the breathing vibrations of sp^3 carbon, whereas the G-band is assigned to the in-plane vibrational motion of sp^2 carbon [30]. The increased ratio of I_G/I_D demonstrates an abrupt increment in sp^2 content upon annealing at 200 or 220 °C, accompanied by the transition of carbon states from three-dimensional (3D) to two-dimensional (2D) assembly. In other words, the carbon dopants change from 3D clusters to 2D graphite-like structure above a critical temperature, driven by the high pressure imposed by the lattice confinement with the assistance of elevated temperature. Such an increase in sp^2 content provides more unsaturated π bonds, thus promoting the charge separation and facilitating the hole transport in BiOCl crystals during photocatalytic reactions. This is justified by the lower transfer resistance at BiOCl/electrolyte interface (see EIS results in Figure S8) and higher photocurrent generation with high sp^2 content. According to the results obtained in this study, it is believed that, in principle, the photocatalytic activity of C-BiOCl will be enhanced when all of the sp^3 are completely converted to sp^2 , as the sp^2 hybridization promotes the charge separation and facilitates the hole transport in the crystals. However, in practice further increment in I_G/I_D ratio is limited by the formation of bismuth (Bi) and bismuth oxides (Bi_2O_3) particles with elevated temperature above 220 °C, as shown in Figure S9. As such, the highest I_G/I_D ratio of 1.86 is achieved at 220 °C with best photocatalytic performance in this study. Besides, it is also difficult to fully convert the sp^3 hybridization to sp^2 , as the carbon atoms interact with the BiOCl crystals. This results in defects in the assembled sp^2 state, thus tends to exist as sp^3 hybridization state [36].

Figure 5. Schematic illustration of the transition of carbon dopants from sp^3 to sp^2 hybridization in BiOCl crystal with elevated temperature.

Based on the above results, the formation and transition process of carbon doping is illustrated in Figure 5. In the process of glucose treatment, the glucose molecules are adsorbed on the BiOCl surface first, and the carbonaceous species block and stabilize the implanted carbon atoms. The lattice has a self-purification effect [37], resulting in doping only within the surface layer. With the increasing temperature, carbon atoms energetically prefer to substitute Cl terminals in each [Cl-Bi-O-Bi-Cl] unit, leading to the lattice expansion along the [001] direction. Meanwhile, carbon dopants are confined between the [Cl-Bi-O-Bi-Cl] units, causing the transformation from sp^3 to sp^2 hybridization with the assistance of elevated temperature. Such a transition enhances the charge separation process and accelerates the hole transport, thus benefiting the photocatalytic activity.

4. Conclusion

In this study, surface disorders are introduced into BiOCl crystals by carbon doping at the (010) facets, where the chlorine terminals in each [Cl-Bi-O-Bi-Cl] are replaced by carbon dopants. Meanwhile, a transition from sp^3 to sp^2 hybridization occurs for the dopants at elevated temperature, corresponding to a transition of assembly state from 3D clusters to 2D graphite-like structure. This significantly increases the photocatalytic activity toward phenol degradation under visible light, i.e., from 38.9×10^{-4} to $134.7 \times 10^{-4} \text{ min}^{-1}$. It is attributed to the enhanced visible light absorption and promoted charge separation. This study sheds light on manipulating the sp^2

transition of dopants for designing high performance semiconductors toward application in photocatalysis and energy conversion.

Acknowledgment

We gratefully acknowledge the helpful and informative discussion with Prof. Zhipan Li, Dr. Yuan Yuan and Mr. Yuqi Zhang. This work was supported by the National Natural Science Foundation of China (No.51302329, 51501024) and the Fundamental Research Funds for the Central Universities (No.106112015CDJXY130010, 106112016CDJZR135506). The electron microscopy (S.Z.Y.) was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division. This research used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. This work used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation Grant No ACI-1053575 and Grant No DMR160118.

Appendix A. Supplementary data

Supporting Information: SEM images and corresponding EDS mapping of pure and carbon-doped BiOCl. XRD pattern, UV-vis spectra and electrochemical impedance spectra of pure and carbon-doped BiOCl. The XRD patterns of silicon wafer for the (111), (220), (311) peaks of standard Silicon sample. The XRD patterns of C-BiOCl annealing at 240 °C. The structure simulation results and Density of States calculation of pure BiOCl and carbon intercalated BiOCl. Table of Elemental contents (at.%) in pure and carbon-doped BiOCl. The Supplementary data associated with this article can be found in the online vision.

References

- [1] Chen, X., Liu, L., Peter, Y. Y., Mao S. S. *Science* 331 (2011) 746-750.
- [2] Zhang, K., Liu, C., Huang, F., Zheng, C., Wang, W. *Appl Catal B-Environ* 68 (2006) 125-129.
- [3] Cheng, H., Huang, B., Dai, Y. *Nanoscale* 6 (2014) 2009-2026.
- [4] Ye, L., Deng, K., Xu, F., Tian, L., Peng, T., Zan, L. *Phys. Chem. Chem. Phys.* 14 (2012) 82-87.
- [5] Jiang, J., Zhao, K., Xiao, X., Zhang L. Z. *J. Am. Chem. Soc.* 134 (2012) 4473-4479.
- [6] Liu, X., Su, Y., Zhao, Q., Du, C., Liu, Z. *Scientific Reports* 6 (2016).
- [7] Giordano, F., Abate, A., Baena, J. P. C., Saliba, M., Matsui, T., Im, S. H., Graetzel, M. *Nat. Commun* 7 (2016).
- [8] Yang, Y., Fan, X. L., Pan, R., Guo, W. J. *Phys. Chem. Chem. Phys* 18 (2016) 10152-10157.
- [9] Chen, X., Burda, C. *J. Am. Chem. Soc.* 130 (2008) 5018-5019.
- [10] Zheng, Y., Jiao, Y., Ge, L., Jaroniec, M., Qiao, S. Z. *Angew Chem Int Ed* 125 (2013) 3192-3198.
- [11] Yu, J., Wei, B., Zhu, L., Gao, H., Sun, W., Xu, L. *Appl. Surf. Sci.* 284 (2013) 497-502.
- [12] Di, J., Xia, J., Ji, M., Wang, B., Yin, S., Zhang, Q., Li, H. *ACS Appl. Mater. Inter* 7 (2015) 20111-20123..
- [13] Xia, J., Xu, L., Zhang, J., Yin, S., Li, H., Xu, H., Di, J. *Cryst Eng Comm* 15 (2013) 10132-10141.
- [14] Jiang, Z., Liu, Y., Jing, T., Huang, B., Wang, Z., Zhang, X. Dai, Y. *RSC Advances* 5 (2015) 47261-47264.
- [15] Li, J, Zhao, K., Yu, Y., Zhang, L. Z. *Adv. Funct. Mater.* 25 (2015) 2189-2201.
- [16] Yu, X., Kim, B., Kim, Y. K. *ACS Catalysis* 3 (2013) 2479-2486.
- [17] Chen, X., Liu, L., Liu, Z., Marcus, M. A., Wang, W. C., Oyler, N. A., Guo, J. *Scientific reports* 3 (2013) 1510.

- [18]Lu, J., Dai, Y., Jin, H., Huang, B. *Phys. Chem. Chem. Phys.* 3 (2011) 18063-18068.
- [19]Blöchl, P. E. *Phys. Rev. B* 50 (1994) 17953.
- [20]Kresse, G.; Joubert, D. *Phys. Rev. B* 59 (1990) 1758.
- [21]Kresse, G.; Furthmüller, J. *Comput. Mater. Sci.* 6 (1996) 15-50.
- [22]Kresse, G.; Furthmüller, J. *Phys. Rev. B* 54 (1996) 11169.
- [23]Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* 77 (1996) 3865.
- [24]Davies, J E D. *J. Inorg. Nucl. Chem.* 35 (1973) 1531-1534.
- [25]Ferrari, A. C., Meyer, J. C., Scardaci, V., Casiraghi, C., Lazzeri, M., Mauri, F., Geim, A. K. *Phys Rev Lett* 97 (2006) 187401.
- [26]Huang, M., Yan, H., Heinz, T. F., Hone, J. *Nano Lett* 10 (2010) 4074-4079.
- [27]Gong, L., Kinloch, I. A., Young, R. J., Riaz, I., Jalil, R., Novoselov, K. S. *Adv. Mater.* 22 (2010) 2694-2697.
- [28]Nemmannich, R. *J. Phys Rev B* 20 (1979) 392-420.
- [29]Oliveira, M. H., Schumann, T., Gargallo-Caballero, R., Fromm, F., Seyller, T., Ramsteiner, M., Trampert, A., Geelhaar, L., Lopes, J. M. J., Riechert, H. *Carbon* 56 (2013) 339-350.
- [30]Saito, R., Hofmann, M., Dresselhaus, G., Jorio, A., Dresselhaus, M. S. *Adv Phys* 60 (2011) 413-550.
- [31]Blank, V. D., Denisov, V. N., Kirichenko, A. N., Kulnitskiy, B. A., Martushov, S. Y., Mavrin, B. N., Perezhogin, I. A. *Nanotechnology* 18 (2007) 345601.
- [32]Lau, D. W., McCulloch, D. G., Marks, N. A., Madsen, N. R., Rode, A. V. *Phys Rev B* 75 (2007) 233408.
- [33]Akhavan, O., Ghaderi, E., Aghayee, S., Fereydooni, Y., Talebi, A. *J. Mater. Chem* 22 (2012) 13773-13781.
- [34]Xu, C., Wang, X., Zhu, J. J. *Phys. Chem. C* 112 (2008) 19841-19845.
- [35]Yu, Y., Cao, C., Liu, H., Li, P., Wei, F., Jiang, Y., Song, W. *J. Mater. Chem. A* 2 (2014) 1677-1681.

- [36]L. G. Cançado, A. Jorio, E. H. Martins Ferreira, F. Stavale, C. A. Achete, R. B. Capaz, M. V. O. Moutinho, A. Lombardo, T. S. Kulmala, A. C. Ferrari. *Nano Lett* 11 (2011), 3190-3196.
- [37]Chen, D., Viswanatha, R., Ong, G. L., Xie, R., Balasubramanian, M., Peng, X. *J. Am. Chem. Soc.* 131 (2009) 9333-9339.