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Efficient Photocatalytic Reduction of Aqueous Cr(VI) over Porous BNNSs/TiO_2 Nanocomposites under Visible Light Driven

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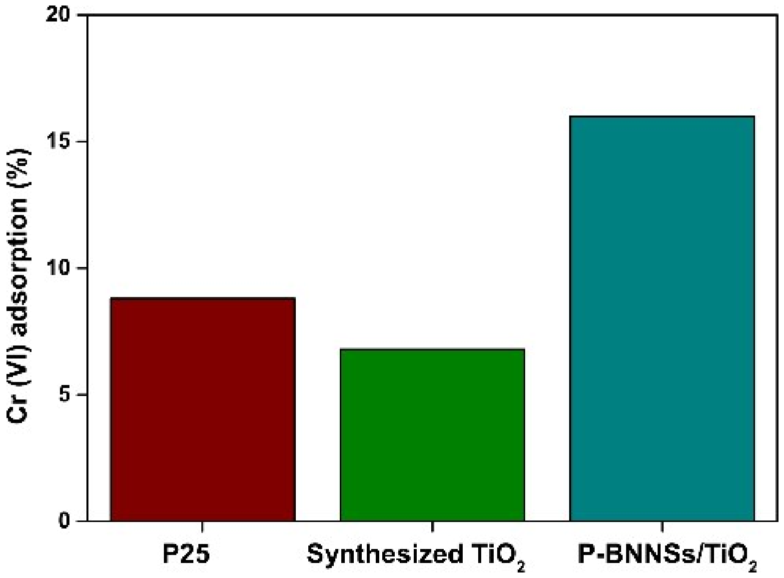

Figure S1. (a) Cr(VI) adsorption percentage by P25, synthesized TiO_2 and P-BNNSs/TiO_2 composites in the dark condition for 1 h. (The concentration of Cr(VI) solution was 25 mg L^{-1}; the quantity of TiO_2 was maintained at 25 mg).

As shown in Figure S1, after stirring the Cr(VI) solutions with P25, synthesized TiO_2 and P-BNNSs/TiO_2 composites, respectively, in dark condition for 1 h. Cr(VI) adsorption percentage on P-BNNSs/TiO_2 composites almost twice the figure for both synthesized TiO_2 and P25. Given that the photo reaction species are mainly located on the surface of photocatalysts, higher Cr(VI) adsorption increased the contact of Cr(VI) and photo reaction species, hence facilitating the Cr(VI) reduction.

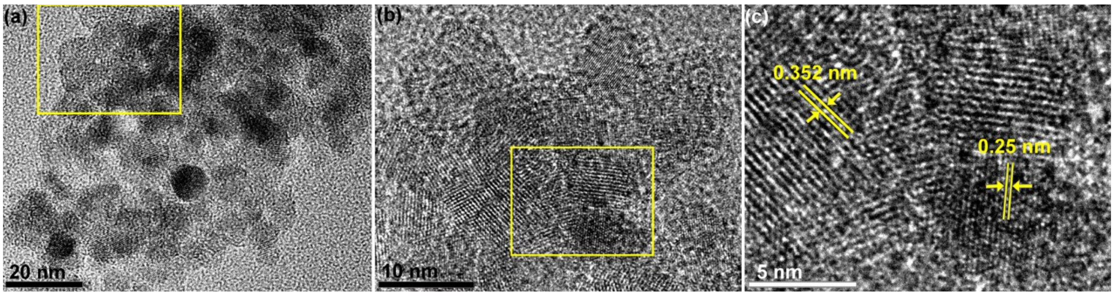

Figure S2. (a) TEM and HRTEM images of the P-BNNSs/TiO_2 composites after photocatalytic reduction of Cr(VI); (c) is the enlarge image of the rectangular area in (b).

It can be seen from Figure S2a that after the photocatalytic reduction of Cr(VI), the P-BNNSs/TiO_2 composites are densely decorated with a number of particles. These particles are either the loaded TiO_2 nanoparticles or the adsorbed Cr_2O_3, which were confirmed by the (101) plane of anatase TiO_2 with a lattice spacing of 0.352 nm and (110) plane of Cr_2O_3 with a lattice spacing of 0.25 nm, respectively (Figure S2c).

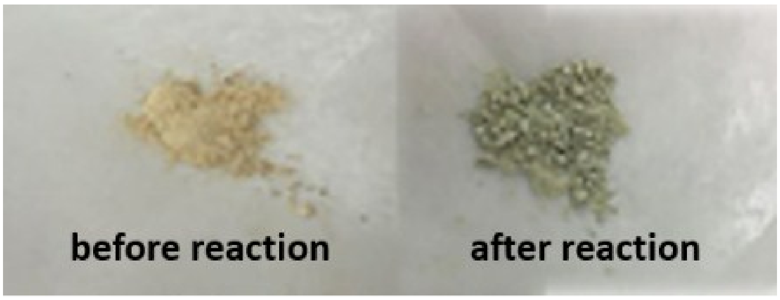

Figure S3. The color of P-BNNSs/TiO_2 composites before and after Cr(VI) photocatalytic reduction.

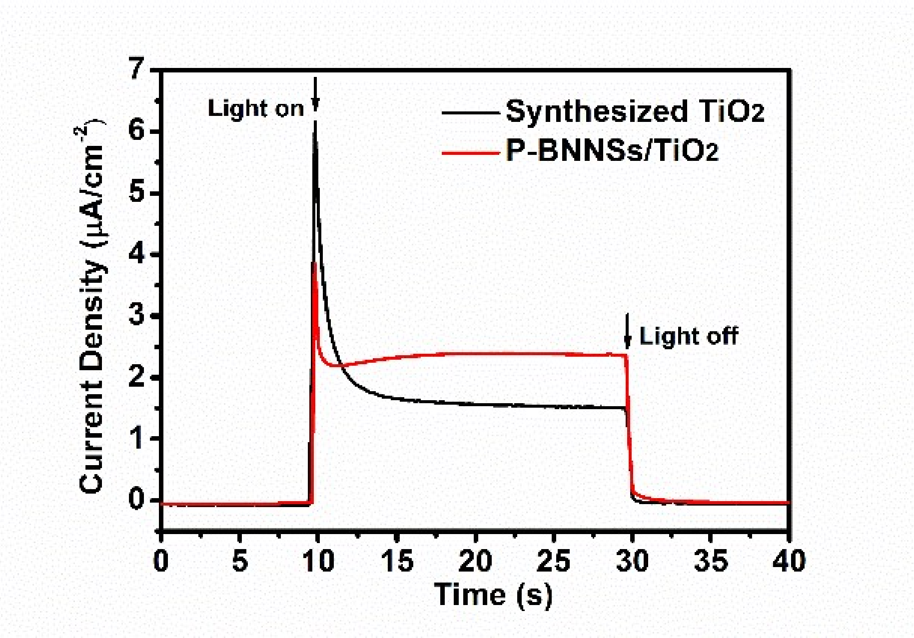

Figure S4. Photocurrent responses of synthesized TiO_2 and P-BNNSs/TiO_2 composites under simulated solar light irradiation.

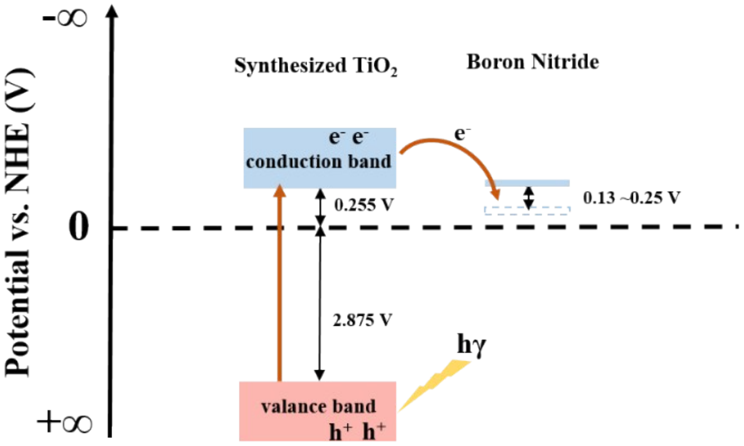

Figure S5. Schematic illustrations for electron transfer from TiO_2 nanoparticles to porous BNNSs.

The band structure of the synthesized TiO_2 was obtained using the followed Equation (1) – (3):

$$X= [x (A)^{a} x (B)^{b} x(C)^{c} x (D)^{d}]^{1/(a+b+c+d)} \tag{1}$$

$$E_{CB}=X-0.5E_g-E_e \tag{2}$$

$$E_{VB}= E_{CB} + E_g \tag{3}$$

Where E_{VB} and E_{CB} are the valence band (VB) and conduction band (CB) edge potential, respectively. E_e is the energy of free electrons vs. normal hydrogen electrode (NHE) (4.5 V) and Eg is the band gap energy of a semiconductor. X is the absolute electronegativity of semiconductor (a, b, c and d are the atomic number of compounds). Based on the band gap of synthesized TiO_2 obtained from the Tauc plot, the valence and conduction band potentials of synthesized TiO_2 can be obtained. Specifically, the conduction and valence band of synthesized TiO_2 were determined as -0.255 eV and 2.875 eV, respectively. These values are similar to the previously reported results of anatase TiO_2.[1]

Although it is still unclear of the conduction band potential of BN, calculations showed that conduction band of semi-hydrogenated h-BN monolayered nanosheets (-0.25 V vs. NHE) is similar to that of anatase TiO_2. Previous research also revealed that BN can yield O_2^- in water thus concluded that the conduction band potential of BN should be negatively greater than the O_2/O_2^- reduction potential, which is -0.13 V (vs. NHE). In this regard, conduction band potential of BN was summarized to lie between -0.13 V (vs. NHE) and -0.25 V (vs. NHE). [2] In terms of synthesized TiO_2, its conduction band potential is 0.255 V (vs. NHE), higher than the conduction band potential of BN as mentioned above. Therefore, the transfer of photo-induced electrons from TiO_2 to porous BNNSs is thermodynamically feasible. The transfer process is presented in Figure S5. The achievable electron transfer can promote the charge transfer and inhibit the electron-hole recombination.

References

[1] Q. Huang, S. Tian, D. Zeng, X. Wang, W. Song, Y. Li, W. Xiao, C. Xie, ACS Catal. 3 (2013) 1477-1485.
[2] Y. Ide, K. Nagao, K. Saito, K. Komaguchi, R. Fuji, A. Kogure, Y. Sugahara, Y. Bando, D. Golberg, Phys. Chem. Chem. Phys. 18 (2015) 79-83.

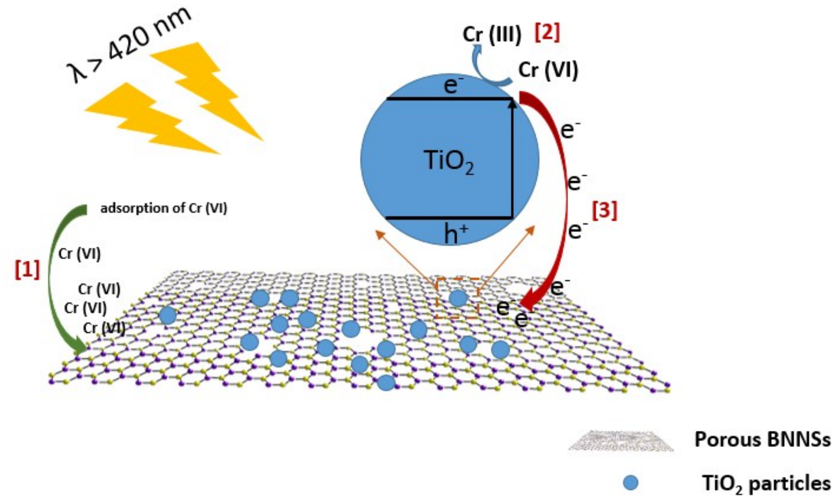

Figure S6. Scheme of photo reduction of Cr (VI) by P-BNNSs/TiO_2 composites

The photocatalytic mechanism of P-BNNSs/TiO_2 composites toward the reduction of Cr (VI) under visible light irradiation (λ >420 nm) can be summarized as Figure S6. Briefly, once the P-BNNSs/TiO_2 composites are dispersed in the Cr (VI) solution, Cr (VI) ions can be quickly adsorbed on the porous BNNSs [Path 1]. When the visible light irradiation (λ >420 nm) is applied, the loaded TiO_2 nanoparticles produce the electrons and holes. The photo-induced electrons can reduce the Cr (VI) which are either in the solution or on the porous BNNSs [Path 2]. Meanwhile, the produced electrons can transfer to the porous BNNSs due to the intimate interaction between TiO_2 nanoparticles and porous BNNSs [Path 3]. These electrons' transfer inhibit the electron-hole recombination, which can increase the number of electrons for Cr (VI) reduction.