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Advances in water disinfection by photocatalysis

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TITOLO
I progressi nella disinfezione dell'acqua attraverso la fotocatalisi

KEY WORDS
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Disinfezione dell'acqua, fotocatalisi, nanogiunzione, *E. coli* K-12, specie reattive

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Summary
An AgBr-Ag-Bi_2WO_6 nanojunction was synthesized by a facile deposition-precipitation method. Two VL-active components (AgBr and Bi_2WO_6) and the electron-transfer component (Ag) were spatially fixed in this nanojunction system. The VLD photocatalytic disinfection of *E. coli* K-12 by the AgBr-Ag-Bi_2WO_6 nanojunction, which could completely inactivate 5×10^7 cfu mL^{-1} of bacterial cells within 15 min, was greatly superior to other reported VLD photocatalysts. The mechanism of VLD photocatalytic disinfection was also investigated. It was found that the diffusing •OH, generated by both the oxidative and the reductive pathways of photocatalysis, was the major reactive species to inactivate bacterial cells, and that the direct contact between the AgBr-Ag-Bi_2WO_6 nanojunction and the bacterial cells was not required.

Riassunto
Una nanogiunzione AgBr-Ag-Bi_2WO_6 è stata sintetizzata con un facile metodo di deposizione-precipitazione. Due componenti VL-attivi (AgBr e Bi_2WO_6) e il componente donatore di elettroni (Ag) sono stati fissati spazialmente in questo sistema di nanogiunzione. La disinfezione fotocatalitica VLD di *E. coli* K-12 da parte della nanogiunzione AgBr-Ag-Bi_2WO_6, che potrebbe inattivare completamente 5×10^7 ufc ml^{-1} di cellule batteriche in 15 minuti, è risultata di gran lunga superiore ad altri fotocatalizzatori VLD riportati. In questo lavoro è stato anche analizzato il meccanismo di disinfezione fotocatalitico VLD. Si è scoperto che gli •OH diffusi, generati sia dal pathway ossidativo che riduttivo della fotocatalisi, erano la principale specie reattiva ad inattivare le cellule batteriche e che non era richiesto il contatto diretto tra la nanogiunzione AgBr-Ag- Bi_2WO_6 e le cellule batteriche.

Photocatalysis has been proven to be an effective treatment for water decontamination (1, 2). It has been used to degrade organic pollutants and inactivate microbes in contaminated water samples. Photocatalysis is a heterogeneous advanced oxidation process (AOP). Upon irradiation of appropriate light source, the charged species, namely, electron (e^-) and hole (h^+) are generated in the conduction and valence bands, respectively, of a semiconductor. The h^+ can react with hydroxyl ion (OH^-) or water to form hydroxyl radical (·OH), while the e^- reacts with O_2 produces superoxide ($\cdot O_2^-$). $\cdot O_2^-$ further reacts with proton and electron to produce hydrogen peroxide (H_2O_2). Reaction of H_2O_2 with another photogenerated e^- leads to the production of ·OH (Figure 1). Thus, the photocatalysis produces reactive charged species (i.e. e^- and h^+) and oxidative species ($\cdot O_2^-$, ·OH and H_2O_2). Each of these reactive species can be involved in the degradation of organic compounds and disinfection of microbes (3).

The most commonly used semiconductor as a photocatalyst is titanium dioxide (TiO_2) due to its low cost, and is stable, efficient and non-toxic (4, 5). However, because of its large band-gap between the valence and conduction bands (3.2 eV), TiO_2 can only be activated by UV light (λ < 380 nm), which occupies only 5% of the spectrum of

Figure 1 - The photocatalysis mechanism (1, 4)

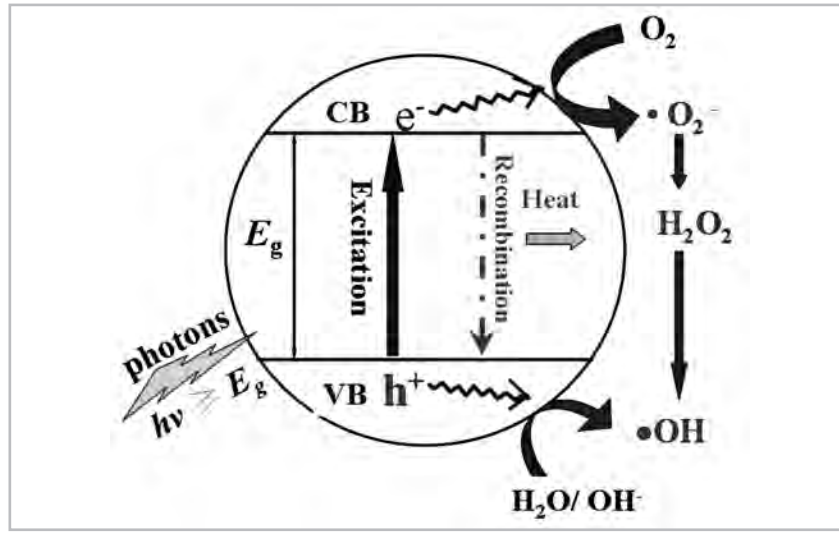
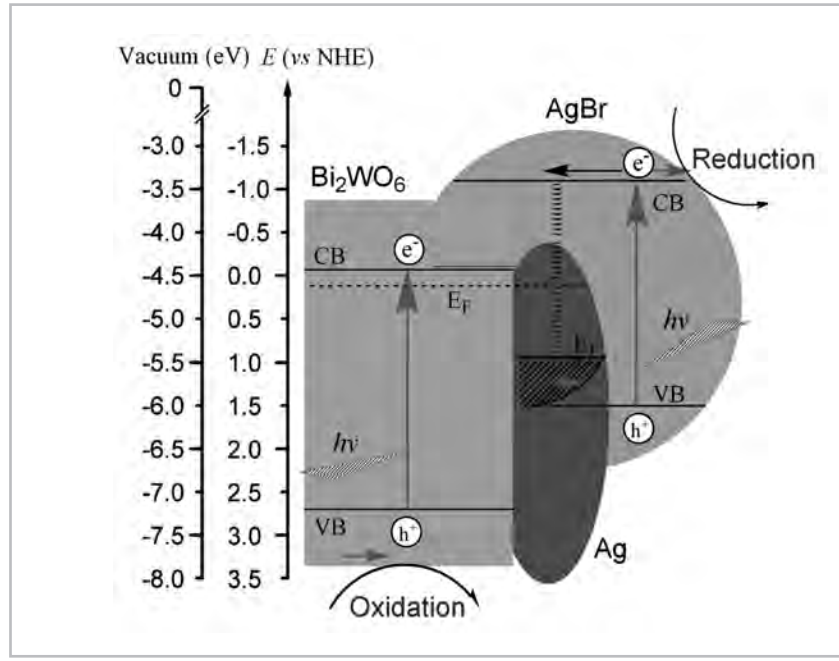


Figure 2 - Proposed photocatalytic reaction process of AgBr-Ag-Bi_2WO_6 (12)



sunlight. In order to maximize the use of sun light for photocatalysis, many studies focus on the design, fabrication and characterization of visible-light-driven (VLD) photocatalysts of efficiently utilizing visible light (VL), which occupies close to 50% of the spectrum of sun light. There are three approaches for the searching of VLD photocatalysts: (1) modifying TiO_2 to extend its absorption into VL spectrum; (2) using non-TiO_2 but traditional semiconductors with a narrow band gap; and (3) exploring new types of VLD photocatalysts. For (1), doping of TiO_2 with metals (6) and non-metals (7) can narrow the band-gap and makes the modified TiO_2 to be VL active. However, these modified TiO_2 usually only respond to a narrow spectrum of VL, and the photocatalytic activity is low. Dye-sensitized TiO_2 also responds to VL, but the drawbacks of the modified photocatalyst are unstability and low efficiency (8, 9). For (2), vanadium oxide (V_2O_5) and ferric oxide (Fe_2O_3) both have a narrow band-gap and are VL active. However they are toxic and of low efficiency (1). Cadmium sulfide has a high VLD photocatalytic activity, but it is unstable (10). For (3), bismuth-based photocatalysts (such as bismuth vanadate ($BiVO_4$)) have high VLD photocatalytic activity, but they can be activated only by a narrow spectrum of VL (11).

Figure 3 - Photocatalytic degradation of Procion Red MX-5B (A) and PCP (B) by different photocatalysts with same weight of each VL-active component under VL (12)

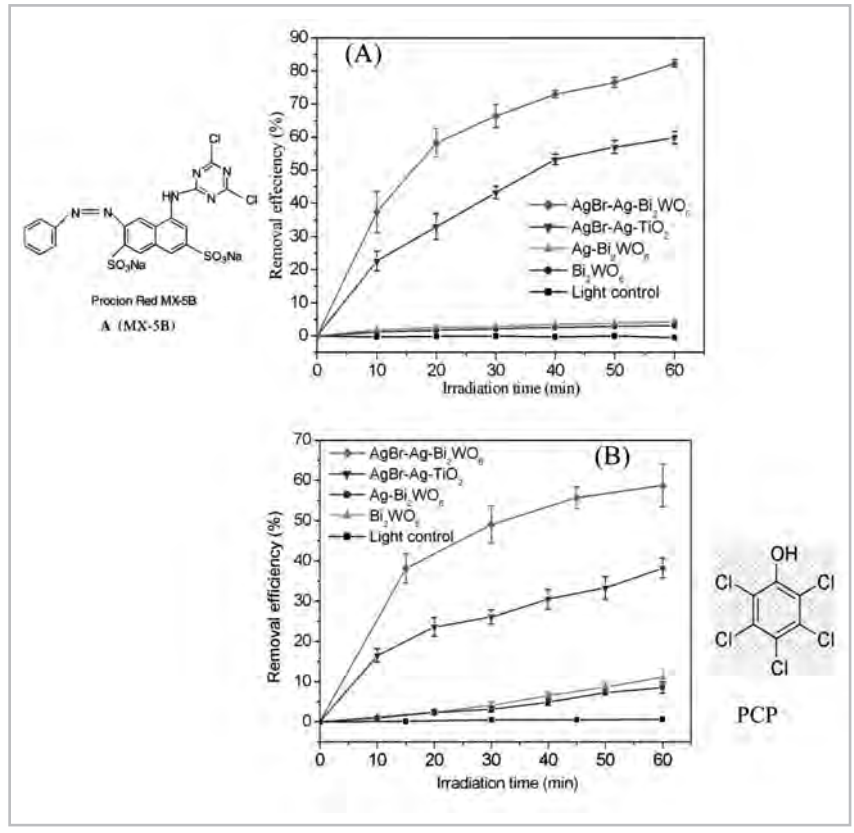


Figure 4 - Photocatalytic disinfection of *E. coli* K-12 by different photocatalysts with the same weight of each VLD component under VL (12)

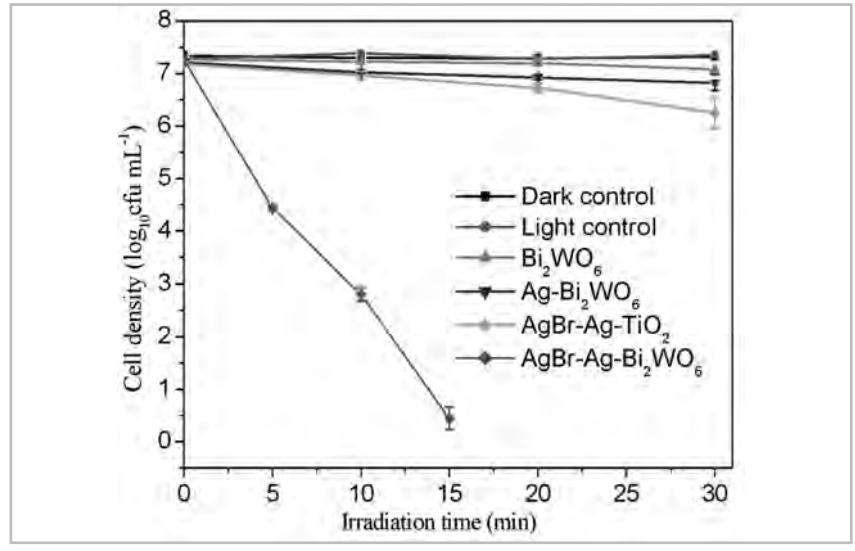
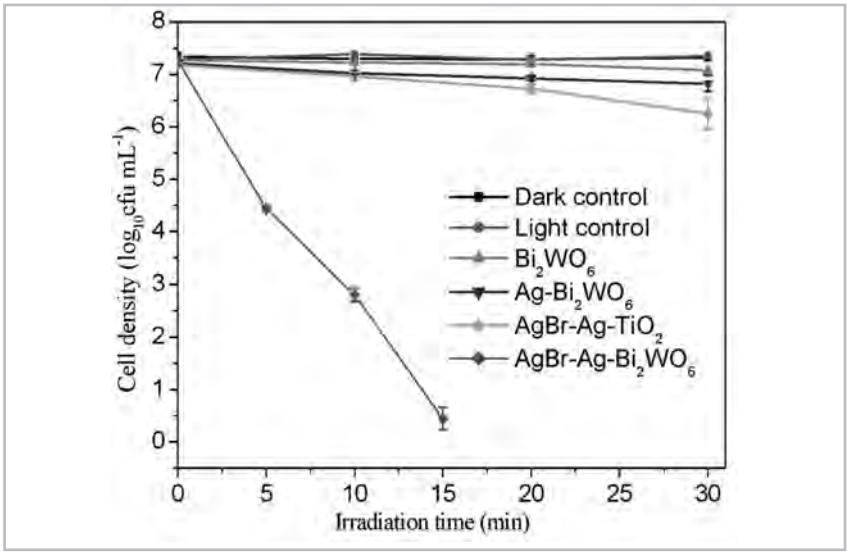
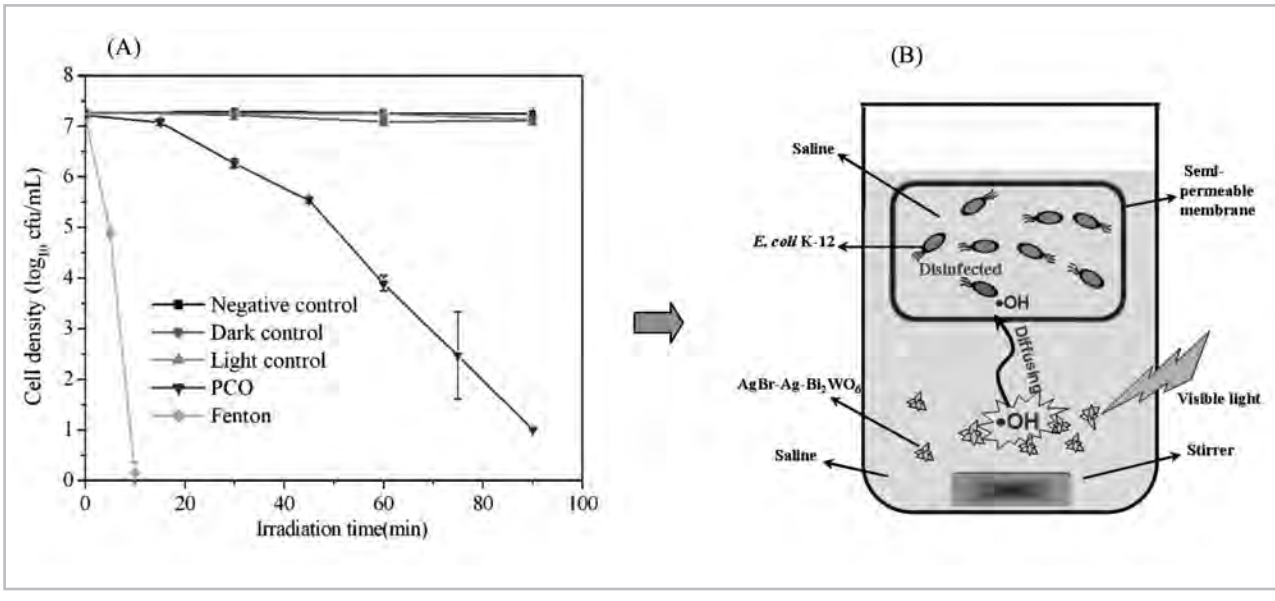


Figure 5 - Photocatalytic disinfection of *E. coli* K-12 by AgBr-Ag-Bi_2WO_6 in the presence of different scavengers (3)



Recently, a silver bromide-silver-bismuth tungstate (AgBr-Ag-Bi_2WO_6) nanojunction was synthesized by a facile deposition-precipitation method (12). Two VL-active components (AgBr and Bi_2WO_6) and the electron-transfer component (Ag) were spatially fixed in this nanojunction system (Figure 2). Due to its double VL active components, AgBr-Ag-Bi_2WO_6 nanojunction exhibited much higher VLD photocatalytic activity than that containing only single VL active component (either AgBr or Bi_2WO_6) for the degradation of an azo dye, Procion Red MX-5B (MX-5B), and pen-

Figure 6 - (A) The photocatalytic disinfection of *E. coli* K-12 by AgBr-Ag-Bi_2WO_6 in the "partition system" (3), and (B) The proposed VLD photocatalytic disinfection mechanism of AgBr-Ag-Bi_2WO_6occurred in the "partition system"



tachlorophenol (PCP) (Figure 3) (12). The photocatalytic performance of AgBr-Ag-Bi_2WO_6 nanojunction was superior to the sum of that of the two individual VLD photocatalysts (i.e. AgBr and Bi_2WO_6), indicating that there was a synergic effect between its two VL-active components (12). On the basis of its energy band, it was suggested that the synergic effect resulted from the vectorial electron transfer driven by the two-step excitation of the two VLD components in AgBr-Ag-Bi_2WO_6 (12).

The VLD photocatalytic disinfection of *E. coli* K-12 by the AgBr-Ag-Bi_2WO_6 nanojunction was also studied (3). The VLD photocatalytic disinfection could completely inactivate 5×10^7 cfu mL^{-1} of bacterial cells within 15 min, which was greatly superior to other reported VLD photocatalysts [Figure 4, (3)]. The mechanism of VLD photocatalytic disinfection was also investigated by scavenger and the "partition system" experiments. The results indicate that the diffusing •OH, generated by both the oxidative and the reductive pathways of VLD photocatalysis of AgBr-Ag-Bi_2WO_6, was one of the major reactive species to inactivate bacterial cells (Figure 5, (3]), and that the direct contact between the AgBr-Ag-Bi_2WO_6 nanojunction and the bacterial cells was not required for the inactivation [Figure 6, (3)]. Therefore, this work does not only develop a powerful VLD photocatalyst, but also reports novel understandings of the VLD photocatalytic degradation of organics and disinfection of bacteria.

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