

Supporting Information

Assembly of CdS nanoparticles on boron and fluoride co-doped TiO₂ nanofilm for solar energy conversion applications

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1. Results and Discussion

1.1 XRD analysis

Fig. 1a confirms that the diffraction peaks of all samples are ascribed to the TiO₂ anatase phase ($2\theta = 25.284^\circ$), Fig. 1b indicates that there has been virtually no phase change in TiO₂ in the process of codoping, regardless of the amounts of dopants. Furthermore, due to the small amount of B and F used for doping, no significant characteristic peak of boron oxide was found in B-F doped TiO₂. In other words, the addition of a small amount of B and F did not change the structure of anatase TiO₂.

1.2 TEM analysis

The coverage of CdS QDs on B-F-TiO₂ film surface and well interconnected among the nanospheroidal particles was clearly demonstrated from TEM image (Fig. 2). TEM image verified that individual B-F-TiO₂ were covered with nanoparticle

aggregate with diameters about 10~15 nm. And it also shows that large aggregates of CdS cover the entrance of the B-F-TiO₂ film. However, the TEM image of the B-F-TiO₂/TGA/CdS-3 film clearly displays that CdS QDs were abundantly deposited inside the B-F-TiO₂ film, which shows that a crystalline CdS QDs with the size ~6 nm was grown on an anatase B-F-TiO₂ film.

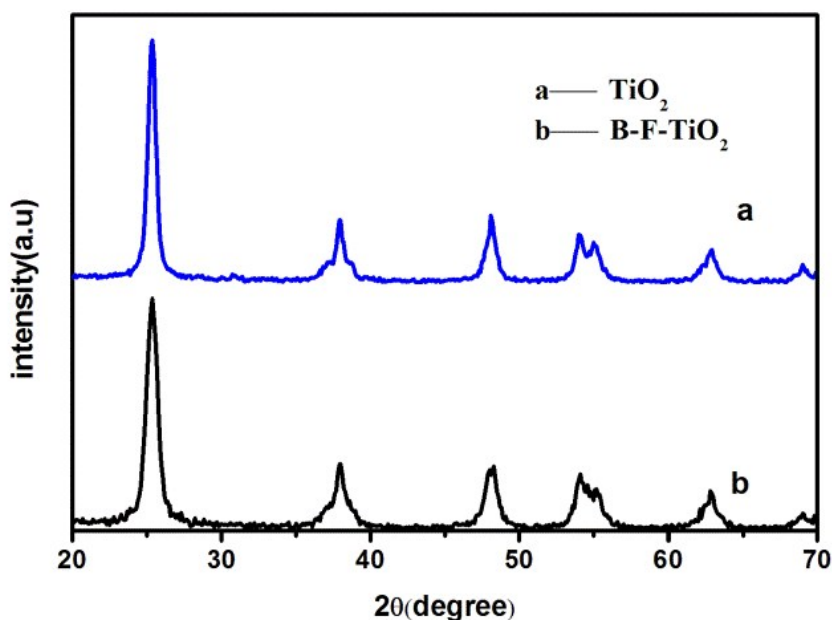


Fig. 1 XRD patterns of the pure TiO₂ (curve a) and 0.5% B-F-doped TiO₂ (curve b).

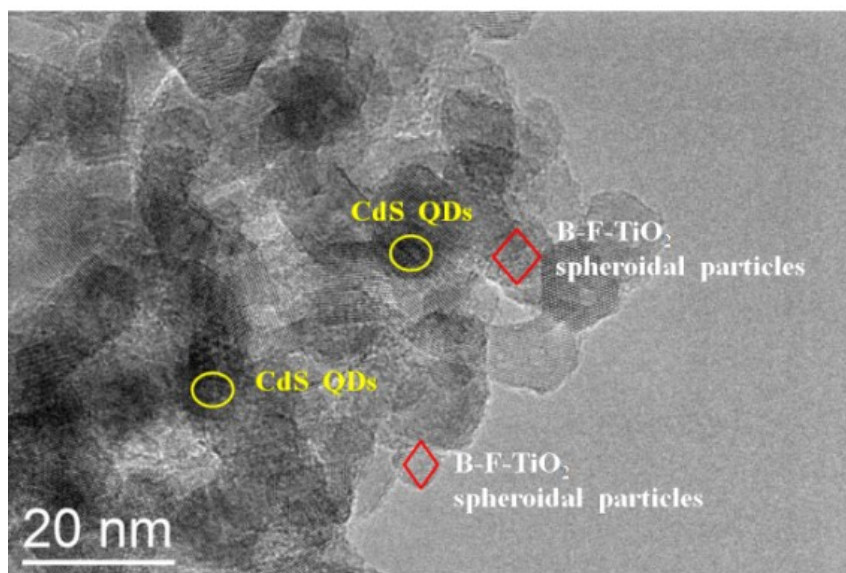


Fig 2. TEM image of CdS QD sensitized B/F co-doped TiO₂ film

1.3 EDS analysis

The EDS analysis of the B/F-doped TiO₂ was conducted with a scanning electron microscope. From Fig. 3, characteristic peaks corresponding to Ti and O elements

were observed, arising from the TiO_2 . The small peak seen for B and F confirms the existence of B and F in the TiO_2 substance, which suggests incorporation of B and F elements.

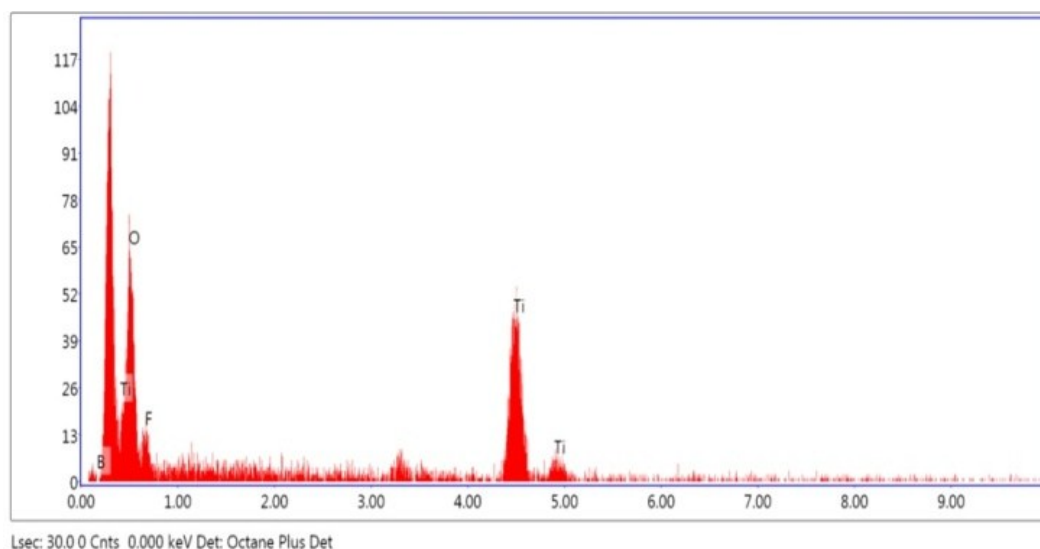


Fig. 3. SEM-EDS analysis of B/F-doped TiO_2 electrode

1.4 XPS analysis

The electronic structure and chemical environment of the elements on the surface were investigated by XPS spectra. We examined three areas, the Ti 2p region around 460 eV (Fig. 4b), and the O 1s region around 530 eV (Fig. 4b): the B 1s region around 193 eV (Fig. 4c), and the N 1s region around 397 eV (Fig. 4d). The nonmetal doping can introduce residual charge, which may result in an decrease in the number of surface O-H groups (which is evidenced by O1s XPS) and then an decrease in the crystallite size. Which was agreed with the XRD. In contrast, although the direct evidence is still absent, Chen et al.⁴⁶ proposed that the doped boron may reduce the surface energy of TiO_2 nanoparticles, which may hinder the increase in the crystallite size. Probably different sample preparation procedures lead to the difference. It has been demonstrated that the B 1s XPS spectrum may be used to identify the boron species on the surfaces of the doped TiO_2 ⁴⁷⁻⁵³. As shown in Fig. 3c, the B1s XPS spectrum of the B-doped TiO_2 exhibits the typical asymmetrical broad peak at 186.7 eV⁵⁴, which may be deconvoluted (carried out by the XPSPEAK41 software package) may be ascribed to interstitial borons. The binding energy of B1s in H_3BO_3 was 193.8 eV while in TiB_2 was 188.2 eV, so here B1s 186.7 eV was between the

binding energy of H_3BO_3 and TiB_2 , so maybe some B replaced O, then formed B-Ti-O bond, this means that the B atom doped into the crystal lattice of TiO_2 . The 2p orbital of B hybridized with the 2p orbital of O, then narrowed the band gap⁵⁵.

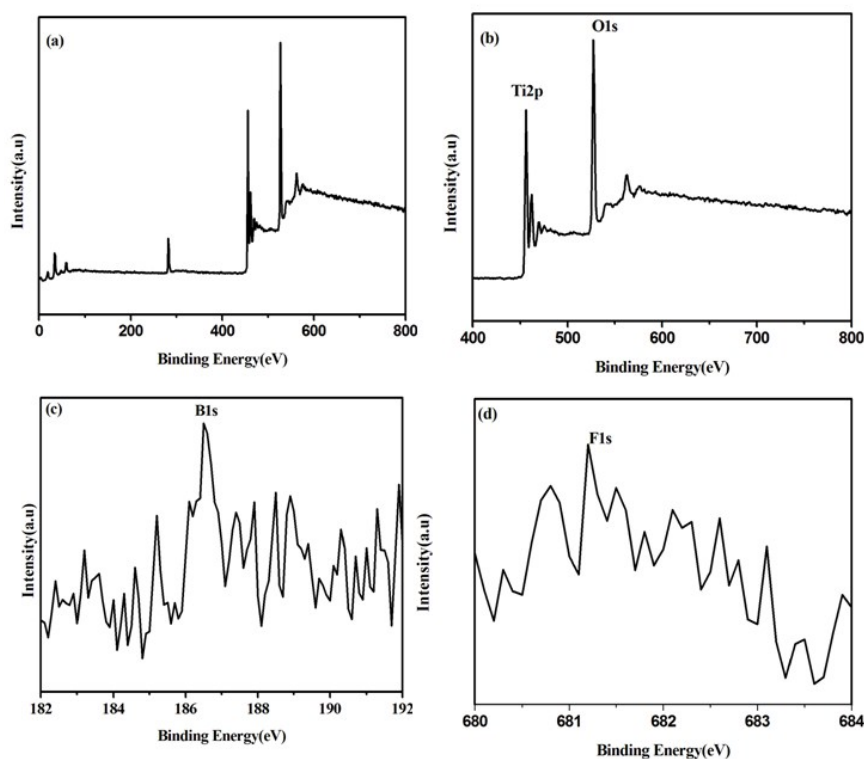


Fig. 4. XPS spectra of B-F- TiO_2 nanocomposite (a), Ti 2p peak and O 1s peak (b), B 1s peak (c), F 1s peak (d) in the composite

The binding energy peaks for F 1s were observed at 681.2 eV, both in good agreement with those reported for surface F species in TiOF_2 ⁵⁶. The fact that only the Ti (2p) components display a variation, and not the O (1s) component, signifies that fluoride must be bonded to titanium forming an O-Ti-F fragment. The location of the boron species cannot be assigned from XPS analysis given its low concentration. Therefore, it indicates that an O-Ti-B-F bond structure may occur in the B, F co-doped anatase TiO_2 film. It can be concluded that fluoride and boron have been actually incorporated into the TiO_2 films by the method used in this study.

1.5 Schematic energy diagram

Schematic energy diagram was shown in Fig.5, the flat-band potential of the bare TiO_2 and B/F co-doped TiO_2 were determined to be -2.097 V and -2.2 V (vs. Ag/AgCl), respectively, clearly the open-circuit potential of the B/F co-doped electrode is negatively shifted by 103 mV compared with the undoped TiO_2 electrode.

This negative movement of the flat-band edge can be due to a shift in the position of the conduction band edge of the nanocrystalline electrodes.

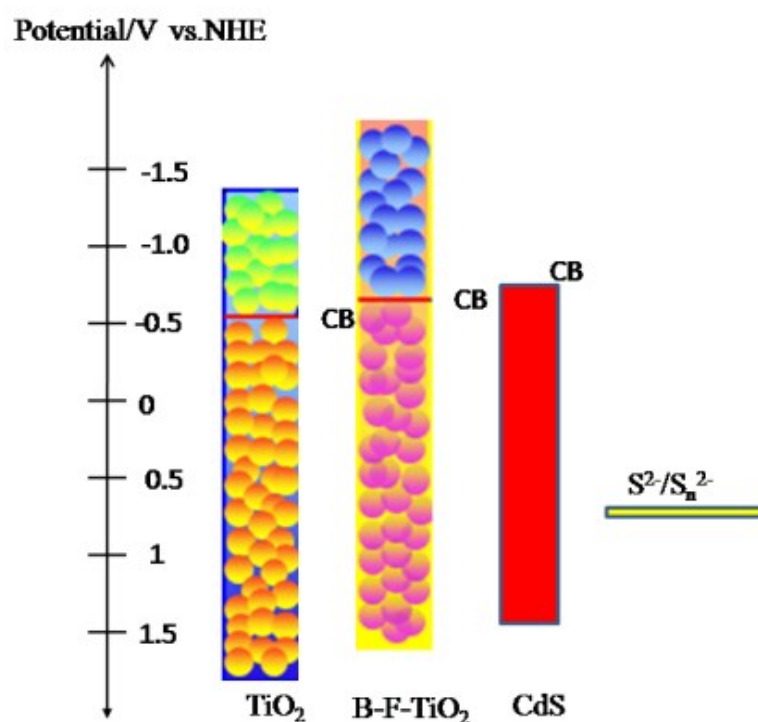


Fig. 5. Schematic energy diagram for QDSSCs based on the undoped TiO₂ electrode, B/F codoped TiO₂ electrode and a S²⁻/S_n²⁻ redox electrolyte.

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