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Ferroelectric polarization effect on surface chemistry and photo-catalytic activity: A review

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Abstract

The current efficiency of various photocatalytic processes is limited by the recombination of photogenerated electron–hole pairs in the photocatalyst as well as the back-reaction of intermediate species. This review concentrates on the use of ferroelectric polarization to mitigate electron–hole recombination and back-reactions and therefore improve photochemical reactivity. Ferroelectric materials are considered as wide band gap polarizable semiconductors. Depending on the surface polarization, different regions of the surface experience different extents of band bending and promote different carriers to move to spatially different locations. This can lead to some interesting interactions at the surface such as spatially selective adsorption and surface redox reactions. This introductory review covers the fundamental properties of ferroelectric materials, effect of an internal electric field/polarization on charge carrier separation, effect of the polarization on the surface photochemistry and reviews the work done on the use of these ferroelectric materials for photocatalytic applications such as dye degradation and water splitting. The manipulation of photogenerated charge carriers through an internal electric field/surface polarization is a promising strategy for the design of improved photocatalysts.

Keywords: Photo-catalysis; Hydrogen production; Ferroelectric; Water splitting; Adsorption; Recombination

Contents

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1. Introduction

Various semiconductors such as TiO_2, CdS, ZnO and WO_3 have been explored for photocatalytic applications such as hydrogen production from water splitting and dye degradation for environmental remediation. The current efficiency of these photocatalytic processes is below what is needed for commercialization. Factors limiting the efficiency include: (i) incomplete absorption of available sunlight, (ii) poor catalyst stability, (iii) fast electron–hole recombination and (iv) slow surface redox reactions [1,2]. In general, charge carrier separation remains the most complex and critical issue. Understanding and addressing the electron hole recombination issue is critical to the success of photocatalysis. Surface redox reactions are the rate limiting step, therefore the charge separation, diffusion and redox reactions must proceed within the lifetimes of photo-excited carriers [3–5].

One concept that can be used to mitigate losses from recombination and back reactions is to use electric fields that may help to separate photogenerated carriers. The best-known examples of electric fields in photo-catalysis are associated with interfaces, such as solution/photo-catalyst interfaces, metal–photocatalyst junctions, and p–n junctions in heterojunction photocatalysts (Fig. 1) [6]. Electric fields associated with metal–photocatalyst Schottky junctions have been widely used to improve their activity. Photocatalysts modified with noble metal nanoparticles such as Pt, Au, Ag, Pd etc. facilitate the charge separation due to the electric field at the junction/interface formed between the co-catalyst and the semiconductor [1–3,7]. Similarly electric fields at p–n junctions with the

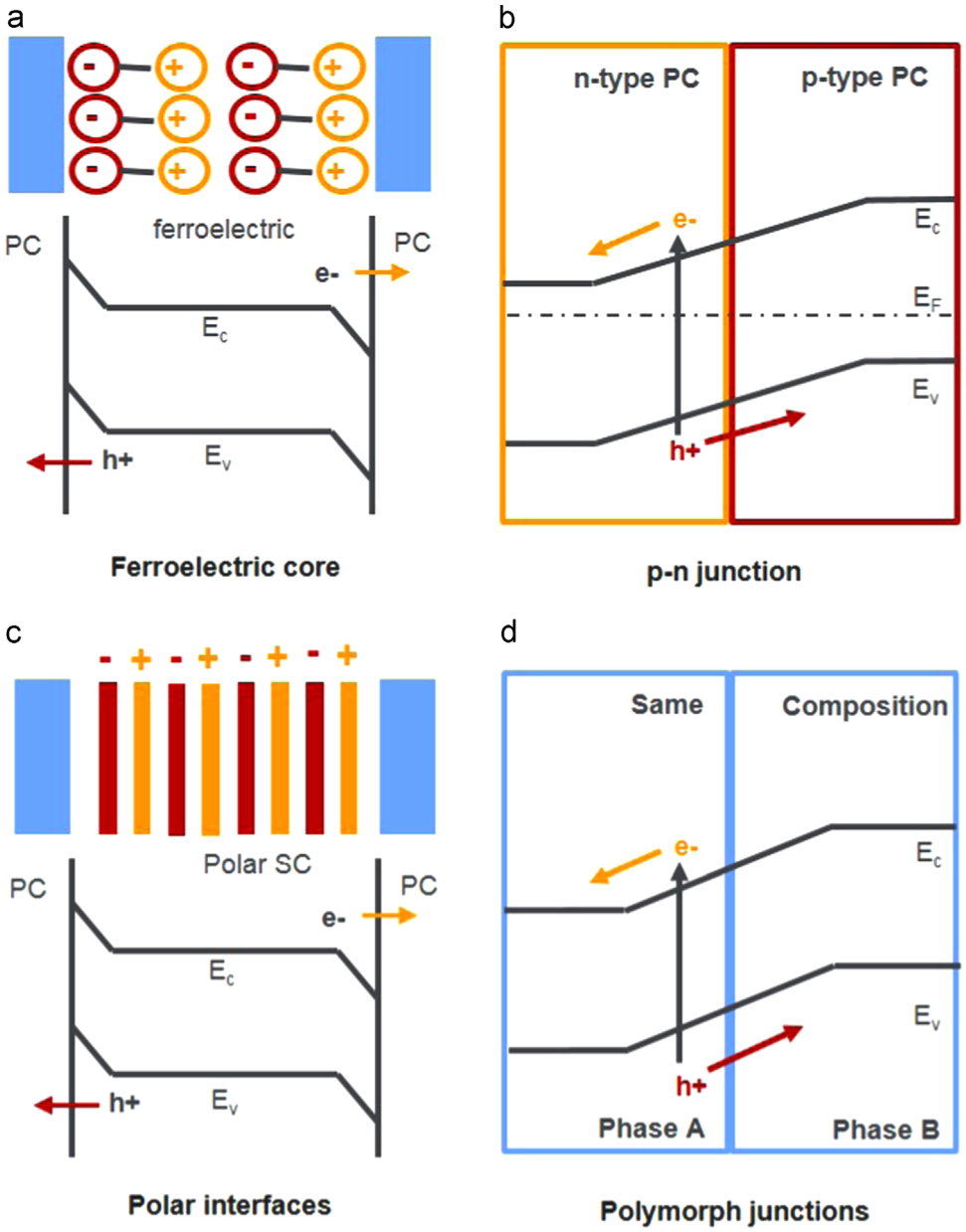

Fig. 1. The internal field enhanced photogenerated charge carrier separation: (a) ferroelectric polarization; (b) p–n junctions; (c) polar surfaces; and (d) polymorph junctions. (PC: photocatalyst; SC: semiconductor) [6].