Investigation of Plasmonic $Ag@Ag_3(PO_4)_{1-x}$/ZnO Nanoarchitectures for Solar-Hydrogen Application

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Global climate warming and environment pollution have spurred scientists to develop new high-efficient and environmental-friendly energy technologies. Hydrogen is an ideal fuel for fuel cell applications. Hydrogen has to be produced from renewable and carbon-free resources using nature energies such as sunlight if one thinks of clean energy and environmental issues. In this regard, a photoelectrochemical (PEC) cell consisting of semiconductor photoelectrodes that can harvest light and use this energy directly for splitting water is a more promising way for hydrogen generation. Recently, researchers have explored the applicability of plasmonic photocatalysis for organic molecule decomposition, catalytic oxidation, and particularly PEC water splitting. However, to the best of our knowledge, there has been rare study to date regarding the $Ag@Ag_3(PO_4)_{1-x}$/ZnO hybrid nanoelectrodes applied into PEC water splitting. In this work, we report the new design of high-activity model in photocatalytic nanosystem comprising an Ag core covered with an approximately 2-nm-thick nanoshell of Ag_3PO_4 ($Ag@Ag_3(PO_4)_{1-x}$) on the ZnO nanorods that are visible-light-sensitive photofunctional electrodes with strong photooxidative capabilities to evolve O2 from water.

The ZnO nanorod arrays were fist grown on ITO substrates using a simple electro-deposition method. The electrochemical deposition approach at room temperature in the case of $Ag@Ag_3(PO_4)_{1-x}$ nanoparticles subsequently resulted in rapid formation of cable-like nanocomposites. The PEC performance of $Ag@Ag_3(PO_4)_{1-x}$ nanoparticle/ZnO nanorod hybrid nanoarchitectures in water splitting without sacrificial reagents was systematically evaluated. The finite-difference time-domain (FDTD) method was then applied to determine the underlying photocatalytic enhancement mechanism. The maximum photoconversion efficiency could be successfully achieved as high as 2 %, with the significant photocurrent of 3.1 mA/cm^2. Furthermore, in addition to achieve the maximum IPCE value of 90%, it could be noted that the IPCE of $Ag@Ag_3(PO_4)_{1-x}$ photosensitized ZnO photoanodes at the monochromatic wavelength of 400 nm is up to 60%. The improvement in photoactivity of PEC water-splitting may be attributed to the enhanced near-field amplitudes resulted from LSPR of Ag-core and absorption edge of $Ag_3(PO_4)_{1-x}$-nanoshell, which increase the rate of formation of electron/hole pairs at the nearby surface of $Ag_3(PO_4)_{1-x}$-nanoshell and ZnO-nanorod, thus enlarging the amount of photogenerated charge contributing to photocatalysis. The capability of developing highly photoactive $Ag_3(PO_4)_{1-x}$-photosensitized ZnO photoanodes opens up new opportunities in various photocatalytic areas, particularly including solar-hydrogen fields.

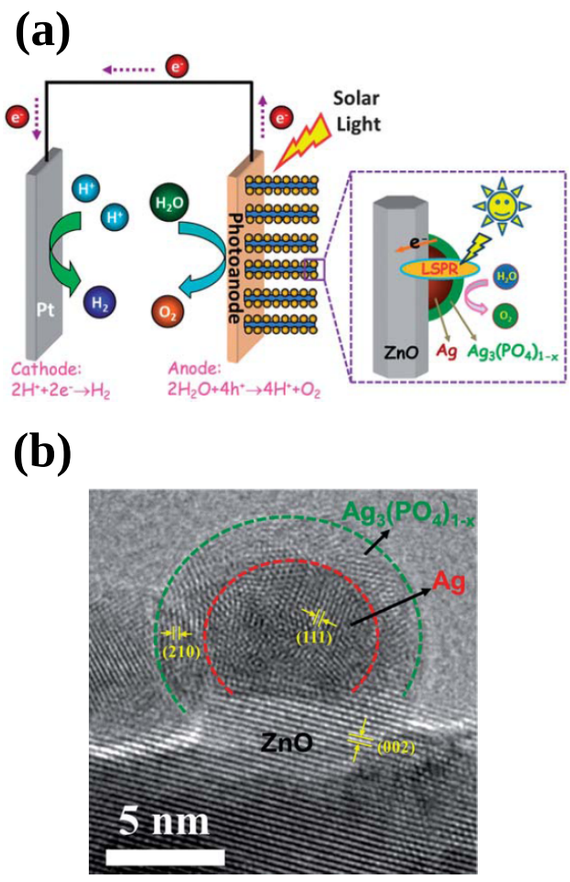

Figure 1. (a) Sketch showing ZnO nanorods decorated with $Ag@Ag_3(PO_4)_{1-x}$ core–shell nanoparticles and plasmonic photocatalysis for driving PEC watersplitting. (b) HRTEM image of a ZnO nanorod decorated with $Ag@Ag_3(PO_4)_{1-x}$ core–shell nanoparticles.

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