Energy Advances

ROYAL SOCIETY OF CHEMISTRY

PAPER

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Cite this: Energy Adv., 2024, 3, 829

Bimetallic and plasmonic Ag and Cu integrated TiO_2 thin films for enhanced solar hydrogen production in direct sunlight†

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Received 27th January 2024, Accepted 7th March 2024

DOI: 10.1039/d4ya00056k

rsc.li/energy-advances

Plasmonic metal nanoparticle-integrated mesoporous TiO_2 nanocomposites (Ag/TiO_2, Cu/TiO_2 and Ag–Cu/TiO_2), prepared by a simple chemical reduction method, have been demonstrated to show superior activity in thin-film form for solar H_2 generation in sunlight. Integration of Ag + Cu on TiO_2 significantly enhances the solar H_2 production due to the combined SPR effect of both metal species and the possible synergistic interaction among Cu + Ag in Ag–Cu/TiO_2. TiAgCu-1 (0.75 wt% Ag and 0.25 wt% Cu on TiO_2) showed the highest H_2 yield of 6.67 mmol h^{-1} g^{-1} and it is 43 times higher than that of bare TiO_2. The thin-film form of TiAgCu-1 shows 5 times higher solar H_2 production than its powder counterpart. 1 wt% of Ag or Cu on TiO_2 shows a H_2 yield of 4.6 or 2 mmol h^{-1} g^{-1}, respectively, which underscores the importance of combined or synergistic effects. The increase in solar H_2 generation in Ag–Cu/TiO_2 is attributed to factors such as the SPR effect of Cu and Ag, and strong interaction between Ag and Cu. The high photocatalytic efficiency of the TiAgCu-1 thin film is attributed to the large dispersion of metallic species with relatively high Ag/Cu surface atomic ratio, enhanced light absorption, a heterogeneous distribution of Ag and Cu species, and high double layer capacitance. The inter particle mesoporous network increases the interfacial charge transfer and reduces the mass transfer limitations. The plausible photocatalytic reaction mechanism could involve the combination of direct electron transfer from metal (Cu/Ag) to TiO_2 as well as the significant field effect due to the Ag–Cu alloy, which is expected to increase the electron excitation locally.

Introduction

The development of electronically integrated photocatalytic materials that could efficiently catalyze water splitting by utilizing solar energy to produce clean H_2 is of great importance, especially in view of the world wide focus on the use of renewable energy and the increasing concern regarding environmental issues.[1–5] Ever since the potential of TiO_2 in photocatalytic applications was realized by Fujishima and Honda in 1972, there has been a perpetual interest in the design and fabrication of visible light-driven photocatalytic materials for practical applications.[5–7] Integration with metal nanoparticles, which also exhibit surface plasmon resonance (SPR), is one of the effective strategies for enhancing the visible light harvesting capability and photocatalytic performance of TiO_2 by suppressing the electron–hole recombination.[8] Recently, we have reported the synthesis of Ag/TiO_2 and M-Au/TiO_2 (M = Ag, Pd and Pt) nanocomposites with accessible mesopores and demonstrated the high potential of this material for solar H_2 evolution.[2] The SPR effect shown by Ag nanoparticles enhances the absorption of visible light.[9–11] However, it is more desirable that the activity of Ag/TiO_2 can be improved in a way by adding a synergistically interacting and catalytically active metal, such as Cu into it; indeed this is expected to make it a bimetal/alloy nanoparticle system,[12] which would improve the charge separation and also provide more active sites for efficient H_2 production.[5,13] Among the 3d transition metal series, Cu is one of the preferred choices due to its SPR nature, co-catalytic ability, and fast electron transfer rate.[14] The combined effect of Cu and Ag in enhancing the photocatalytic activity with Ag–Cu/TiO_2 photocatalysts by taking advantage of the co-catalytic as well as SPR effect of both Ag and Cu has not been reported in the literature.[13] Incorporation of Cu in Ag/TiO_2 brings changes in the physico-chemical characteristics, such as

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† Electronic supplementary information (ESI) available: FESEM, HRTEM-EDS, Ag/Cu atomic ratio, impedance parameters, XPS binding energy values, and H_2 rate comparison. See DOI: https://doi.org/10.1039/d4ya00056k