Hydrogen production using by photocatalysis using silver nanocubes supported on titanium dioxide as photocatalist

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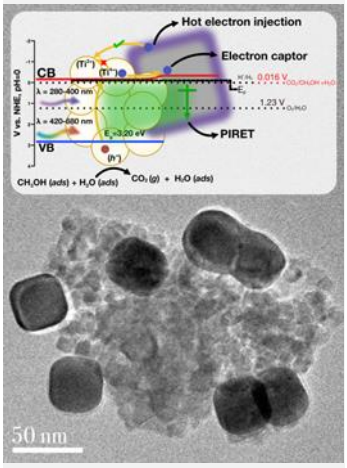

In this study, silver nanocubes (Ag_{NC}) were supported on titanium dioxide nanoparticles in the anatase phase ($aTiO_2NPs$) to evaluate their photoactivity to produce molecular hydrogen (H_2) through a methanol/water (CH_3OH/H_2O) reforming reaction under ultraviolet (280 – 400 nm) and visible (420 – 680 nm) irradiation. The support of Ag_{NC} on $aTiO_2NPs$ significantly improved H_2 production under UV-light irradiation. The $Ag_{1\%}/aTiO_2$ photocatalyst showed four-fold greater H_2 production than the reference material ($aTiO_2NPs$). Under visible light, the reference material showed complete absence of H_2 production. However, the support of Ag_{NC}, especially the $Ag_{1\%}/aTiO_2$ photocatalyst, enhanced H_2 production through localized surface plasmon resonance through the injection of hot electrons into the $aTiO_2NPs$. These results suggest a complex photocatalytic mechanism in which Ag_{NC} play a crucial role as electron captors and facilitators of plasmonic energy transfer.

Introduction

An alternative technology for producing H_2 with low CO_2 emission is the photocatalytic oxidation of H_2O. Unlike other methods, this process uses sunlight to split H_2O into H_2 and O_2. Estimates suggest that H_2 can be produced and sold at a cost of 4 USD/kg or less by using CH_3OH as a sacrificial agent through photocatalysis [1, 2]. However, significant challenges still need to be addressed to enable large-scale application of this technology. The main challenge is the development of highly active, chemically and thermally stable, non-toxic, and environmentally friendly photocatalysts that can be synthesized using low-energy, economical, and environmentally friendly processes [3]. This study focused on preparing Ag_{NC} using the polyol method and supporting them on $aTiO_2NPs$ for use as photocatalysts. The goal was to improve the photocatalytic activity for H_2 production through the division of CH_3OH/H_2O under ultraviolet and visible light irradiation. Additionally, the structural, optical, textural, and morphological properties of these photocatalysts were examined.

Material and Methods

$aTiO_2NPs$ were synthesized using the inverse microemulsion method described by M. J. Muñoz-Batista et al. [4]. Ag_{NC} were synthesized using the polyol method according to the procedure reported by Wang et al. [5]. The Ag_{NC} protected with PVP were dispersed in ethanol (C_2H_6O, Jalmek, ≥ 96%) and mixed with $aTiO_2NPs$, followed by magnetic stirring for 1 h at 25 °C in a N_2 atmosphere, and under dark conditions, different wt. % were obtained for the Ag_{NC} with respect to the $aTiO_2NPs$.

Photocatalytic activities in a liquid medium were assessed using a semi-continuous Pyrex reactor, a Hg-Xe lamp (500 W), and dichroic filters for exposure to ultraviolet or visible wavelengths within specific ranges. H_2 production rates were measured after 3 h of irradiation through mass spectrometry analysis under pseudo-steady-state conditions.

Results and Discussion

Using the parameters modified from the methodology proposed by Wang et al. [5]. We managed to grow Ag_{NC} ranging from 23 nm to 39.5 nm in a period of 15 min to 90 min, the growth of the nanocubes was characterized through the evolution of different plasmonic modes that arise and change as they grow, and which were obtained by UV-Vis. Furthermore, we corroborated the growth of the Ag_{NC} by capturing the TEM images (these results are not shown).

All supported Ag_{NC} were grown for 60 min. TEM images indicated the presence og Ag_{NC} over $aTiO_2NPs$ agglomerates with an average size of 12.5 (Fig. 1a). HRTEM analysis revealed the characteristic interplanar

distances of the anatase and metallic Ag phases, as shown in Fig. 1c. XRD confirmed the single phase of anatase with an average crystallite size of 12.6 ± 0.9 nm (These results are not shown).

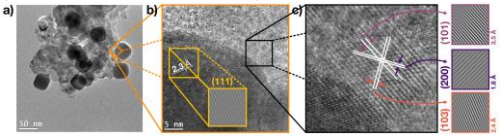

Figure 1. (a) TEM image of $Ag_{2.5\ \%}/aTiO_2$. In image (b), the enclosed region corresponds to the location where the HRTEM image (c) was taken.

Figure 2 shows the absorbance spectra, corrected by Kulbelka-Munk, of the photocatalysts modified with various amounts of Ag_{NC} and the reference material, along with their respective digital photographs. As the amount of Ag_{NC} on the $aTiO_2$NPs increased, a simultaneous increase in absorbance was observed in both width and intensity at approximately 420 nm, which is characteristic of the dipole moment generated in the corners of the Ag_{NC}. Notably, the $Ag_{0.5\%}/aTiO_2$ sample exhibited an increase in the absorption band within the range of 520-800 nm. This phenomenon is attributed to the agglomeration of Ag_{NC}, resulting in the formation of new resonances, which were identified as plasmon hybridizations. Tauc graphs were generated and the band gaps of the resulting photocatalysts were calculated. Both these results and those obtained from the N_2 adsorption-desorption isotherms suggest the formation of metal/semiconductor unions. The physicochemical characteristics of the photocatalysts modified with different amounts of Ag_{NC} and the reference material are presented in Table 1.

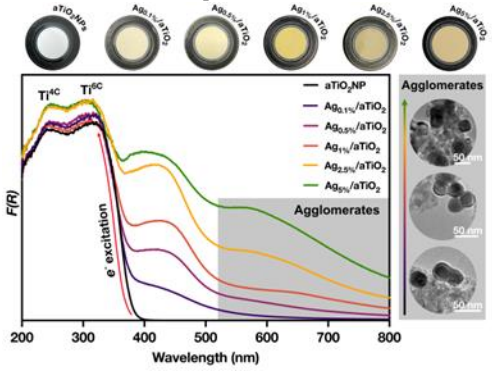

Figure 2. Absorbance spectra of $aTiO_2$NPs and $Ag_x/aTiO_2$.

Table 1. Physicochemical characteristics and water-splitting activity of mesoporous $aTiO_2$NPs and $Ag_x/aTiO_2$ photocatalysts.

Photocatalysts	Cristallite size (nm)	S_{BET} (m^2/g)	Pore zise (nm)	V_p (cm^3/g)	Band gap (eV)	H_2 production rate – UV (μmol/gh)	H_2 production rate – Vis (μmol/g h)
$aTiO_2$NPs	12.7	82.2	5.9	0.15	3.20	128.6	0
$Ag_{0.1\%}/aTiO_2$	12.6	66.5	5.4	0.11	3.01	192.9	76.0
$Ag_{0.5\%}/aTiO_2$	12.8	67.2	5.6	0.12	2.81	214.3	97.5
$Ag_{1\%}/aTiO_2$	12.5	71.2	5.6	0.12	2.57	489.6	272.1
$Ag_{2.5\%}/aTiO_2$	12.5	68.2	5.5	0.12	1.92	383.6	208.9
$Ag_{5\%}/aTiO_2$	12.6	70.0	5.4	0.12	1.46	362.1	192.9

Conclusions

The results of H_2 production by photoreforming of CH_3OH/H_2O demonstrated that supporting Ag_{NC} on $aTiO_2$NPs increased the photocatalytic activity with respect to the reference material. Maximum photoactivity was achieved with the $Ag_{1\%}/aTiO_2$ material under irradiation with ultraviolet and visible light. These results suggest a complex photocatalytic mechanism involving Ag_{NC} as electron captors, hot electron injectors, and charge separators (PIRET).

Acknowledgments

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