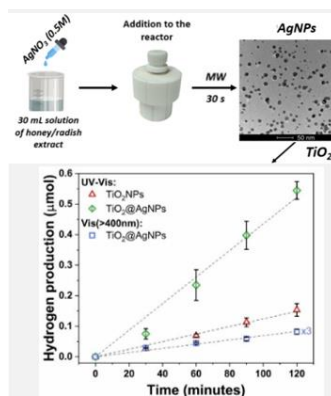


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Here we report a sustainable and fast approach for the preparation of silver nanoparticles based on a microwave-assisted chemistry method (MWAC) in aqueous medium. Honey, root extracts of radish, turnip, and yam were used as green reagent sources. UV-Vis spectra peaks of the silver nanoparticles (AgNPs) were observed after 30 s of MW irradiation. The AgNPs were impregnated onto TiO₂NPs. This photocatalyst was tested for the H₂ generation in the photo-reform of methanol at room temperature. Due to synergistic effects, H₂ evolution increased 3.5 times using TiO₂@AgNPs when compared to pure TiO₂NPs under UV-Vis light. The TiO₂@AgNPs also generated H₂ when exposed to only visible light irradiation. The present study introduces a new sustainable and eco-friendly strategy for designing low-cost photocatalysts for H₂ generation using solar light.

Introduction

AgNPs have attracted attention due to their unique properties which enable their application in sensing, photocatalysis, and electronic devices [1]. However, some methods of synthesis may bring environmentally damaging effects, as they require toxic chemicals and solvents, in addition to time-consuming procedures. [1]. With Green Chemistry becoming a trend, many researchers seek other approaches to overcome AgNPs synthesis drawbacks. Various reports using natural compounds as both the reducing/capping agents are available for the synthesis of AgNPs, providing a sustainable and low-cost method. Honey and leaves of radish are examples of compounds that have been utilized for this purpose, allowing to obtain AgNPs with anticancer activity and a safe and eco-friendly pesticide, respectively [2,3]. However, one limitation remains in AgNPs synthesis applying green reagents: the slow reaction kinetics compared to regular chemical approaches. This drawback can be diminished by incorporating a MWAC as a quick, energy-saving, and uniform source of heating in AgNPs synthesis [4]. In this work, AgNPs were quickly obtained with a sustainable approach using a MWAC synthesis in aqueous medium. Honey, root extracts of pink radish, yam, and white egg turnip acted as the reducing/stabilizing species. The AgNPs were impregnated onto TiO₂NPs and tested for the H₂ generation in the photo-reform of methanol at room temperature.

Material and Methods

The MWAC of AgNPs synthesis method consisted of mixing 30 mL of honey aqueous solution/root extract with AgNO₃ in a beaker with stirring [5]. This

solution was placed in a Teflon reactor and irradiated for 30 s inside a standard MW. The MWAC synthesis of TiO₂NPs was carried out in a commercial instrument MARS 6 (CEM Corporation). Briefly, in a Teflon cup 5 mL of a 50 wt% aqueous titanium(IV) bis(ammonium lactato)dihydroxide (TALH) with 45 mL of NH₃ (0.1 M) solution was irradiated for 15 minutes at 160°C (800W) [6]. The solution was cooled down, dried and calcinated at 400°C for 4h. The TiO₂@AgNPs photocatalyst preparation initiated by dispersing TiO₂NPs in water. AgNPs colloidal dispersion was then added to the TiO₂NPs and stirred for 1h. After resting overnight, the precipitate was calcined for 3h at 400°C. Photocatalytic experiments were carried out using a high pressure Xe/Hg lamp of 350 W (Sciencetech Inc.). 15 mL of water, 2 mL of methanol and 17 mg of the photocatalyst were irradiated for fixed periods of time. H₂ was quantified by gas chromatography on a Shimatzsu (GC-2010 GC) chromatograph.

Results and Discussion

Sustainable syntheses of AgNPs were conducted using honey or vegetable extracts in a MW. The formation of AgNPs was indicated by UV-Vis due to the localized surface plasmon resonance (LSPR) effect. The LSPR phenomena of AgNPs results in a strong absorption peak near 400 nm that depends mainly on the NP mean size and shape distribution [1]. Figure 1a-d shows the characteristic photoabsorption of the prepared AgNPs with honey and several root extracts.

The AgNPs formation were confirmed with a Transmission Electron Microscopy image (Figure 2). The MWAC synthesis led to spheric and small AgNPs with mean size of 11 nm.

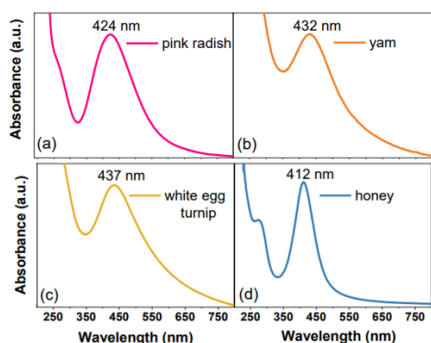


Figure 1. UV-Vis spectra of AgNPs colloidal dispersions synthesized using (a) pink radish, (b) yam, (c) white egg turnip, and (d) honey as natural compounds in a MWAC synthesis.

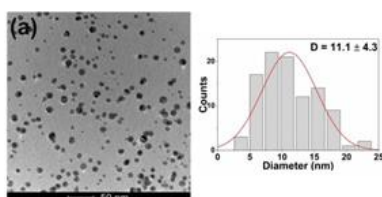


Figure 2. Transmission Electron Microscopy image of AgNPs synthesized from honey. [Honey] = 0.6 g mL⁻¹ [AgNO₃] = 3 mmol L⁻¹

Pristine TiO₂NPs synthesized by a MWAC methodology were impregnated with AgNPs prepared using honey solutions (TiO₂NPs @AgNPs). Figure 3a shows that hydrogen generation evolves steadily under UV-vis and under only visible light.

The hydrogen generation rate on TiO₂@AgNPs photocatalyst is notably lower under visible light compared to UV-vis illumination. However, this highlights the photocatalyst's capacity to remain

Conclusions

A sustainable approach has been used for the synthesis of AgNPs based on a microwave assisted method in aqueous medium. The green and cost-effective preparation of the inorganic nanomaterials led to the production of the TiO₂@AgNPs photocatalyst with higher efficiency than pure TiO₂NPs in H₂ evolution and with visible light activity. The methodology described here for the inorganic NPs can be extended for synthesizing several types of NPs showing the potential for photocatalysts preparation in large amounts using sustainable chemical compounds

Acknowledgments

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active even under visible light exposure. When subjected to UV-vis irradiation, the hydrogen evolution rate of TiO₂@AgNPs surpasses pristine TiO₂NPs by a factor of 3.5, further emphasizing the considerable potential of the eco-friendly photocatalyst for solar-to-hydrogen conversion. Moreover, TiO₂@AgNPs exhibit outstanding recycling capabilities, maintaining consistent hydrogen generation over three consecutive photocatalytic cycles, as depicted in Figure 3b

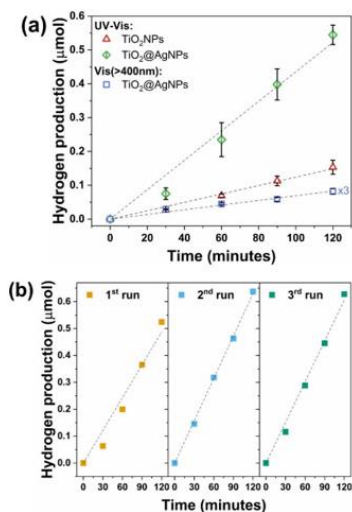


Figure 3. (a) Hydrogen photogeneration experiments under UV-vis and visible radiation using TiO₂NPs and TiO₂@AgNPs. (b) Recycling of the TiO₂@AgNPs under UV-Vis irradiation for 3 cycles. Methanol acted as a sacrificial agent (methanol/water ~1/8 v/v) and the AgNPs were synthesized using [honey] = 0.6 g mL⁻¹, [AgNO₃] = 6 mmol L⁻¹ and pH 3.8