Sustainable and Versatile Synthesis of Silver Nanoparticles and Their Photocatalytic Application

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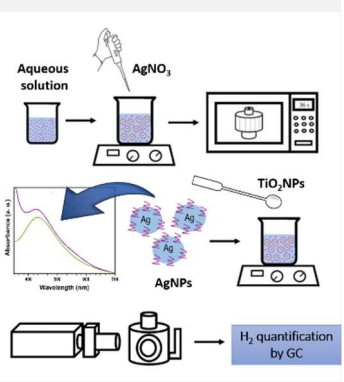

Silver nanoparticles (AgNPs) exhibit distinct properties depending on their size and shape, making them useful in various fields. The development of environmentally sustainable methodologies to obtain these materials represents a critical necessity. In this work, AgNPs were synthesized through microwave assisted chemistry (MWAC) using aqueous solutions of fructose and sodium citrate. The influence of synthesis parameters on the AgNPs optical behavior was investigated by UV-visible spectroscopy. Some of the synthesized AgNPs were loaded onto TiO_2 nanoparticles (TiO_2@AgNPs) and tested for hydrogen photogeneration under UV-visible irradiation. After 2 h of irradiation, an increase in the hydrogen production from 1.6 up to 4.7 times was observed for TiO_2@AgNPs when compared to pristine TiO_2. The effectiveness of hydrogen production was significantly affected by both the synthesis parameters of the AgNPs and the amount of AgNPs incorporated in the TiO_2.

Introduction

Metallic nanoparticles play an important role across various technological areas due to their versatile applications. Silver nanoparticles (AgNPs), in particular, can be used in biomedical, food, environmental, and electronic fields [1,2]. When incorporated into a titanium dioxide (TiO_2) support, AgNPs can serve as co-catalysts in water photo-reduction for hydrogen production [3]. However, a significant challenge in working with nanostructured materials lies in developing synthesis methods that yield nanoparticles with desired properties. For successful synthesis of AgNPs, it is crucial to provide an environment that prevents their tendency to agglomerate owing to their high surface energy [1]. Numerous studies have explored plant extracts and other non-harmful media as stabilizing and reducing agents, aiming to achieve sustainable AgNPs synthesis [1,2,4]. Additionally, microwave assisted chemistry (MWAC) emerges as a promising approach, offering rapid and uniform heating [5].

Hence, the present work suggests a green method utilizing microwave irradiation to synthesize AgNPs, which were subsequently impregnated into TiO_2NPs. A combination of two chemicals commonly used by the food industry, D-fructose and sodium citrate, was employed to both reduce and stabilize the silver nanoparticles. The synthesis parameters were optimized to achieve particle sizes that lead to distinct optical properties. The resulting TiO_2@AgNPs nanostructures were evaluated as photocatalysts for hydrogen production via the photo-reform of methanol at room temperature under UV-Vis irradiation.

Material and Methods

Silver nanoparticles (AgNPs) were prepared using silver nitrate ($AgNO_3$) as the silver precursor and a solution of D-fructose and sodium citrate as both reducing and stabilizing agents. Ultrapure water (Milli-Q®) was the solvent. The following aqueous stock solutions were prepared: i) 0.5 mol/L $AgNO_3$ (Plat LAB - Comércio de Artigos para Laboratórios e Serviços Ltda); ii) 0.5 $g.mL^{-1}$ D-fructose (Carlo Erba Reagents); iii) 0.5 $g.mL^{-1}$ sodium citrate (Vetec Química Fina Ltda). For each synthesis condition, a 30 mL final volume was prepared by adding varying amounts of the stock solutions under stirring, then transferred into a polytetrafluoroethylene (PTFE) reactor. Heating was performed by irradiated in a domestic microwave (MW) oven at maximum power of 1400 W, for 36 s. The colloidal AgNPs obtained were diluted in water for characterization by UV-Visible spectroscopy.

AgNPs were loaded onto titanium dioxide nanoparticles TiO_2NPs also prepared by MWAC using titanium (IV) bis(ammoniumlactato)dihydroxide (TALH), a water-soluble titania precursor, and aqueous ammonia solution [4]. Colloidal AgNPs were added to achieve weight percentages (wt. %) of Ag/TiO_2 from 0.5 – 4.5%. A wet impregnation procedure was employed and the obtained TiO_2@AgNPs samples were oven dried and calcinated in atmospheric air for 3h at 400°C (heating rate of 3°C/min). They were characterized by UV-diffuse.

The photocatalytic behavior of the TiO_2@AgNPs was tested using a high pressure Xe/Hg lamp (Sciencetech Inc. 140 W) [6]. Methanol/water solutions (~1/8 v/v) containing 1 $mg.mL^{-1}$ of the photocatalyst were employed and H_2 production was determined by gas chromatography (Shimadzu GC-2010 equipment with a molecular sieve 5 Å packed column).

Results and Discussion

The synthesis parameters underwent optimization through individual variations of the concentration of each solution. Figure 1 shows the impact of fructose concentration while holding silver precursor and sodium citrate constant. A surface plasmon resonance (SPR) band is discernible for all samples, attributed to the collective oscillation of surface electrons in metallic AgNPs [1,2].

It can be observed that lower concentrations of fructose result in a red shift in the absorption spectra. The sample

synthesized at [fructose] = 0.01 g.mL^{-1} exhibits a maximum wavelength (λ_{max}) at 410 nm, whereas a maximum of 400 nm was observed for [fructose] = 0.10 g.mL^{-1}. The inset in Figure 1 presents a photograph of the synthesis solution after irradiation, which helps to illustrate its distinct behavior. Furthermore, the full width at half maximum (FWHM) indicates that the concentration of 0.01 g.mL^{-1} results in a broader absorption peak, measuring 64 nm, while the sample at 0.10 g.mL^{-1} exhibits a narrower peak, measuring 49 nm. The shift and broadening of the SPR peak observed for AgNPs synthesized at [fructose] = 0.01 g.mL^{-1} suggest a larger size distribution compared to the other samples. Transition electron microscopy analysis is currently in progress in order to confirm these findings.

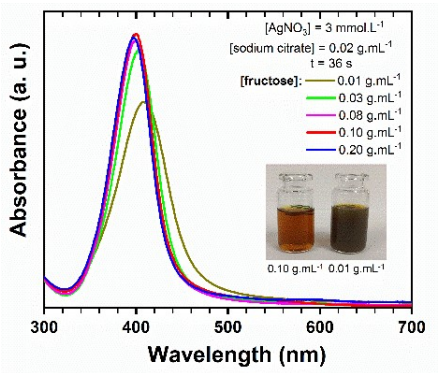

Figure 1. UV-Visible spectra of AgNPs synthesized with 3 mmol.L^{-1} $AgNO_3$ and 0.02 g.mL^{-1} of sodium citrate in the presence of variable amounts of fructose. Inset: photograph of two solutions after the MW irradiation.

The results (not shown) from optimizing the concentrations of sodium citrate and silver precursor did not exhibit a notable shift in either the λ_{max} or the FWHM of the SPR band.

The AgNPs synthesized using fructose concentrations of 0.01 and 0.10 g.mL^{-1} were selected for testing H_2 photogeneration. Results after 1h and 2h of irradiation are depicted in Figure 2 for samples with varying amounts of AgNPs loaded onto TiO_2. In all samples, H_2 production was enhanced following the incorporation of AgNPs. However, increasing the amount of AgNPs resulted in markedly different behaviors for each synthesis condition. For AgNPs synthesized using [fructose] = 0.01 g.mL^{-1}, the increase in the H_2 generation correlated with the quantity of AgNPs. On the other hand, when the fructose concentration was 0.10 g.mL^{-1}, the best result was achieved at 0.5 wt.% Ag/TiO_2. These findings suggest that the size of the AgNPs significantly influences the impregnation process, which directly affects the H_2 production.

Results from the characterization of TiO_2NPS before and after impregnation with the AgNPs via UV-Vis diffuse reflectance spectroscopy revealed no significant alterations in the band gap. These results suggest the potential for optimizing the impregnation process, which could improve hydrogen production of the TiO_2@AgNPs samples.

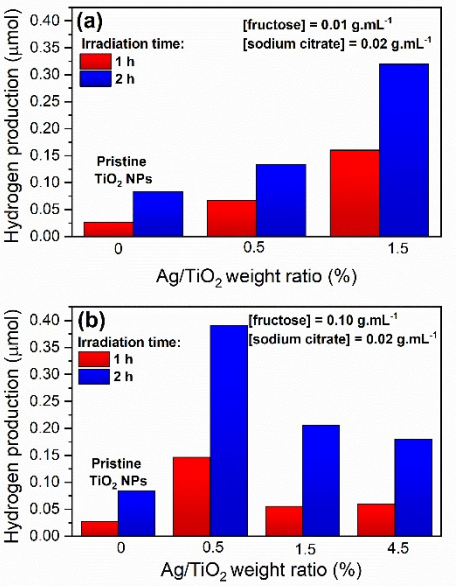

Figure 2. Photocatalytic hydrogen production under UV-Visible irradiation using the TiO_2@AgNPs. AgNPs were synthesized using [$AgNO_3$] = 3 mmol.L^{-1} and a solution of **(a)** [fructose] = 0.01 g.mL^{-1} and [sodium citrate] = 0.02 g.mL^{-1}; or **(b)** [fructose] = 0.10 g.mL^{-1} and [sodium citrate] = 0.02 g.mL^{-1}. Results for the pristine TiO_2 NPs are shown for comparison. In all cases methanol was used as sacrificial agent (methanol/water solution: ~1/8 v/v).

Conclusions

The synthesis method utilized in this study successfully produced stable AgNPs, employing a combination of fructose and sodium citrate. Results demonstrate the influence of aqueous media on the properties of AgNPs synthesized by MWAC. Preliminary data indicate that loading AgNPs onto pristine TiO_2NPs enhances their photocatalytic activity in the H_2 evolution reaction under UV-Vis irradiation by 1.6 up to 4.7 times. Ongoing efforts involve further characterization of the AgNPs by microscopy and optimization of the impregnation process. These endeavors hold promise for enhancing the photocatalytic efficacy of the TiO_2@AgNPs system.

Acknowledgments

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References

[1] C. V. Restrepo, C. C. Villa, *Environmental Nanotechnology, Monitoring & Management*, 15 (2021) 100428.
[2] O. Pryshchepa, P. Pomastowski, B. Buszewski, *Advances in Colloid & Interface Science*, 284, (2020) 102246.
[3] F. Conte, I. Rossetti, G. Ramis, C. Vaulot, S.Hajjar-Garreau, S. Bennici, *Materials*, 15 (2022) 2915.
[4] G. B. Strapasson, M. Assis, C. W. Backes, S. A. Corrêa, E. Longo, D. E. Weibel, *International Journal of Hydrogen Energy*, 46 (2021) 34264.
[5] A. Kumar, K. Yun, L. Zheng, X. Sun, *Materials Today Nano*, 11 (2020) 100076.
[6] G. B. Strapasson, F. R. Scheffer, S. W. Cendron, F. C. Silva, N. H. Lazzari, C. Azambuja, A. Peyrot, D. E. Weibel, *SN Applied Sciences*, 2 (2020) 543.