22º Congresso Brasileiro de Catálise
25 a 29 Setembro de 2023
Bento Gonçalves / RS

SBCAT
SOCIEDADE BRASILEIRA DE CATÁLISE

Synthesis of silver nanoparticles using plant extracts and microwave assisted chemistry and their potential application for hydrogen production

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Abstract

In this contribution, we report on a simple and rapid synthesis of silver nanoparticles (AgNPs) using microwave (MW) assisted chemistry, with different natural extracts. The extracts obtained from plants were used to reduce/stabilize AgNPs and $AgNO_3$ acted as metal precursor in aqueous medium. The samples were characterized by UV-Vis spectroscopy, revealing the presence of a plasmonic band associated with AgNPs around 410-460 nm. Furthermore, the stability over time for AgNPs prepared using white cabbage was monitored, showing that AgNPs remained stable for at least 21 days. AgNPs were impregnated into titanium dioxide nanoparticles (TiO_2@AgNPs) also prepared by MW irradiation. The photocatalytic activity of TiO_2@AgNPs was tested for H_2 evolution in the photo-reform of methanol under UV-Vis irradiation, demonstrating greater efficiency compared with the TiO_2NPs counterparts.

Keywords: AgNPs, green synthesis, microwave, photocatalysis, H_2 evolution

Introduction

In recent decades, the escalating apprehension regarding the detrimental impact of fossil fuels on the environment has led to an increased focus on the concept of green chemical efficiency, since it can offer a simple and non-polluting alternative (1). One area of focus has been the investigation of cleaner and renewable energy sources to replace those based on fossil fuels. In this context, the use of photocatalysts to generate hydrogen through water splitting has emerged as a significant option. However, to be suitable for sustainable hydrogen production via water splitting, a photocatalyst must meet several criteria (2,3). It should have an appropriate band gap energy and be able to absorb visible light across a wide range. Additionally, it must possess excellent chemical stability and maintain its catalytic activity over a long period of time. Lastly, the photocatalyst should be cost-effective and readily available for large-scale commercialization.

In the search for a suitable photocatalyst for H_2 generation via water splitting it is a well stablish procedure to add a co-catalyst to a nanostructured material in order to further improve its efficiency. Metallic nanoparticles are of great interest as co-catalysts because they exhibit an optical behavior under light irradiation called Localized Surface Plasmon Resonance (LSPR) (4). Among metallic nanoparticles, silver nanoparticles (AgNPs) are particularly noteworthy due to their unique properties that enable a broad range of potential applications. In addition to being used in catalysis and photocatalysis, AgNPs have been employed in environmental applications (5), as antibacterial agents (6), and in anticancer therapies (7), among other fields. Consequently, there is significant motivation to synthesize AgNPs with precisely controlled characteristics.

An environmentally friendly approach to synthesizing AgNPs involves using plant extracts, which has been demonstrated previously (4). This method is simple, utilizes mild conditions, and requires a short time for nanoparticle synthesis. Cabbage and turnip extracts are examples of plants that can serve as reducing agents and stabilizers in AgNP synthesis (8,9). Additionally, microwave-assisted (MW) synthesis is a green chemistry approach that provides faster and more homogeneous heating than other methods. This study aims to develop a green synthesis method for generating silver nanoparticles using plant extracts as reducing and stabilizing agents in domestic microwaves. The objective is to demonstrate a simple, cost-effective, and environmentally friendly method with a high yield of metallic nanoparticles that can be utilized as co-catalysts for H_2 generation.

Experimental

Preparation of Plant Extract

In order to prepare extracts from white and red cabbage, the plants were first chopped separately and blended in a blender with Milli-Q water until a uniform mixture was formed. For passion fruit, turnip kabu, and chayote plants, their bark was removed, and their pulp was blended. The mixture obtained for each plant was then filtered using a Buchner filter. The concentration of the extract was determined by calculating the ratio between the mass of the plant used and the amount of water that was added during the blending process.

Microwave-assisted synthesis of nanoparticles

The synthesis of the silver nanoparticles (AgNPs) was performed using the plant extract, to reduce and to stabilize the nanoparticles that were formed. A stock solution of silver nitrate ($AgNO_3$) with 0.5 mol.L^{-1} concentration was added under agitation in order to obtain the desired concentration of silver precursor in the solution. For each synthesis, the solution was introduced into a Teflon reactor and submitted to microwave (MW) irradiation in a domestic microwave (1600 W), for 36 seconds. The concentration of the extract was varied in a series of syntheses. The silver concentration was previously investigated and it was fixed as 3 mmol.L^{-1} for all the synthesis.

Titanium dioxide (TiO_2) nanoparticles (TiO_2NPs) were also synthesized by microwave assisted chemistry in aqueous medium. For that, a commercial microwave was used (MARS6 – CEM Corporation) and Titanium(IV) bis(ammoniumlactato)dihydroxide (TALH, 50 wt% in H_2O) and aqueous ammonia solution (28.0–30.0% of NH_3) were used, flowing the methodology described in a previous work (9).

The photocatalyst TiO_2@AgNPs was prepared by wet impregnation of selected AgNPs in the TiO_2NPs. The dry and calcinated TiO_2NPs were dispersed in water and sonicated and a desired amount of the colloidal AgNPs solution was added and stirred for 1h. The material was kept overnight and the precipitate was recovered by centrifugation, dried and calcinated for 3h at 400°C.

Characterization

In order to evaluate the formation of the nanoparticles, each colloidal solution obtained after the synthesis was diluted with water and measured by UV-Vis spectroscopy in the wavelength range of 200 – 800 nm, using a Cary® 50 UV-VIS – Varian. The photocatalytic experiments were carried out using a high pressure Xe/Hg lamp of 350 W (Scientech). The photocatalyst to be tested was suspended on a methanol/water solution (~1/8 v/v) and sonicated for 30 minutes before being placed in a photochemical reactor (24.16 ± 0.01) made of PTFE. The photocatalytic activity was evaluated by gas chromatography (Shimatzsu GC-2010 chromatograph) using a molecular sieve 5A packed column. Further details on photocatalytic evaluation procedure can be found elsewhere (10).

Results and Discussion

Ag nanoparticles synthesis and characterization

Silver nanoparticles (AgNPs) were synthesized by microwave irradiation using $AgNO_3$ as silver precursor, and different plant extracts were used as reducing and stabilizing agents. Table 1 displays the wavelengths at which each extract reaches its maximum absorption band (λ_{max}) in a fixed concentration of extract and $AgNO_3$, specifically 0.5 g/mL and 3 mmol/L, respectively. The optical absorption spectra obtained after the syntheses show an absorption band in the visible region of about 430 to 460 nm, associated with the presence of AgNPs, for all samples. These absorptions are originated mainly from the LSPR effect of AgNPs (4). Despite presenting relatively close absorbance peaks, the extracts exhibited different band widths (results not shown). Furthermore, the chayote extract did not reveal any absorbance peak, demonstrating that each extract plays a distinct role in the formation of silver nanoparticles.

Table 1. Comparison of the wavelength of the maximum absorption band (λ_{max}) of the extracts used for the green synthesis of AgNPs. The synthesis was performed using the same concentrations of plant extract and $AgNO_3$ for all samples: 0.5 g.mL^{-1} and 3 mmol.L^{-1}, respectively.

Plant name	**Scientific name**	λ_{max} **(nm)**
White cabbage	*Brassica oleracea var. capitata*	431
Passion fruit	*Passiflora edulis*	463
Red cabbage	*Brassica oleracea var. capitata f. rubra*	437
Turnip Kabu	*Brassica rapa subsp. rapa*	442
Chayote	*Sechium edule*	-

The most favorable results were obtained through the synthesis process utilizing white cabbage. The intense and distinct absorption band observed strongly suggests successful formation of AgNPs with a uniform size distribution. Moreover, the low wavelength value of the observed λ_{max} indicates that the nanoparticles are of small size. Due to this reason, the synthesis process utilizing white cabbage was further optimized. The concentration of the silver precursor was kept constant at 3 mmol.L^{-1}, since it already led to a high intensity in the UV-Vis spectrum and the concentrations of the white cabbage extract was varied.

The absorption spectra for the synthesis with different concentrations of the extract are shown in Figure 1. One can notice that the most promising result was for a concentration of 1.25 g of extract per mL of water. In Figure 1, it can also be seen that there is a decrease in the absorption when a certain threshold concentration is reached. Therefore, there is an optimal proportion between the silver precursor and the plant extract that leads to the reduction of the Ag^+ to form the metallic nanoparticles that are stabilized by the extract.

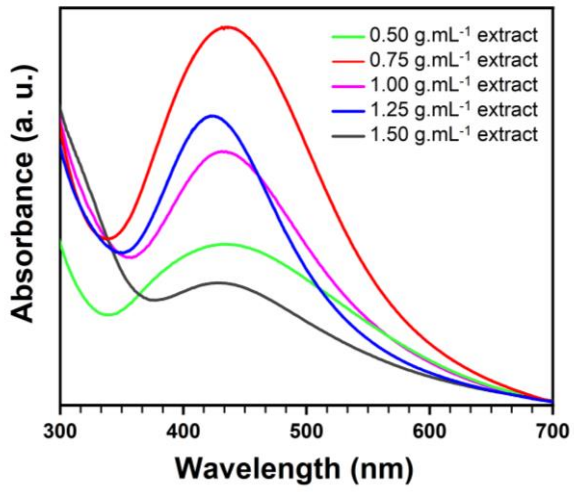

Figure 1. UV-Vis spectra of AgNPs, 3 mmol of silver precursor were added in the synthesis.

Stability tests of the AgNPs

Ensuring good stability of nanoparticles over time is crucial. Therefore, the stability of the AgNPs was monitored using UV-Vis spectroscopy, and the results are presented in Figure 2. Notably, the AgNPs exhibited remarkable stability for at least 21 days, as evidenced by the consistent intensity and width of the absorption band over time.

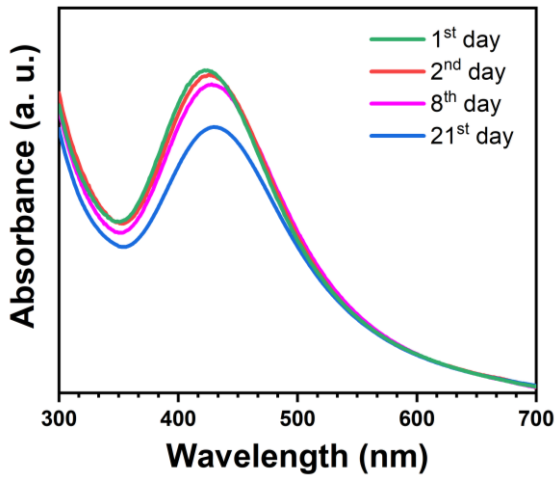

Figure 2. AgNPs stability demonstrated by UV-Vis after several days.

Photocatalytic hydrogen generation

The AgNPs synthesized using white cabbage extract with 1.25 $g.mL^{-1}$ concentration and a final concentration of 3 $mmol.L^{-1}$ of $AgNO_3$ were impregnated into TiO_2NPs in order to obtain the photocatalyst TiO_2@AgNPs with a Ag/TiO_2 weight ratio of 1%. The photocatalytic results for H_2 evolution using methanol as the sacrificial agent are shown in Figure 3, for the TiO_2@AgNPs photocatalyst compared with the TiO_2NPs without AgNPs impregnation. Results for two sequential runs of photocatalytic experiment using the TiO_2@AgNPs are displayed in Figure 4, revealing that the activity of the photocatalyst for the H_2 evolution reaction was stable for at least 8 h of continuous irradiation.

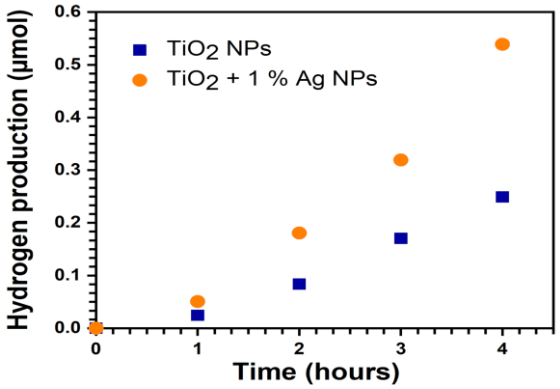

Figure 3. Photocatalytic hydrogen production under UV-Vis irradiation.

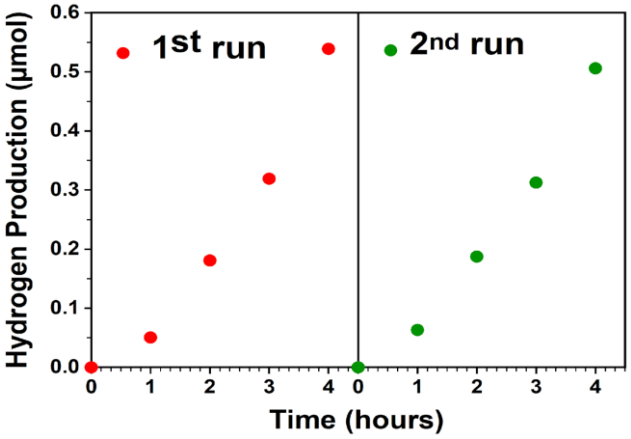

Figure 4. Hydrogen evolution rate for two sequential runs using the TiO_2@AgNPs.

Conclusion

Based on the results obtained in this work, we can conclude that the microwave-assisted synthesis of silver nanoparticles using plants extracts, especially, white cabbage extract, is a technique with great potential, proving to be effective, fast and sustainable. The prepared silver nanoparticles were impregnated in titanium dioxide nanoparticles and later used in hydrogen photogeneration

experiments demonstrating its superior performance compared to pure titanium dioxide nanoparticles. Furthermore, the nanoparticles proved to be stable for a considerable period of time and demonstrated their potential to increase hydrogen production when compared to TiO_2 NPs.

Acknowledgments

The authors would like to thank to CNPq, CAPES and FAURGS for the financial support.

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