



Photocatalytic Performance of AgNPs-Zeolite Composite by Hydrothermal Synthesis for Water Splitting

Rua'a F. Ahmed*, Mohamed K. Dhahir

Institute of Laser for Postgraduate Studies, University of Baghdad, Baghdad, Iraq

* Email address of the Corresponding Author: ruaa.fawzi1201a@ilps.uobaghdad.edu.iq

Article history: Received 1 Apr 2023; Revised 1 July 2023; Accepted 5 July 2023; Published online 15 Dec 2023

Abstract: Two samples of (Ag NPs-zeolite) nanocomposite thin films have been prepared by easy hydrothermal method for 4 hours and 8 hours inside the hydrothermal autoclave at temperatures of 100°C. The two samples were used in a photoelectrochemical cell as a photocatalyst inside a cell consisting of three electrodes: the working electrode photoanode (AgNPs-zeolite), platinum as a cathode electrode, and Ag/AgCl as a reference electrode, to study the performance of AgNPs-zeolite under dark current and 473 nm laser light for water splitting. The results show the high performance of an eight-hour sample with high crystallinity compared with a four-hour sample as a reliable photocatalyst to generate hydrogen for renewable energies.

Keywords: nanocomposite, PEC water splitting, catalyst, hydrothermal synthesis, zeolite.

1. Introduction

Water splitting via photoelectrochemical cell (PEC) technology offers a sophisticated method and useful strategy for dealing with the issues of energy and environmental crises by converting light energy to produce hydrogen fuel by splitting water reactions, which divide water into O₂ and H₂ (2H₂O→2H₂+O₂). In the PEC process, the water-splitting reaction needs photon energy to be catalyzed by a photocatalyst. To resist the positive free energy result from PEC water splitting. Where it needs stable electrodes, effective photoelectrodes, and scalable PEC cells with cost-effective operation for large-scale hydrogen production [1,2], as shown in Fig.1.

Noble metal nanoparticles were used in PEC cells, where metallic nanoparticles (NP) are attracting the interest of chemists due to their novel properties, which include a high surface area and exceptional surface activity that provide excellent catalytic, optical, and electrical properties. where specifically found in noble metals such as gold and silver or the subnanometric particles contained in zeolites. Zeolite, an alkali or alkaline-earth metal hydrated aluminosilicate mineral, has received a lot of attention lately as a readily accessible and affordable natural mineral [4], which is a significant class of functional materials. Porous zeolites are anticipated to attain high H₂ evolution efficiency due to their distinctive and large surface area.



The family of zeolites is well-known as a class of crystalline porous materials with high catalytic activity, well-confined periodic porous structure, acid resistance, and ion exchange capability [5].

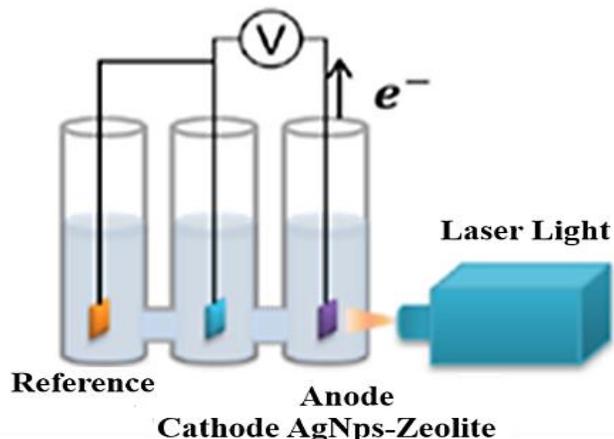


Fig.1: A diagram explaining a PEC cell with a standard three-electrode arrangement [3].

The progress made shows that the improved adsorption performance as well as the high separation and transfer efficiency of photogenerated charge carriers are crucial for the photocatalytic enhancement of zeolite-based composites. Because of their well-defined pore and channel architectures, these materials are commonly utilized as ion exchangers, catalysts, and adsorbents in industry [6]. The zeolite structure can be filled with transition metal atoms through conventional impregnation, hydrothermal processes, photosynthesis, or cation exchange using a traditional ion exchange approach [7].

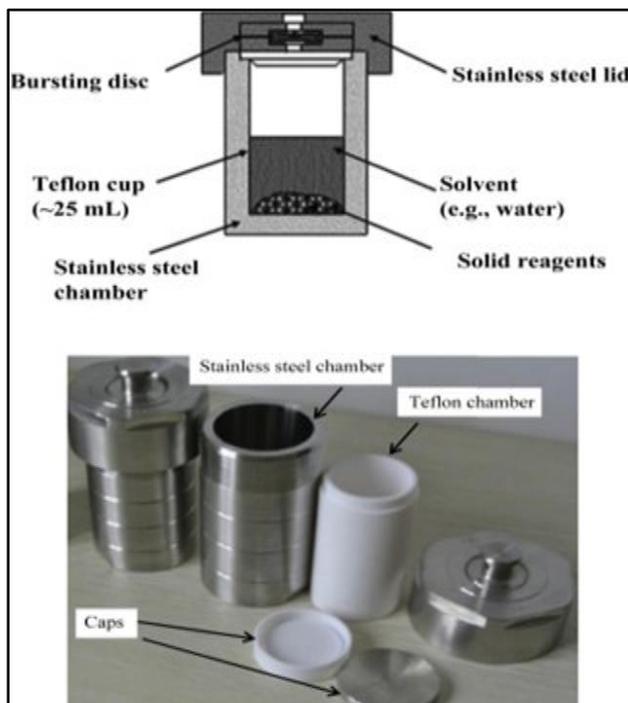


Fig.2: Image of stainless-steel autoclaves with Teflon lining and internal parts (upper). The reaction chamber, which is made of stainless steel, contains the Teflon chamber. The stainless-steel chamber in the lower image is lined with Teflon and is commercially available [9].

Recently, researchers' interest in the single-pot hydrothermal approach has increased [6]. The process of hydrothermal synthesis is used to create materials at low temperatures with high vapor pressure. This approach is thought to be the most energy-efficient and environmentally benign because the reaction is carried out in closed-system settings. Typically, hydrothermal synthesis is performed in aqueous solutions using a Teflon-lined stainless-steel autoclave, as shown in Fig.2 [8]. Employing laser light as an excitation source to research photocatalyst activity has an extremely high degree of feasibility. A diode laser (473 nm) has the specific characteristics of a special laser light source, including high intensity and monochromaticity.

In this paper, AgNPs-Zeolite composites were synthesized by the hydrothermal method using an autoclave with different crystallization times (4 and 8 hours), and then the structure and morphology characterization were investigated. Also, a comparison between the samples as the best-performing catalyst in photocatalytic water splitting.

2. Materials and Methods

Ag NPs-zeolite has been synthesized by the hydrothermal method, where silver nanoparticles (0.2 g, 20 nm particle size, spherical) from Hongwu International Group Ltd., China, were dissolved in 5 mL of deionized water and 10 mL of polyethylene glycol 600 (PEG 600) from the manufacturer, Alpha Chemika, made in India, at (250C) for 30 min with stirring, and nanozeolite particles of size 50 SSA: 340 m²/gr were added (0.2 g) also with 20 mL from an absolute ethyl alcohol manufacturer. Alpha Chemika, made in India, was added to the mixture gradually with stirring for 2 hours. Finally, the crystallization method was easy; the mixture was placed inside a hydrothermal autoclave and then a thermal oven that was kept at 100 OC for 4 and 8 hours for two samples, respectively, as shown in Figure 3. The Ag-NPs-Zeolite composite was obtained after steps of filtration and drying at 100 OC for 1 hour in the oven, with the pH kept near neutral during the step of the filtration process. Then it is deposited by the distillation method on a fluorine-doped tin oxide (FTO) substrate and used as an electrode in the applications of PEC for water splitting.

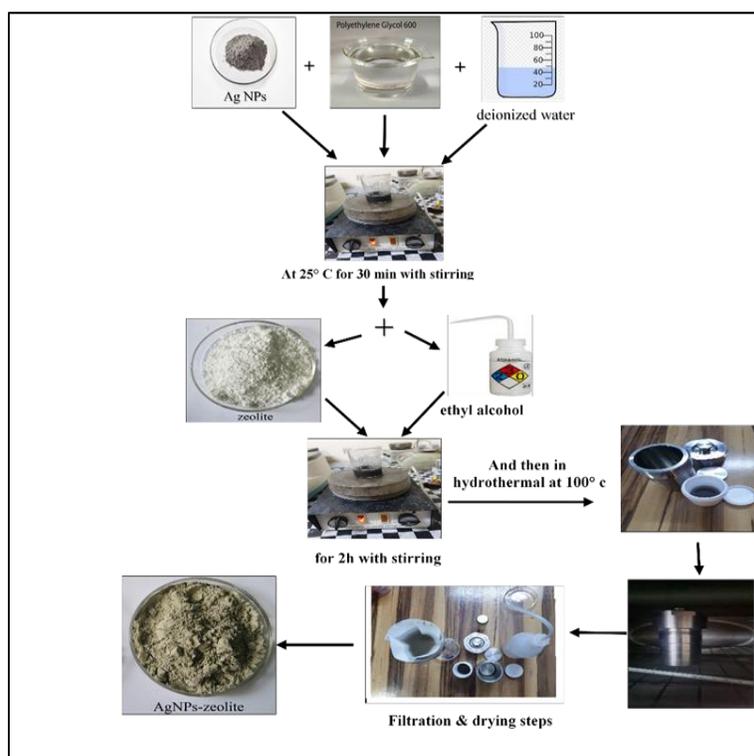


Fig.3: Ag NPs-Zeolite composite preparation steps.

3. Characterization

The X-ray diffraction (XRD-6000) SHIMADZU 220V/50Hz (Japan) patterns of the samples were recorded using a diffractometer operating with a Cu -K α radiation in the 2θ angle range 50–800 with a step of 0.05° and with 0.60 s of accumulation at each point. A field emission scanning electron microscope (FESEM) (FEI Japan) was used to determine the morphology and particle size of Ag (Np)-zeolite. The SHIMADZU UV-VIS-NIR 1800 240V (Japan) spectrophotometer was obtained using a UV-vis spectrometer, the spectra between 190 and 1100 nm were captured and the Zeta potential analysis was performed (Zeta plus Brookhaven, 90 Bundle Instruments Corporation, USA).

4. Results and Discussion

4.1 X-Ray Diffraction Analysis

Figure 4 depicts the XRD patterns of the Ag-NPs-Zeolite composite. The purpose of the XRD investigation was to learn more about the crystalline nature of the synthesized nanocomposites. The good crystalline quality of the produced samples is confirmed by the sharp peaks [10]. The absorption peaks for zeolite appeared at $2\theta = 22.40, 23.10, 26.50,$ and 27.10 . All of the Zeolites' diffraction patterns clearly correspond to those on the Zeolite standard card (JCPDS 39-0223) [6]. From Fig.4, it is shown that the zeolite is crystalline. Also, it is observed that the Ag NPs-zeolite composite has notable peaks around $2\theta = 38.60, 44.70, 64.90,$ and 77.80 , which correspond to the silver nanoparticles. (111), (200), (220), and (311) crystal planes, these peaks' development shows that the crystalline phase of silver has developed within the Zeolite framework, which, when matched with standard silver values (JCPDS 04-0783) [11], can be indexed using the facets of silver's face-centered cubic crystal structure with the lattice constants ($a = b = c = 4.082975 \text{ \AA}$). These peak heights are consistent with the values in the standard card, like in the earlier reports [12,13]. Also, Fig. 4 shows that the crystallinity of the sample increases with aging time. The aging process allows for crystal size regulation. According to [14], the production of impurity phases is reduced and crystallization is accelerated. So, the longer crystallization time of the composition of (Ag NPs-Zeolite) produced a highly crystalline phase, as evidenced by the XRD peak intensity of sample 8 hours, which was more desirable in comparison with sample 4 hours.

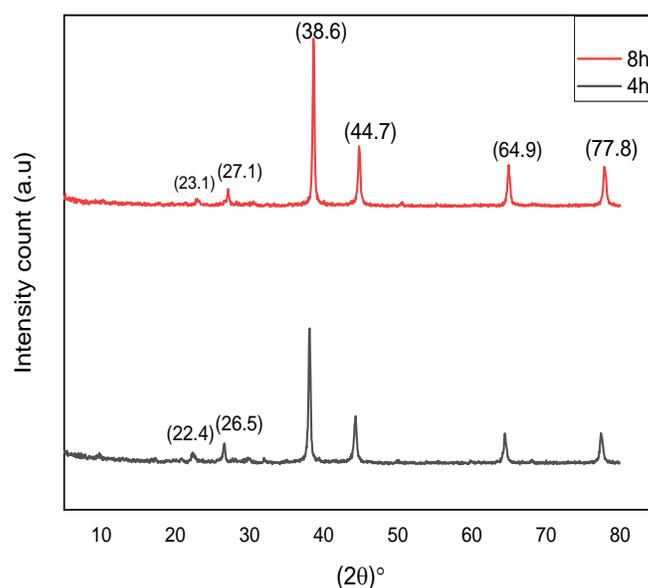


Fig. 4: XRD patterns of (Ag NPs-Zeolite) composite for two samples.

4.2 FESEM Analysis

AgNPs-zeolite electrodes were tested using field emission scanning electron microscopy. FESEM can specify the shape and particle size of samples. Figure 5(a) shows FESEM images for zeolite nanoparticles. From FESEM analysis, the morphology of the Zeolite surface appears as flakes, and their size ranges from (43-50) nm. The morphology of the composite for two samples shows a good distribution of silver nanoparticles in zeolite; this result agrees with the study in [15]. Also, silver nanoparticles are stable inside the pores of zeolite, and some of the AgNPs form clusters on the surface of the zeolite as shown in Fig. 5(b) for the sample after 4 hours with particle sizes ranging between (88–183) nm. Figure 5(c) illustrates an AgNPs-Zeolite nanocomposite for an 8-hour sample, with particle sizes ranging between (56-193) nm. Also, Fig.5(d) represents that the longer the crystallization time, the larger the average particle size; this means that the higher the crystallization time for (Ag NPs-Zeolite) composite, the more metallic particles will be made up, which means convert nanoparticles to bulk material, which begin to enlarge clearly after aging time for 4 hours and 8 hours, which agrees with research [16].

The composite in the previous figures displayed a rough surface with a spherical structure for silver nanoparticles and showed many silver clusters. At 100-200 °C in a hydrothermal autoclave, reduction results in the creation of silver clusters on the surface of zeolite; this agrees with [17]. Also, some shiny spots corresponding to the AgNPs appeared on the surface of the Zeolite nanoparticle; therefore, the AgNPs were rather well distributed in the Zeolite nanoparticles. This agrees with [18].

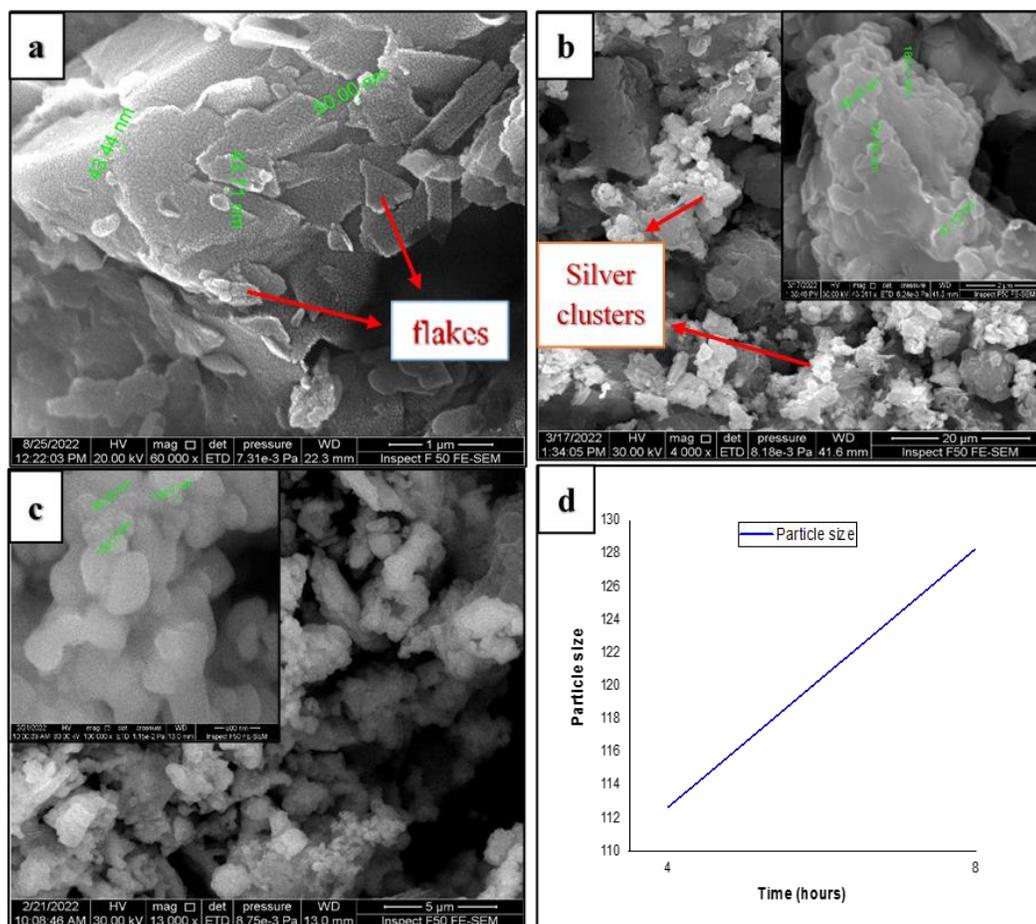


Fig.5: FESEM images for Zeolite and (Ag NPs-Zeolite) composite for two samples: (a) Zeolite, (b) a four-hour sample, (c) an eight-hour sample, and (d) the average particle size for two samples.

4.3 UV-Visible Spectral Study

Two samples exhibit a high level of absorption in the region of UV absorption. Figure 6(a) shows the highest peak of zeolite absorption at the peaks of (248,288) nm, while Fig.6 (b) shows the highest peak at (284) nm for silver. Ag species with more Ag atoms often produce UV-Vis bands at a longer wavelength, and the bands at 260 and 284 nm are attributed to Ag $n\delta^+$ ($n = 4-8$) clusters. This is in agreement with the research [19,20]. The reflectance spectra of the materials used (Ag NPs-Zeolite) in the visible and ultraviolet ranges were recorded below 300 nm; also, non-exchanged zeolites were observed. The silver-loaded zeolites produced stronger signals in the UV range (200–300 nm).

Figure 6 depicts the absorption peaks for (Ag NPs-Zeolite) composite for two samples: 4 hours (c) and 8 hours, (d) at (291,309) and (291,296) nm, respectively. These signals have previously been linked to isolated silver ions that are present at particular locations within the zeolite framework. It also shows that the intercalation of silver ions into the zeolite structure has slightly altered the zeolite's electron structure, which is well in line with other reports [16,21]. The process of prolonging the crystallization time increases the intensity of the absorption, as shown in the 8-hour sample in Fig.6 (d), indicating the growth of the amount of metal Ag particles according to [16].

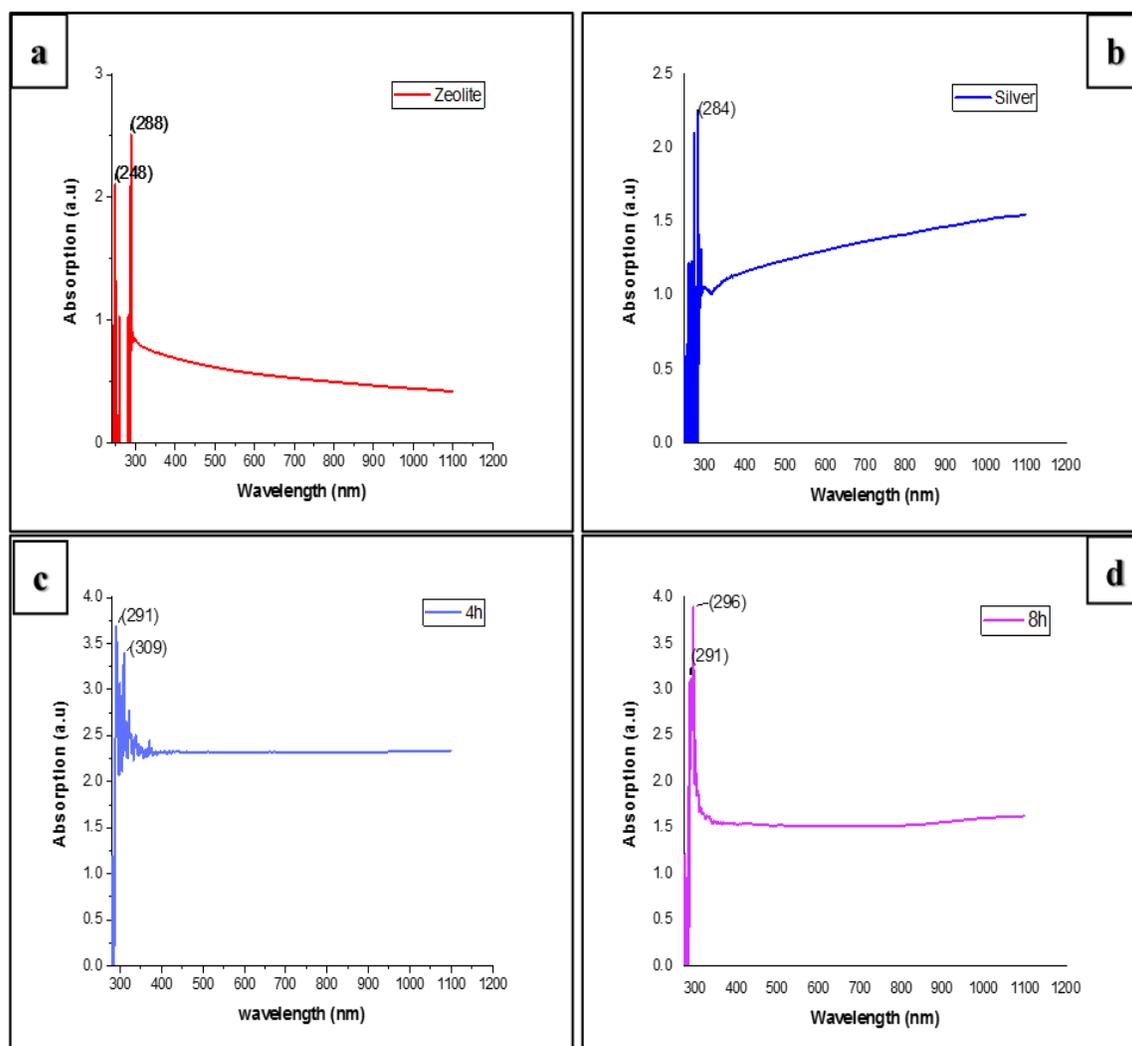


Fig.6: UV-visible spectrum for Zeolite, Silver NPs, and (Ag NPs-Zeolite) composites for two samples (a) Zeolite; (b) Silver (Ag NPs); (c) a 4-hour sample; (d) an 8-hour sample.

4.4 Zeta Potential Analysis

The zeta potential is the total charge that a particle picks up in a specific medium. The surface charge of the (AgNPs-Zeolite) composite dissolved by the solvent solution after the crystallization process by hydrothermal autoclave to obtain the measurement of (AgNPs-Zeolite) by zeta-potential. Zeta potential was typically used to gauge a surface's resistance to agglomeration. The stability of an (AgNPs-Zeolite) composite in colloidal form can be predicted using the zeta potential, with a value of greater than +30 mV or less than -30 mV suggesting the least amount of particle aggregation brought on by electrostatic attraction. Where the electrical stability of colloids increases when their zeta potentials, whether negative or positive, are enhanced, whereas aggregates and agglomerates are described by low zeta potential values, which is supported by [22, 23]. The surface charge for Zeta potential for the (Ag NPs-Zeolite) composite is illustrated in Fig.7. It has low stability of the (Ag-Zeolite) nanoparticles, mobility values, and zeta potential values for the two samples observed in Table 1. This explains the presence of silver nanoclusters on the surface of the zeolite in the above FESEM images.

Table 1: The values of the zeta potential and the mobility of the (Ag-Zeolite) nanoparticle solution.

The Nanoparticle solution	Zeta potential (mV)	The mobility ($\text{m}^2 \text{V}^{-1} \text{s}^{-1}$)
Ag-Zeolite	- 25.01	-1.95

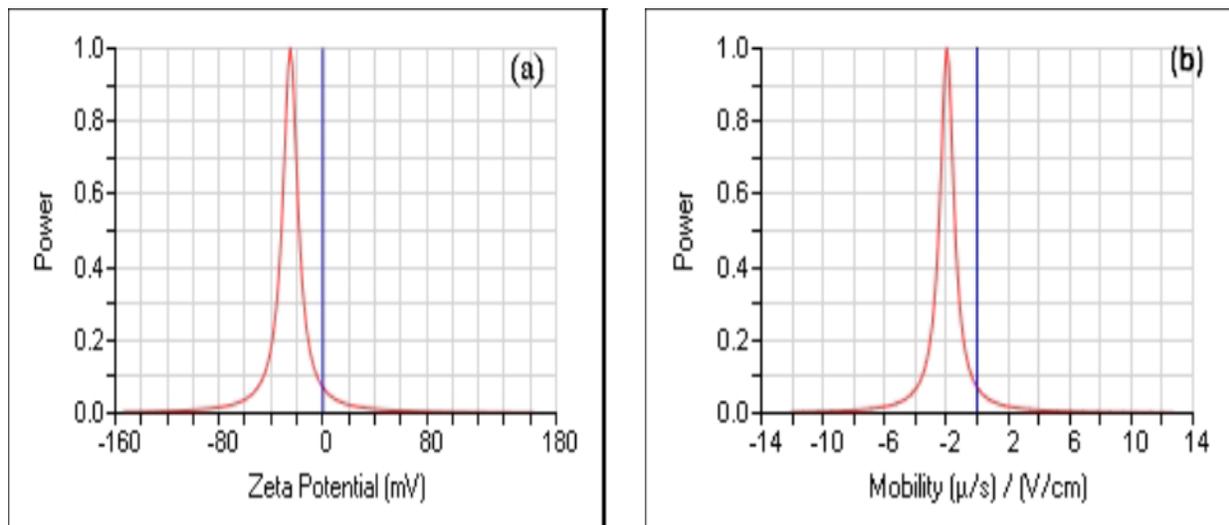


Fig.7: (a) the (Ag-Zeolite) nanoparticle solution's zeta potential (mv); (b) the (Ag-Zeolite) nanoparticle solution's mobility ($\text{m}^2 \text{V}^{-1} \text{s}^{-1}$).

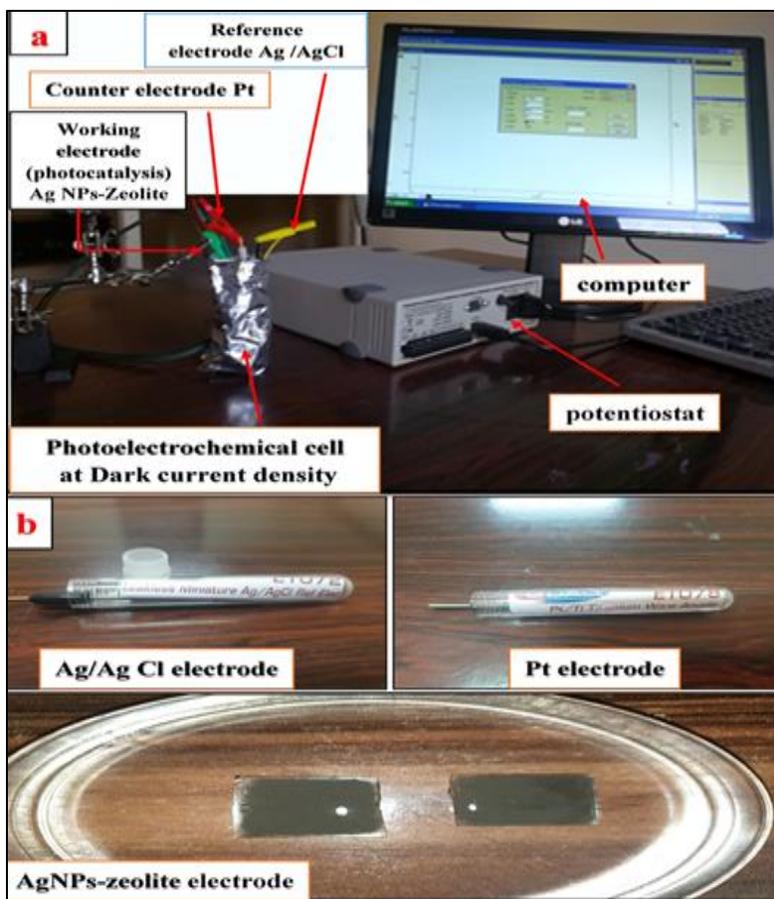
5. Characterization of AgNPs-Zeolite Photocatalyst Performance in a Photoelectrochemical Cell at Dark Current Density and 473nm Laser Illumination

A photoelectrochemical cell containing three electrodes with an electrochemical workstation from (ER466, EDAQ company Australia, potential stat) was used to study the behavior of Ag NPs-Zeolite Photocatalyst. Firstly, at dark current density, and secondly, at 473 nm laser illumination, as shown in Fig.8.



Table 2: The J values at dark current and 473 nm laser illumination for each sample at 1 volt.

NO.	The samples	J mAcm ⁻² at Dark current	J _{laser} (473nm) mA cm ⁻² at (200 mW cm ⁻²)
1	AgNPs-Zeolite at 4 hours	0.0427	0.05061
2	AgNPs-Zeolite at 8 hours	0.0731	0.08511

**Fig.8:** (a) AgNPs-Zeolite Photocatalyst at Dark Current Density (b) Three Electrodes for Photoelectrochemical Cell.

The electrodes of a photocatalyst of (AgNPs-zeolite) nanocomposite were fabricated and employed as a photoanode to study the effectiveness of photoelectrochemical (PEC) water-splitting for AgNPs-zeolite under dark and laser light irradiation. The PEC water splitting performance of the AgNPs-zeolite nanocomposite was measured using linear sweep voltammetry (LSV) techniques to estimate the current density for PEC. Table 2 and Fig.9 of two samples show the electrode's current density increased gradually from (0.0427 to 0.05061) for a 4-hour sample and from (0.0731 to 0.08511) for an 8-hour sample upon exposure to 473 nm laser light, compared with dark current at a given voltage (0–1) V versus Ag/AgCl for 60 s of a cycle. The photo-responsive property of the synthesized catalyst is demonstrated by the enhancement in the current density of (AgNPs-zeolite) nanocomposite photoanode after exposure to laser light. I-V parameters of the (AgNPs-zeolite) photoanode for PEC water-splitting results show that under

laser light illumination as compared to dark current showed a six-fold enhancement in the photocurrent density and therefore enhanced PEC performance this agrees with researchers [24].

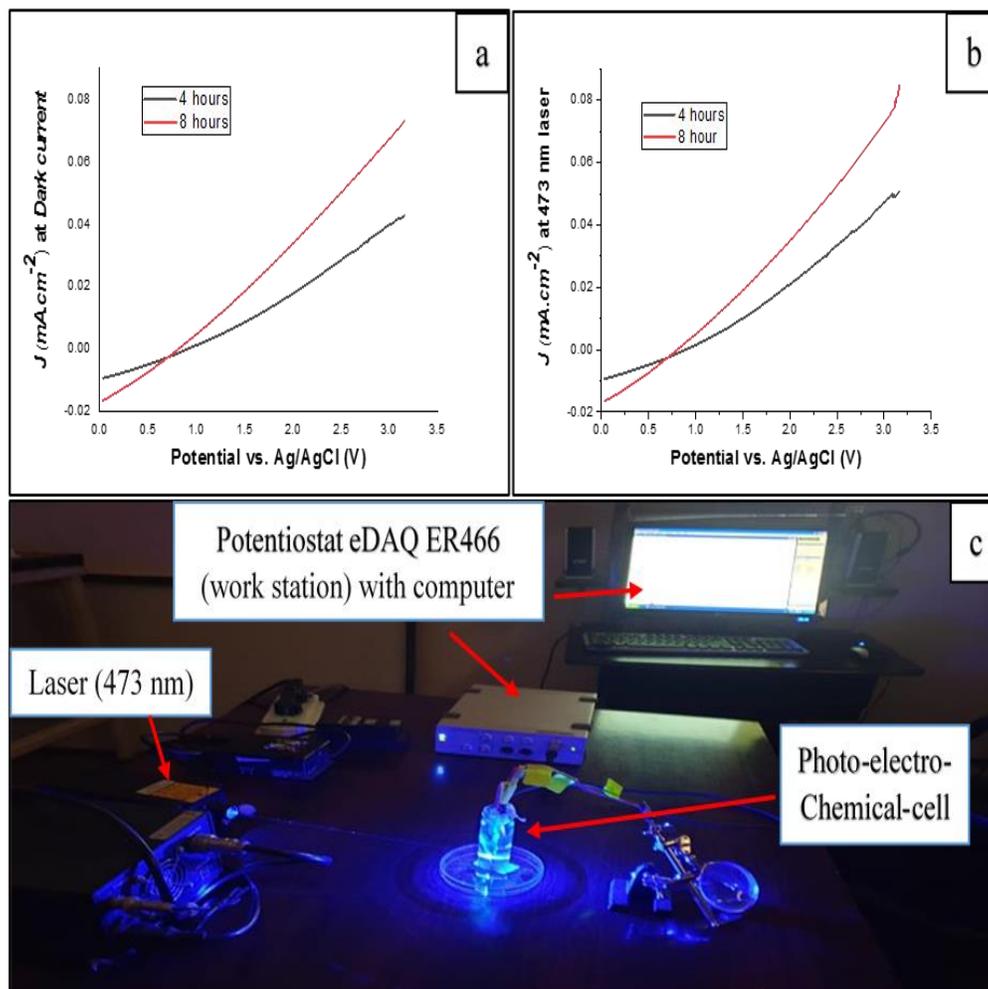


Fig.9: (a) and (b) show the linear sweep voltammetry response of (AgNPs-zeolite) nanocomposite photoanodes of two samples under dark and 473 nm laser light irradiation, respectively; (c) the AgNPs-zeolite photo anodes test for two samples under 473 nm laser light.

6. Conclusions

The results show that the (AgNPs-zeolite) photocatalyst is active in improving the performance of the photoelectrochemical cell for water splitting, and the speed of response for the catalyst is good. Also, the longer crystallization time of the AgNPs-zeolite nanocomposite during the manufacturing phase inside the hydrothermal autoclave made the performance of an eight-hour sample with high crystallinity better than a four-hour sample as a reliable photocatalyst to generate hydrogen for renewable energies.

References

- [1] Landman A, Halabi R, Dias P, Dotan H, Mehlmann A, Shter GE, Halabi M, Naserldeen O, Mendes A, Grader GS, Rothschild A. "Decoupled photoelectrochemical water splitting system for centralized hydrogen production" *Joule*, **4**(2),448-71 (2020).



- [2] Chang JH, Kumar M, Shen SY. "Fundamentals of photoelectrochemical water splitting" Nanostructured Materials for Photoelectrochemical Water Splitting IOP Publishing Ltd (2021).
- [3] Lee WC. "Photoelectrochemical water splitting and gas ionisation sensing using metal oxide nanostructures" (Doctoral dissertation, University of Sussex).
- [4] Torkian N, Bahrami A, Hosseini-Abari A, Momeni MM, Abdolkarimi-Mahabadi M, Bayat A, Hajipour P, Rourani HA, Abbasi MS, Torkian S, Wen Y. "Synthesis and characterization of Ag-ion-exchanged zeolite/TiO₂ nanocomposites for antibacterial applications and photocatalytic degradation of antibiotics" Environmental Research., **207**,112157(2022).
- [5] Cheng J, Gao C, Jing M, Lu J, Lin H, Han Z, Ni Z, Zhang D. "Photo-catalysis water splitting by platinum-loaded zeolite A." Materials Research Express, **5**(5),055506 (2018).
- [6] Hu X, Bai J, Wang J, Li C, Xu W. "Preparation of 4A-zeolite-based Ag nanoparticle composite catalyst and research of the catalytic properties" RSC Advances, **5**(4), 2968-73 (2015).
- [7] Shi Y, Ye S, Liao H, Liu J, Wang D. "Formation of luminescent silver-clusters and efficient energy transfer to Eu³⁺ in faujasite NaX zeolite. Journal of Solid State Chemistry" **285**,121227 (2020).
- [8] Hussain SA, Muhammad SK, Alkhayatt AH. "Hydrothermally growth of TiO₂ Nanorods, characterization and annealing temperature effect" Kuwait Journal of Science" **48**(3),(2021).
- [9] Kafle BP. "Introduction to nanomaterials and application of UV-Visible spectroscopy for their characterization" Chemical analysis and material characterization by spectrophotometry, **6**(2020).
- [10] Salem MA, Elsharkawy RG, Ayad MI, Elgendy MY. "Silver nanoparticles deposition on silica, magnetite, and alumina surfaces for effective removal of Allura red from aqueous solutions" Journal of Sol-Gel Science and Technology, **91**,523-38 (2019).
- [11] Agasti N, Kaushik NK. "One pot synthesis of crystalline silver nanoparticles" Am. J. Nanomater, **2**(1),4-7(2014).
- [12] Sowmya T, Lakshmi GV. "Soymida febrifuga aqueous root extract maneuvered silver nanoparticles as mercury nanosensor and potential microbicide" World Scientific News, **114**,84-105 (2018).
- [13] Hamid MK, Ghafoor DA, Obaid SA. "Characteristic and anticancer activity of silver nanoparticles of graviola (ANNONA) fruit juice as a reducing agent" Biochemical & Cellular Archives, **21**(1) 2021.
- [14] Nazir LS, Yeong YF, Sabdin S. "Formation of pure NaX zeolite: Effect of ageing and hydrothermal synthesis parameters" InIOP Conference Series: Materials Science and Engineering, IOP Publishing, **458**, 012002, (2018).
- [15] Das S, Pérez-Ramírez J, Gong J, Dewangan N, Hidajat K, Gates BC, Kawi S. "Core-shell structured catalysts for thermocatalytic, photocatalytic, and electrocatalytic conversion of CO₂". Chemical Society Reviews., **49**(10), 2937-3004(2020).
- [16] Temerev VL, Vedyagin AA, Iost KN, Afonassenko T, Tsyrlunikov P. "Enhanced adsorption properties of Ag-loaded β -zeolite towards toluene" InMaterials Science Forum Trans Tech Publications Ltd., **917**, 180-184 (2018).
- [17] Lopes CW, Martinez-Ortigosa J, Góra-Marek K, Tarach K, Vidal-Moya JA, Palomares AE, Agostini G, Blasco T, Rey F. "Zeolite-driven Ag species during redox treatments and catalytic implications for SCO of NH₃" Journal of Materials Chemistry A, **9**(48), 27448-58 (2021).
- [18] Mintcheva N, Panayotova M, Gicheva G, Gemishev O, Tyuliev G. "Effect of Exchangeable Ions in Natural and Modified Zeolites on Ag Content, Ag Nanoparticle Formation and Their Antibacterial Activity" Materials. **14**(15),4153(2021).
- [19] Temerev VL, Vedyagin AA, Iost KN, Pirutko LV, Cherepanova SV, Kenzhin RM, Stoyanovskii VO, Trenikhin MV, Shlyapin DA. "Purification of exhaust gases from gasoline engine using adsorption-catalytic systems. Part 1: trapping of hydrocarbons by Ag-modified ZSM-5" Reaction Kinetics, Mechanisms and Catalysis. **127**(2),945-59 (2019).
- [20] Shimizu K, Sawabe K, Satsuma A. "Unique catalytic features of Ag nanoclusters for selective NO_x reduction and green chemical reactions" Catalysis Science & Technology, **1**(3), 331-412011.
- [21] Mazzocut A, Coutino-Gonzalez E, Baekelant W, Sels B, Hofkens J, Vosch T. "Fabrication of silver nanoparticles with limited size distribution on TiO₂ containing zeolites" Physical Chemistry Chemical Physics, **16** (35),186903(2014).
- [22] Inbaraj BS, Chen BY, Liao CW, Chen BH. "Green synthesis, characterization and evaluation of catalytic and antibacterial activities of chitosan, glycol chitosan and poly (γ -glutamic acid) capped gold nanoparticles" International Journal of Biological Macromolecules, **161**,1484-95 (2020).
- [23] Yahiya LZ, Dhahir MK, Faris RA. "Novel and low-cost synthesis of ZNO nanorod coated by graphene oxide for enhanced physical absorption of ZNR from UV to VIS-IR region" Plant Archives, **20**(2),1005-8(2020).
- [24] Baig U, Khan A, Gondal MA, Dastageer MA, Falath WS. "Laser induced anchoring of nickel oxide nanoparticles on polymeric graphitic carbon nitride sheets using pulsed laser ablation for efficient water splitting under visible light" Nanomaterials, **10** (6),1098 (2020).



أداء التحفيز الضوئي لمركب AgNPs-Zeolite عن طريق التوليف الحراري المائي لتقسيم الماء

رؤى فوزي احمد*, محمد كريم ظاهر

معهد الليزر للدراسات العليا، جامعة بغداد، بغداد، العراق

*البريد الإلكتروني للباحث: ruaa.fawzi1201a@ilps.uobaghdad.edu.iq

الخلاصة: تم تحضير عينتين من الغشاء الرقيق (Ag NPs-zeolite) باستخدام طريقة حرارية مائية سهلة لمدة 4 ساعات و 8 ساعات داخل الأوتوكلاف الحراري المائي عند درجات حرارة 100 درجة مئوية. تم استخدام العينتين في خلية كهروكيميائية كمحفز ضوئي داخل خلية تتكون من ثلاثة أقطاب كهربائية: القطب الكهربائي العامل الضوئي (AgNPs-zeolite)، البلاتين كقطب كاثود، و Ag / AgCl كقطب مرجعي لدراسة أداء AgNPs-zeolite تحت تيار مظلم وضوء ليزر 473 نانومتر لتقسيم الماء. تظهر النتائج الأداء العالي لعينة مدتها ثماني ساعات مع تبلور عالٍ مقارنة بعينة مدتها أربع ساعات كمحفز ضوئي موثوق لتوليد الهيدروجين للطاقات المتجددة.

