Photo-enhanced piezocatalytic hydrogen evolution activity of clay based catalyst

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Introduction

The use of piezoelectric charges in catalytic applications has been investigated in recent years[1]. Studies have shown that negative and positive piezoelectric charges generated by mechanical vibration can be used for catalytic redox reactions[2]. Although the conduction band for photocatalytic hydrogen production is more positive than the potential for hydrogen reduction, a sufficiently strong piezoelectric field can bend the conduction band[3]. The asymmetrical distribution of ions in the crystal lattice structure causes the formation of electrical dipoles and positive and negative charges when mechanical stress is applied. In particular, it has been observed in studies that semiconductors with hexagonal crystal structure show high piezocatalytic activity[4]. The piezo catalytic activity of ZnO can be increased by increasing the charge separation with different inorganic semi-conductor surfaces[5]. In this study, ZnO was studied for piezocatalytic hydrogen production by forming nanocomposites with laponite clay. Laponite has the chemical formula $Na_{0.7}Si_8Mg_{5.5}Li_{0.3}O_{20}(OH)_4$ and its isomorphic layered structure produces negative charge, causing the surface to be negatively charged[6].

Experimental Section

Synthesis of Laponite/ZnO composite: Laponite/ZnO nanocomposite was synthesized by hydrothermal polyol method. Commercial laponite is dispersed in pure water, then laponite dispersion prepared by dissolving $Zn(NO_3)$ in diethylene glycol is added and the synthesis process is carried out in a balloon at 300 °C for 6 hours.

Piezocatalytic Hydrogen Evolution Experiments: 10 mg of catalyst was weighed and pyrlex was added to the cell, followed by the addition of 5% TEAO (pH=9) 20 ml as scravanger. Nitrogen was passed through the glove-box to remove the oxygen in the reaction cell. Piezocatalytic hydrogen production is carried out in the ultrasonic bath by closing the mouth of the reaction cell with a rubber septum. The hydrogen produced was taken with a syringe on the head-space of the reaction cell and analyzed in gas chromatography.

Results and Discussion

The XRD pattern confirms the trioctahedral character characteristic of the laponite clay structure (Figure 1.). There are peaks at 19.4°, 27.5° and 60.4° for Laponite clay, corresponding to the crystal planes [100], [005] and [300], respectively. In addition reflections observed of ZnO at 31.7°, 34.6°, 36.4°, 47.6°, 56.5°, 62.7° can be indexed to [100], [002], [101], [102], [110] and [103] crystal planes.

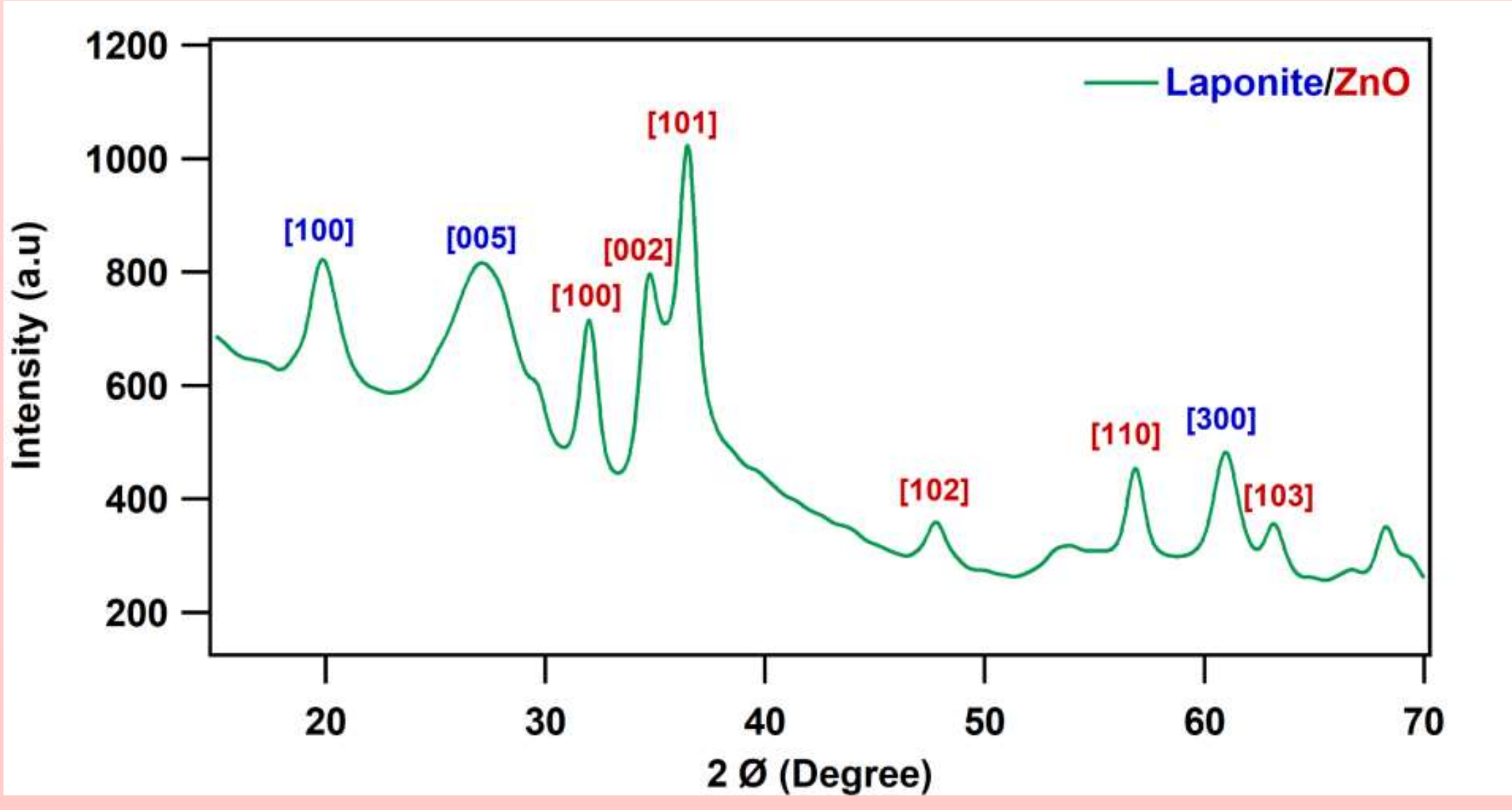


Figure 1. Comparative XRD patterns of the LPZ piezocatalyst

The surface morphology and further purity of Laponite/ZnO piezocatalyst were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis. Accordingly, from the SEM images obtained, it was clearly observed that there were homogeneous ZnO particles on the surface of Laponite clay. TEM images show that the laponite particles crystallize and have a diameter of about 20-30 nm.

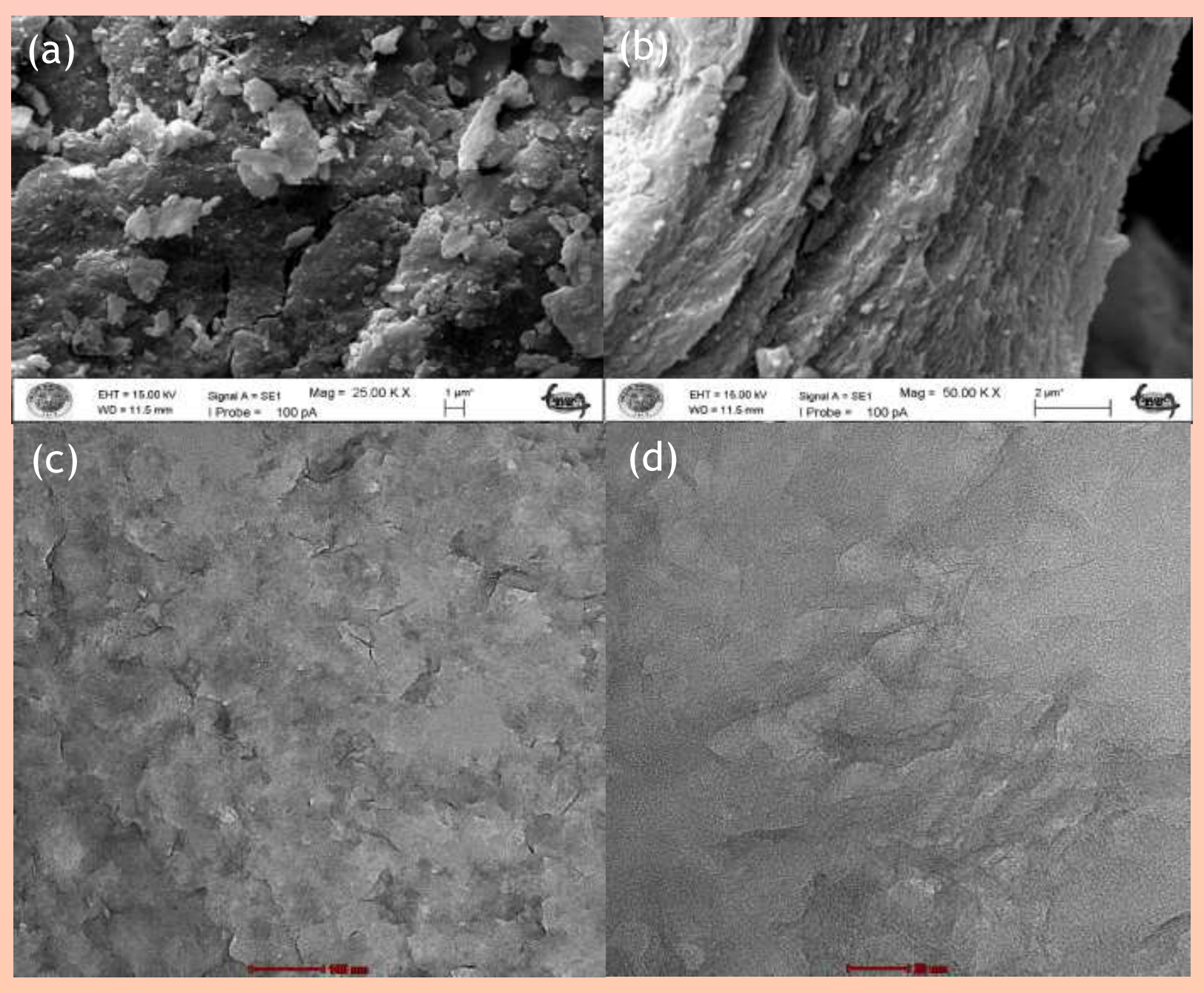
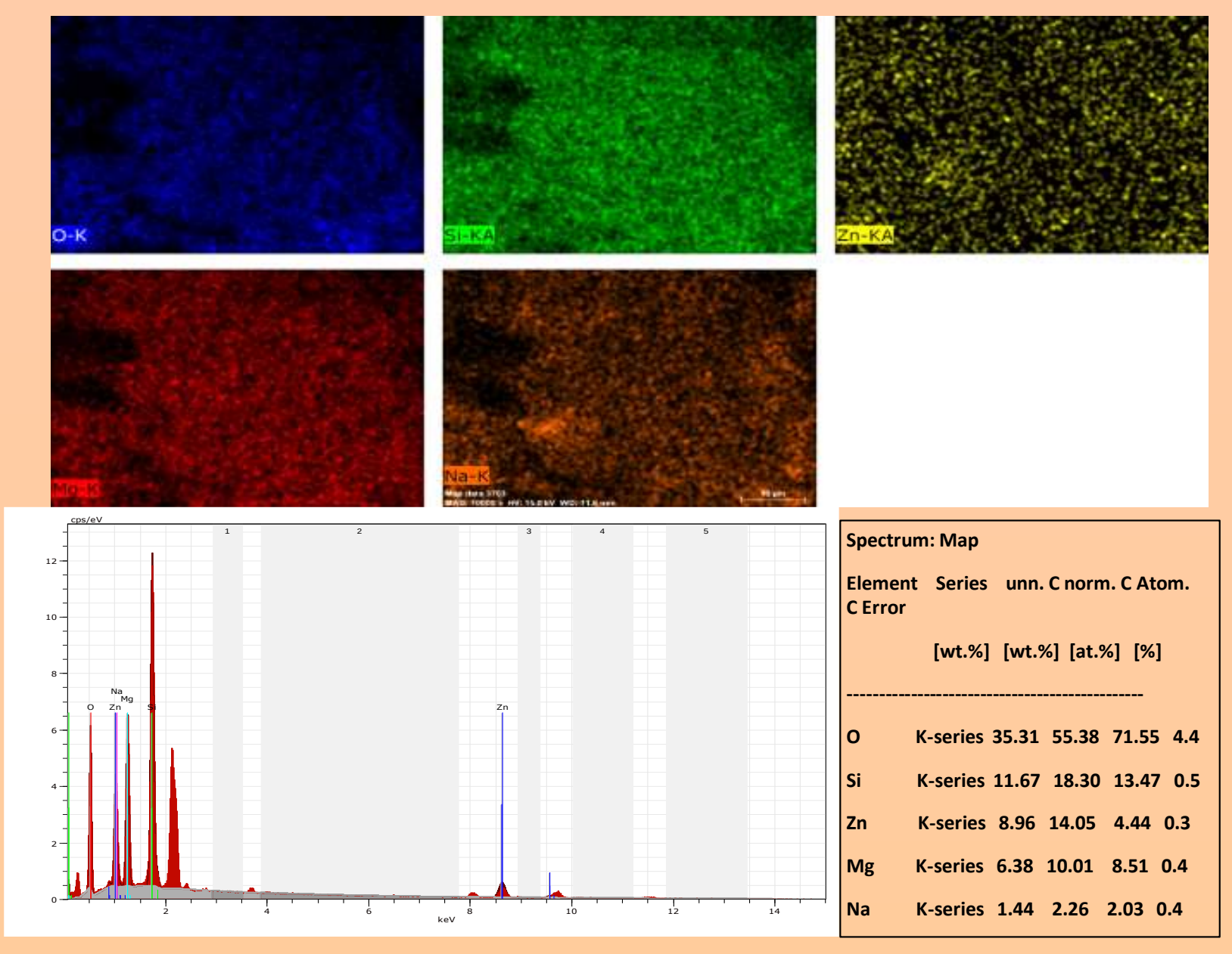


Figure 2. SEM (a, b) and TEM (c, d) images of the Laponite/ZnO

According to EDX and elemental mapping analysis results given in Figure 3, the structure of Laponite clay was investigated stoichiometrically, and it was observed that the elemental distribution of the structure was in accordance with the Laponite structure. In addition, the formation of ZnO on the Laponite surface and its proper stoichiometric distribution have been proven with EDX and elemental mapping analysis.



Spectrum: Map

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
O	K-series	35.31	55.38	71.55	4.4
Si	K-series	11.67	18.30	13.47	0.5
Zn	K-series	8.96	14.05	4.44	0.3
Mg	K-series	6.38	10.01	8.51	0.4
Na	K-series	1.44	2.26	2.03	0.4

Figure 3. EDX and elemental mapping analysis results of the Laponite/ZnO

Photo/piezocatalytic Hydrogen Production Results: Laponite, ZnO, Laponite/ZnO catalysts were investigated for piezocatalitic hydrogen evolution using TEOA as scravanger. Laponite and ZnO showed 265.76 µmol g^{-1} h^{-1} and 260.46 µmol g^{-1} h^{-1} piezocatalytic hydrogen production under ultrasonic sound respectively. Laponite/ZnO nanocomposite displayed 1198.26 µmol g^{-1} h^{-1} piezocatalytic hydrogen production under ultrasonic sound which enhanced about 5-times when compared free forms. In photo enhanced piezocatalytic hydrogen production studies, Laponite/ZnO composite displayed 2136.03 µmol g^{-1} h^{-1} piezocatalytic hydrogen production which is approximately 2-times greater than dark conditions.

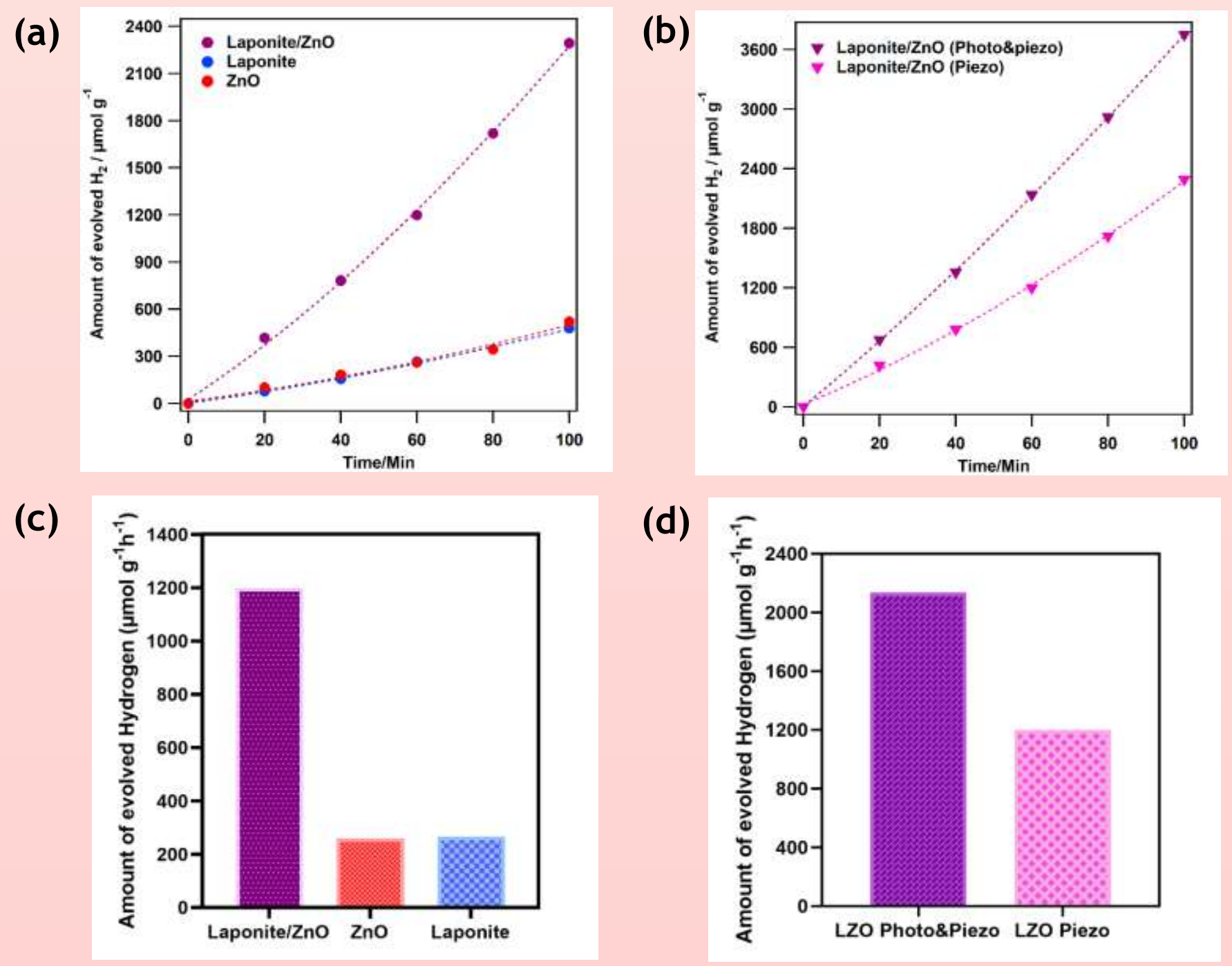


Figure 4. The **(a, c)** piezocatalytic HER performance comparison of Laponite, ZnO and Laponite/ZnO. Piezocatalytic and photopiezocatalytic HER performance comparison **(b,d)** of Laponite/ZnO in the absence and presence of light illumination.

Furthermore, chronoamperometry measurements were performed under light and dark conditions to confirm the piezocatalytic activities by using Laponite, ZnO and Laponite/ZnO . As shown in Figures 5, Laponite/ZnO exhibited a significant increase in the current response compared to both Laponite and ZnO under ultrasonication. The piezocurrent responses of Laponite/ZnO were also significantly enhanced by light illumination. These chronoamperometry results pointed out the amount of generated charge carriers in the presence of mechanical stress and light illumination which are directly related to the redox reactions, as well as in accordance with piezocatalytic and photopiezocatalytic results.

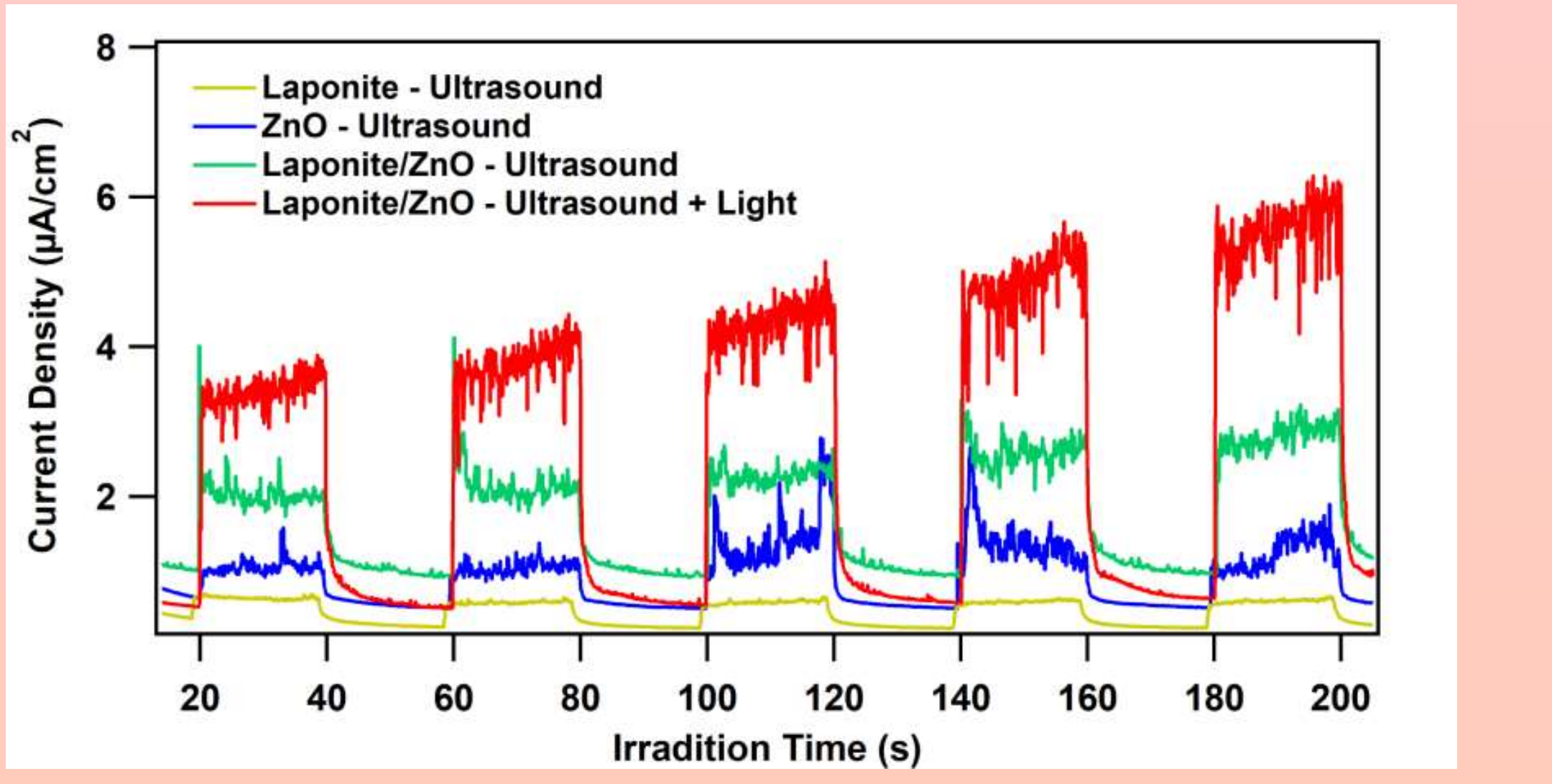


Figure 5. The comparison results of **(a)** photocatalytic HER performance in TEOA solution with $BaTiO_3/MoS_x$, $SrTiO_3/MoS_x$, $BaTiO_3/Pt$ and $SrTiO_3/Pt$ **(b)** UV-Vis absorption spectrums of reaction solutions before and after 8 h illumination.

Conclusion

We reveal that clays, which are inexpensive and environmentally friendly materials, can be used for piezocatalysis, which is a prominent method for hydrogen production in recent years. The catalytic activity of ZnO, which is a known piezocatalyst, has increased considerably thanks to the excellent physicochemical properties of Laponite clay. Due to the fast intermolecular charge transfer and increased charge separation between Laponite and ZnO, a very high increase in catalytic activity has been achieved. In addition to the advantage of the conduction band, which is tilting by the effect of the piezoelectric field, for hydrogen evolution, the participation of photo-excited electrons in the redox reaction has provided a great increase in hydrogen production.Based on all these results, we propose clays as support material to increase charge migration and separation of piezocatalysts in piezocatalytic hydrogen production studies.

References

1. Yu, Jiuyang, et al. "Co 4 N–WN x composite for efficient piezocatalytic hydrogen evolution." Dalton Transactions 51.18 (2022): 7127-7134.Zhu, Jiefang, and Michael Zäch. "Nanostructured materials for photocatalytic hydrogen production." *Current Opinion in Colloid & Interface Science* 4.14 (2009): 260-269.
2. Hu, Cheng, et al. "Exceptional cocatalyst-free photo-enhanced piezocatalytic hydrogen evolution of carbon nitride nanosheets from strong in-plane polarization." Advanced Materials 33.24 (2021): 2101751.
3. Xu, Wenxiu, et al. "Piezodeposition of Metal Cocatalysts for Promoted Piezocatalytic Generation of Reactive Oxygen Species and Hydrogen in Water." ChemCatChem 14.16 (2022): e202200312.
4. Du, Yumeng, et al. "High-efficient piezocatalytic hydrogen evolution by centrosymmetric Bi2Fe4O9 nanoplates." Nano Energy 104 (2022): 107919.
5. Wu, Yizhang, et al. "Integrated unit-cell-thin MXene and Schottky electric field into piezo-photocatalyst for enhanced photocarrier separation and hydrogen evolution." Chemical Engineering Journal 439 (2022): 135640.
6. Jatav, Shweta, and Yogesh M. Joshi. "Chemical stability of Laponite in aqueous media." Applied Clay Science 97 (2014): 72-77.

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