Poly(vinylpyrrolidone) mediated synthesis of TiO₂ with enhanced photocatalytic activity and stability

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Improving photocatalytic activity and stability of titanium dioxide (TiO_2) is crucial for its application in wastewater treatment. Incorporating polymer ligands into the synthetic process is an important way to improve the catalytic performance of TiO₂. In this work, a water-soluble, non-toxic, and non-ionic polymer, polyvinylpyrrolidone (PVP), was used to regulate the synthesis of TiO₂ by using hydrothermal method. It was observed that PVP-regulated TiO₂ had enhanced photocatalytic performance comparing with the pure TiO₂, mainly due to the enhanced light absorption, the suppressed charge recombination efficiency, the increased oxidation power of photogenerated holes and specific surface area. Additionally, the catalytic stability of the catalyst was also improved. As a result, TiO₂ assisted with PVP exhibited a significant improvement in catalytic stability after four cycles of methyl orange degradation. Our research results can provide experimental and theoretical basis for the development of photocatalysts with excel-lent stable catalytic performance.

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1. Introduction

Many scientists have acknowledged TiO_2 as a semiconductor photocatalyst that is utilized in various applications, such as wastewater treatment, solar energy conversion, and hydrogen production[1], due to its low synthesis cost, simple and reliable synthesis methods, and excellent resistance to corrosion by natural light[2-3]. It is widely recognized that anatase, rutile, and brookite are the metastable phases of TiO_2 . Among the three crystal structures of TiO_2 , the anatase phase demonstrates superior photocatalytic activity[4-5]. However, the anatase of TiO_2 lacks stability and reusability[6-7]. In the process of tackling industrial pollution, the notable drop in performance after a single degradation event undoubtedly escalates the cost of environmental remediation, which hinders its application in degrading organic pollutants. Therefore, photocatalysts that both exhibit good catalytic activity and catalytic stability have become the goal of many researchers[8]. Utilizing organic polymeric material for surface modification of

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photocatalysts offers a gentle, cost-efficient, and environmentally-friendly approach to enhance their surface functionality[9]. By incorporating TiO_2 into a polymer matrix, the composite can enhance its photocatalytic efficiency by expanding the light absorption range and improving charge separation and migration through the formulation of some heterojunctions[10]. What's more, polymers can act as stabilizers, preventing particle aggregation and maintaining the dispersion of TiO_2 in the solution[11]. Additionally, polymers can improve the mechanical strength of the composite, allowing for easier separation and reuse[12].

Jiaguo Yu's group investigated the enhanced reduction power of polydopamine-modified TiO_2 [13]. The enhanced photocatalytic activity can be attributed to efficient separation and transfer of photogenerated charge carriers facilitated by the S-scheme heterojunction formed between TiO_2 and PDA, the improved light absorption and increased reduction capability of photogenerated electrons. Zhang et al. achieved the ability to photocatalyze the conversion of CO₂ by modifying TiO_2 with covalent porphyrin polymers[14]. The phenomenon can be attributed to enhanced charge transfer between two components facilitated by a robust interaction between them. Ping Lei et al. enhanced the degradation capability of methyl orange (MO) by modifying TiO_2 with polyvinyl alcohol (PVA) using a hydrothermal method. After 25 cycles of catalytic degradation, the catalytic performance only exhibited a slight decrease [15]. What's more, previous research has also demonstrated that incorporating polymer ligands into TiO₂ systems yielded beneficial outcomes in terms of enhancing performance and catalytic stability through suppressing the charge carriers recombination[16]. PVP is a water-soluble, non-toxic, non-ionic polymer with advantages such as solubility and heat resistance. It has wide-ranging applications in fields such as biology and material science, and its molecular structure contains numerous carbonyl and nitrogen groups. These functional groups allow PVP to form complexes with inorganic precursors[17-18], potentially expanding the opportunities for surface and microstructural modifications of the synthesized TiO₂ particles.



Scheme. 1. Schematic diagram of PVP-regulated synthesis of TiO₂.

In this study, PVP was used as an organic template agent. The titanium source employed in this study was titanium butoxide, while oxalic acid (OA) was utilized as a reaction inhibitor to regulate the hydrolysis rate. The carbonyl and nitrogen groups in PVP were coordinated with titanium atoms using a hydrothermal method (Scheme 1). Finally, the PVP-modulated TiO₂ was obtained by calcination at 650°C. The study revealed that the addition of PVP in the reaction system led to an in-creased length of the TiO₂ particles. Consequently, the recombination rate of photoinduced electron-hole pairs (e^-h^+) experienced a considerable reduction. This reduction in recombination effectively improved the photocatalytic performance of TiO₂. The degradation rate

of MO was also improved. Further investigation into the catalytic stability of TiO_2 showed that PVP modulation greatly enhanced the catalytic stability of TiO_2 .

2. Experimental

2.1. Reagents

Polyvinylpyrrolidone (PVP, average molecular weight: 58000, CAS: 9003-39-8), tert-butanol (TBA, 99.8%, CAS: 75-65-0) were purchased from Chengdu Chron Chemical Co., Ltd. (Cheng-du, China), methyl orange (MO, 96%, CAS: 547-58-0) were supplied by Aladdin Chemical Co., Ltd. (Shanghai, China), Titanium butoxide (TBOT, 98%, CAS: 5593-70-4), ethanol (99.5%, CAS: 64-17-5), 1,4-benzoquinone (BQ, 97%, CAS: 106-51-4), Ammonium oxalate (AO, 99.8%, CAS: 1113-38-8), oxalic acid (OA, 99%, CAS: 144-62-7). All chemicals used in the experiment were of analytical grade and employed without additional purification. The water used in the experiment was deionized.

2.2. Synthesis of PVP-regulated TiO₂

The synthesis process of PVP-modified TiO₂ has two primary steps. During the initial step, a three-neck flask was used, to which 20 mL of anhydrous ethanol and 6.8 mL of TBOT were carefully introduced. The mixture was then subjected to thorough stirring to ensure complete homogenization. Subsequently, to achieve a controlled and uniform precursor and to slow down the hydrolysis rate, 4.5 g of solid OA and 100 mL of deionized water were introduced into the mixture. The resulting solution was maintained under stirring within an ice-water bath at temperatures ranging from 3-5 °C for a period of 3 hours. Following that, solid PVP was incorporated into the solution, as indicated in Table S1. The resulting mixture was then transferred to a water bath set at a temperature of 90 °C. The solution was allowed to react and thermally process for a duration of 8 hours. After an aging period of approximately 14 hours at room temperature, the precursor solution exhibited phase separation and formed a layered liquid. The supernatant was carefully removed, leaving behind a lower milky white suspension. This suspension was subjected to drying in an oven for roughly 5 hours, leading to the formation of a white precursor solid. In the subsequent step, the obtained white precursor solid was finely ground into a powder form. This powder was then subjected to calcination in an air environment at a

temperature of 650 °C. The heating rate during the calcination process was maintained at 5 °C

/min, and the powder was held at this temperature for a period of 2 hours. Through this calcination process, the PVP-modified TiO_2 mate-rial was synthesized. The resulting powder, with a PVP con-centration of x g/L, was named TiO_2 -PVPx.

2.3. Photocatalytic performance of TiO₂-PVPx

To simulate natural sunlight, a xenon lamp with a power out-put of 250 W and an irradiance of 35 mW/cm² was employed as the light source for the photocatalytic experiments of TiO₂. To analyze the UV-visible absorption spectra of the TiO₂ samples, a UV-2800A UV-Vis

spectrophotometer from Shanghai Unico Instrument Co., Ltd. was utilized. In this study, the experimental setup involved adding 0.1 g of TiO₂ samples to a 20 mL solution of Methylene Orange (MO) with a concentration of 20 mg/L. The mixture was stirred magnetically in the dark for 30 min, allowing adsorption-desorption equilibrium to be established between the TiO₂ and MO molecules. After the adsorption-desorption equilibrium was reached, the light source was turned on to initiate the photocatalytic process. To monitor the degradation of MO over time, 1 mL of the solution was collected at regular intervals of 15 min. To separate the supernatant from the TiO₂ samples, the collected solution underwent centrifugation at a speed of 8000 rpm for 10 min. This centrifugal force caused the TiO₂ particles to settle at the bottom, while the supernatant (containing the degraded MO) remained as the top layer. The absorbance of the MO supernatant was then measured at a specific wavelength of λ =470 nm using a spectrophotometer. The degradation ratios (D) were calculated using Formula (1).

$$D = \frac{A_0 - A_t}{A_0} \times 100\% = \frac{C_0 - C_t}{C_0} \times 100\%$$
(1)

In the given formula, the variables A_0 and C_0 represent the initial absorbance and concentration of the supernatant, respectively. On the other hand, the variables A_t and C_t represent the absorbance and concentration of the solution at a specific time point, denoted as t, under illumination. These variables are used to analyze and quantify the changing properties of the solution over time, particularly in relation to its absorbance and concentration levels.

2.4. Characterization

Morphological analysis was conducted using a scanning electron microscope (SEM, FEI Corporation, Hillsboro, USA). The UV-visible diffuse reflectance spectra (DRS, Shimadzu Group Company, Kyoto, Japan) were obtained using a spectrophotometer. X-ray diffraction pattern (XRD) was obtained using an X-ray diffractometer (XRD, Dandong Hao yuan Instrument Co., Ltd., Dandong, China). The infrared spectrum of the sample was obtained using a Fourier transform infrared spectrometer (Thermo Nicolet iS50 FTIR). X-ray photoelectron spectra were obtained with an X-ray photoelectron spectrometer (XPS, Kratos Ltd., Manchester, UK) for analyzing the elemental compositions and chemical states of the surfaces of the samples. Photoluminescence spectra (PL, Hitachi, Ltd., Hita-chi, Japan) were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Surface area measurements were per-formed on nitrogen adsorption-desorption data using Brunauer–Emmett–Teller (BET, Mike Instrument Company, Atlanta, GA, USA).

3. Results and discussion

3.1. Effect of PVP on the morphology of TiO₂

To investigate the impact of the addition of PVP on the morphology of the TiO₂ samples, SEM analysis was employed in this study. In the absence of PVP regulation, the morphology of TiO₂-PVP0 particles (Fig.1ab) displayed a regular and well-dispersed hexagonal prism shape, with a length of approximately 0.615 \pm 0.026 µm. When the PVP concentration was 1 g/L (Fig.1cd), the image of TiO₂-PVP1 showed a disrupted regular morphology of the particles compared with TiO₂-PVP0. The aspect ratio of the particle size increased. As the PVP concentration further

increased to 2 g/L (Fig.1ef), the aspect ratio of TiO₂-PVP2 particles continued to increase, and the edges of the hexagonal prisms became gradually blurred. The statistic data were shown in Table S2. It was found that when the PVP concentration was 0, 1, and 2 g/L, the aspect ratios of the particles were 2.544 ± 0.289 , 2.75 ± 0.092 and 2.996 ± 0.543 , respectively. As the PVP concentration increased to 2 g/L, the particle aspect ratios increased. The SEM analysis revealed that the addition of PVP allows for the modulation of TiO₂ morphology at the micro-nano scale. The originally observed hexagonal prisms with smaller lengths increase in size upon the addition of PVP.



Fig. 1. SEM images of the TiO₂ regulated by PVP with different concentration of PVP (mg/L): (a, b) TiO₂-PVP0, (c, d) TiO₂-PVP1, (e, f) TiO₂-PVP2.

3.2. Analysis of Photocatalytic Performance of TiO₂ under PVP Regulation

To assess the photocatalytic performance of PVP-regulated TiO₂, we chose MO as a colored dye for degradation by the samples. During a 30 min dark reaction, we observed that PVP regulation did not improve the adsorption performance of TiO₂. The average adsorption values of all samples for MO remained around 4%. After the dark reaction, the absorption spectra of MO were recorded every 15 min. Under xenon lamp-simulated illumination, it was observed that the absorbance of MO decreased to varying degrees with increasing illumination time. Fig.2a demonstrated the significantly de-creased absorption of MO when TiO₂-PVP2 was used as a photocatalyst. Fig.2b illustrated the variation of degradation ratio (D) vs. reaction time. It can be observed that when using TiO₂-PVP2 as the photocatalyst, the degradation ratio of MO is the fastest. When the illumination time was set to 30 min, D for TiO₂-PVP0, TiO₂-PVP1, and TiO₂-PVP2 were 69.9%, 73.5%, and 83.7% respectively. The catalytic performance of TiO₂-PVP3 was also considered (Fig.S1). With the increased concentration of PVP, the catalytic activity of TiO₂ first increased and then decreased. 2 g/L PVP is the optimal concentration.

For better industrial applications, the stability of the TiO_2 -PVP0 and TiO_2 -PVP2 was investigated. Although the performance of both samples decreased to some extent with increasing cycle number, it can be observed that the 4 completed degradation cycles times of TiO_2 -PVP2 decreased by 105 min compared to TiO_2 -PVP0. This demonstrates that the introduction of PVP can significantly enhance the catalytic stability of TiO_2 .



Fig. 2. Photocatalytic performance of PVP-regulated TiO₂. (a) The absorption spectra of MO degraded by TiO₂-PVP2. (b) The degradation rate of MO degraded by TiO₂-PVP0, TiO₂-PVP1, and TiO₂-PVP2. The cycling degradation rate of MO with (c) TiO₂-PVP2 and (d) TiO₂-PVP0.

3.3. Composition of TiO₂ Crystals

XRD analysis was employed to examine the crystal structure of the samples in this study. As shown in Fig.3a, after calcination at 650°C, XRD analysis of TiO₂-PVP0, TiO₂-PVP1, and TiO₂-PVP2 samples showed distinct peaks at 25°, 38°, 48°, and 55°.which can be attributed to the (101), (103), (200), and (211) crystal facets of the TiO₂ anatase phase. These crystal facets were identified based on the Powder Diffraction File (PDF) reference number 89-4921. Therefore, it can be concluded that all the samples exhibited the crystal structure of anatase TiO₂. Furthermore, the peak intensity at (101) position decreased with the addition of PVP, and the full width at half maximum (FWHM) also slightly increased. This indicated that PVP regulation slightly inhibited the crystallization of TiO₂.

The FTIR spectra of samples TiO₂-PVP0, TiO₂-PVP1, and TiO₂-PVP2 were shown in Fig.3b. Based on the results obtained, it is evident that the peaks observed in the range of 3200-3700 cm⁻¹ in three samples can be attributed to the stretching vibration of O-H bonds[19-20]. These peaks indicate the presence of water molecules that have been adsorbed onto the surface of the samples. The characteristic peak observed at 1630 cm⁻¹ in samples primarily corresponds to the stretching vibration of C-N bonds[20]. Although TiO₂-PVP0 itself contains little C and N contaminants, the C-N bonds of the PVP molecules were more pronounced. The enhanced C-N stretching vibrations observed in TiO₂-PVP1 and TiO₂-PVP2 demonstrated the successful coordination of PVP into TiO₂. The peaks observed at 1396 cm⁻¹ and 1402 cm⁻¹ in TiO₂-PVP1 and TiO₂-PVP2 correspond to the bending vibrations of -CH₂ groups present in PVP[21]. The peak at 1100 cm⁻¹ in TiO₂-PVP0, at 1120 cm⁻¹ in TiO₂-PVP1 and at 1113 cm⁻¹ in TiO₂-PVP2 were attributed to the stretching vibrations of Ti-O-C bonds[22]. The peaks observed in TiO₂-PVP0, TiO₂-PVP1, and TiO₂-PVP2 in the range of 400-660 cm⁻¹, known as the "bread roll" peaks, correspond to the stretching vibrations of Ti-O-Ti bonds from TiO₂[20,22-23]. However, due to the influence of PVP, the peaks in TiO2-PVP1 and TiO2-PVP2 located in this region undergo planar deformation, further supporting the incorporation of PVP into TiO₂ through various forms of bonding, such as C-N and Ti-O-C bonds, in the precursor.



Fig. 3. (a) XRD patterns and (b) FTIR spectra of TiO₂-PVP0, TiO₂-PVP1, and TiO₂-PVP2.

3.4. Mechanism of enhanced catalytic performance of TiO₂

To explore the mechanism behind the influence of PVP regulation on the photocatalytic performance of nano-sized TiO₂, a series of analysis was conducted. We first analyzed the samples TiO₂-PVP0, TiO₂-PVP1, and TiO₂-PVP2 based on the diffuse reflectance spectra (DRS) shown in Fig.4a. Each sample in the experiment demonstrated remarkable ultraviolet (UV) light absorption. With the introduction of PVP, the absorption intensities of the three samples can be clearly observed as TiO₂-PVP2 > TiO₂-PVP1 > TiO₂-PVP0. The energy band (Eg) of the photocatalyst

can be determined by employing the former analysis mothed[24-25]. Therefore, we obtained the Eg values of TiO₂-PVP0, TiO₂-PVP1, and TiO₂-PVP2 as 3.34, 3.25, and 3.31 eV, respectively. The slight difference in the Eg values among the three samples suggests that their capability to enable electron transitions from the VB to the CB is relatively comparable. The XPS spectra of TiO₂-PVP0, TiO₂-PVP1, and TiO₂-PVP2 are shown in Fig.S2. The binding energies of Ti 2p3/2 (458.8, 458.5, 458.5 eV) and Ti 2p1/2 (464.4, 464.2, 464.2 eV) indicate the chemical valence state of Ti as +4 for all three samples[26]. The binding energies of lattice oxygen (O₂⁻) for TiO₂-PVP0, TiO₂-PVP2 are 529.9, 529.7, and 529.7 eV, respectively. All three samples exhibit C-C, C-O, and C=O bonds[27-28]. Based on the XPS spectra, it can be observed that the intro-duction of PVP does not have a significant impact on the elemental valence states and chemical bond types of TiO₂. The XPS valence band (VB) spectra of the samples are shown in Fig.4c. The estimated valence band values (E_{VL}) are obtained by identifying the x-coordinate where the tangent to the up-ward section of the curve intersects with the horizontal line. The E_{VL} values for the samples are 1.80, 2.09, and 2.87 eV, severally. The actual VB can be calculated using Formula (2)[29]

$$E_{NHE} = \phi \Box E_{VL} \Box \Box 4 \tag{2}$$

In the formula, E_{NHE} represents the standard hydrogen electrode potential, and Φ represents the work function of the instrument (4.6 eV)[30]. Using these values, the final VB values of TiO₂-PVP0, TiO₂-PVP1 and TiO₂-PVP2 were calculated to be 1.96 eV, 2.25 eV, and 3.03 eV, respectively. It can be observed that the modulation of PVP has a significant impact on the VB values of TiO₂. As the VB value increases, the oxidative power of the samples can become stronger.



Fig. 4. The mechanism of improved photocatalytic performance. (a) UV-Vis DRS spectra, (b) bandgap curves, (c) VB-XPS spectra and (d) electronic band structure diagram of TiO₂-PVP0, TiO₂-PVP1, and TiO₂-PVP2.

The oxidative capacities of the three samples follow the order: TiO_2 -PVP0 < TiO_2 -PVP1 < TiO_2 -PVP2. The CB values for TiO_2 -PVP2, TiO_2 -PVP1, and TiO_2 -PVP0 can be calculated from the Eg and VB values and are determined to be -0.28, -1.00, and -1.38 eV, respectively. Fig.4d represents a schematic diagram of the Eg, CB, and VB for each sample.

In order to investigate the roles of various radicals in the photocatalytic degradation process of PVP-modulated TiO₂. By using ammonium oxalate (AO), 1,4-benzoquinone (BQ) and tert-butanol (TBA) as radical scavengers, the effects of h^+ , superoxide radicals(O₂⁻), and hydroxyl radicals(·OH), and to enhance the efficiency or selectivity of the catalytic reaction were investigated[31]. Fig.5a presents the degradation results of TiO₂-PVP2. Without these radical scavengers, the D of MO was initially deter-mined as 95%. However, when AO was introduced into the catalytic process, the degradation efficiency was decreased to 34.7%, indicated O₂⁻⁻ affected the degradation process. Similarly, when TBA and BQ was introduced, the D of MO decreased to 84.8% and 38.6%. It is evident that the photogenerated ·OH species in the catalyst played a crucial role in the degradation process after the introduction of PVP.

The specific surface area of a catalyst is a critical factor that directly impacts its catalytic efficiency. As shown in Fig.5b, when TiO_2 was modulated with increased concentration of PVP, there was an observed increase in the specific surface area of the samples. This trend aligns with the sequence of photocatalytic activity exhibited by the samples, further confirming the reason for the improvement in photocatalytic performance with the addition of PVP.

PL is a phenomenon that arises from the recombination of photoexcited electron-hole pairs. The higher the recombination rate of e^{-h^+} pairs, the stronger the intensity of PL[32]. As shown in Fig.5c, the order of PL intensity was TiO_2 -PVP0 > TiO_2 -PVP1 > TiO_2 -PVP2. Thus, the introduction of PVP significantly reduced the recombination rate of e^-h^+ pairs in TiO₂, which is beneficial for enhancing photocatalytic activity. In TiO₂-PVP2 and TiO₂-PVP1 samples, a notable decrease in the recombination rate of e^{-h^+} pairs were observed compared to TiO₂-PVP0. Particularly, the recombination rate of e^{-h^+} pairs of TiO₂-PVP2 was reduced by approximately 90%. By testing the PL spectrum of TiO₂-PVP3, we found that the PL intensity of TiO₂-PVP3 was obviously increased comparing with TiO₂-PVP2 (Fig.S3), indicating a significant increase in charge re-combination efficiency. So it causes a decrease in catalytic activity (Fig.S1). It may be due to the formation of N-scheme heterojunction between TiO₂ and PVP, resulting in controllable separation and transfer of photogenerated charge carriers. SEM images indicate that TiO₂-PVP0 exhibited better particle dispersion than the other two samples. As a result, the catalytic activity of TiO₂-PVP0 is not significantly disadvantaged compared to TiO₂-PVP1 and TiO₂-PVP2. However, as the material undergoes repeated cycles of use, the catalytic activity and stability gap between TiO₂-PVP0 and TiO₂-PVP2 gradually widened.



*Fig. 5. (a) The degradation rate of TiO*₂-*PVP2 in the presence of different radical scavenger. Specific surface area (b) and PL spectra (c) of TiO*₂-*PVP0, TiO*₂-*PVP1, and TiO*₂-*PVP2.*

4. Conclusion

In summary, the employment of the polymer PVP in the syn-thetic process of TiO_2 increased the length of the particle diameters to some extent and reduced the crystallinity of the particles slightly. However, the introduction of PVP enhanced the absorption of TiO_2 in the ultraviolet region and greatly reduced the recombination rate of e^-h^+ pairs in the catalyst, thus improving the photocatalytic activity of TiO_2 . In the sub-sequent recycling and reusability experiments, it was found that the catalytic stability of the catalysts modified with PVP was significantly enhanced. Particularly, when the concentration of PVP in the reaction system was 2 g/L, the initial degradation rate of MO was increased by 13.8%. After four cycles of MO degradation, the required degradation time was reduced by 105 min, indicating a substantial improvement in stability compared to the unmodified catalyst. Thus, this study provided valuable insights for the fabrication of the photocatalysts with high catalytic activities and stability.

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References

[1] X. Zhang, Chen J., Jiang S., Zhang X., Bi F., Yang Y., Wang Y., Wang Z., J. Colloid Interface Sci., 588, 122 (2021), https://doi.org/10.1016/j.jcis.2020.12.042 [2] X. Zhu, Zhu R., Pei L., Liu H., Xu L., Wang J., Feng W., Jiao Y., Zhang W., J. Mater. Sci. Mater. Electron., 30, 21210 (2019); https://doi.org/10.1007/s10854-019-02494-4 [3] Y. Sun, Gao Y., Zeng J., Guo J., Wang H., Mater. Lett., 279, (2020), https://doi.org/10.1016/j.matlet.2020.128506 [4] J. Ma, Gao S., ACS Nano, 13, 13658 (2019); https://doi.org/10.1021/acsnano.9b03555 [5] S.M. Amorim, Steffen G., de S Junior J.M.N., Brusamarello C.Z., Romio A.P., Domenico M.D., Polym. Polym. Compos., 29, 1055 (2020); https://doi.org/10.1177/0967391120949489 [6] P.K. Prajapati, Kumar A., Jain S.L., ACS Sustainable Chemistry & Engineering, 6, 7799 (2018); https://doi.org/10.1021/acssuschemeng.8b00755 [7] J. Hou, Zhou J., Liu Y., Yang Y., Zheng S., Wang Q., J. Alloys Compd., 849, (2020), https://doi.org/10.1016/j.jallcom.2020.156493 [8] Y. Cheng, Gao J., Shi Q., Li Z., Huang W., Alloys Compd., 901, (2022), https://doi-org-ssl.8611.top/10.1016/j.jallcom.2021.163562 [9] R.J. Sengwa, Dhatarwal P., P.Opt. Mater., 113, (2021); https://doi.org/10.1016/j.optmat.2021.110837 [10] H. Nawaz, Umar M., Maryam R., Nawaz I., Razzaq H., Malik T., Liu X., Adv. Energy Mater., 24, (2022); https://doi.org/10.1002/adem.202200844 [11] E. Bet-moushoul, Mansourpanah Y., Farhadi K., Tabatabaei M., Chem. Eng. J., 283, 29 (2016), https://doi.org/10.1016/j.cej.2015.06.124 [12] C. Cazan, Enesca A., Andronic L. Polymers, 13. 2017 (2021), https://doi.org/10.3390/polym13122017 [13] A. Meng, Cheng B., Tan H., Fan J., Su C., Yu J., Appl. Catal. B, 289, 120039 (2021), https://doi.org/10.1016/j.apcatb.2021.120039 [14] Y. Zhang, Zhang G.-L., Wang Y.-T., Ma Z., Yang T.-Y., Zhang T., Zhang Y.-H., J. Colloid Interface Sci., 596, 342 (2021), https://doi.org/10.1016/j.jcis.2021.03.104 [15] P. Lei, Wang F., Gao X., Ding Y., Zhang S., Zhao J., Liu S., Yang M., J. Colloid Interface Sci., 227-228, 185 (2012), https://doi.org/10.1016/j.jhazmat.2012.05.029 [16] D.M. El-Mekkawi, Abdelwahab N.A., Mohamed W.A.A., Taha N.A., Abdel-Mottaleb M.S.A., J. Clean. Prod., 249, (2020), https://doi.org/10.1016/j.jclepro.2019.119430 [17] H. Najafi-Ashtiani, Appl. Surf. Sci., 455, 373 (2018),

660

https://doi.org/10.1016/j.apsusc.2018.06.010

[18] L. Qiu, Mei D., Chen W.-H., Yuan Y., Song L., Chen L., Bai B., Du P., Xiong J., Sol. Energy Mater Sol. Cells, 248, (2022); <u>https://doi.org/10.1016/j.solmat.2022.112032</u>

[19] Y. Song, Zhao F., Li Z., Cheng Z., Huang H., Yang M., RSC Adv, 11, 23901 (2021); https://doi.org/10.1039/D1RA03917B

[20] M.V. Someswararao, Dubey R.S., Subbarao P.S.V., Singh S., Results Phys., 11, 223 (2018), https://doi.org/10.1016/j.rinp.2018.08.054

[21] J. Oyim, Amuhaya E., Nyokong T., J Macromol Sci Phys, Part A, 60, 192 (2023); https://doi.org/10.1080/10601325.2023.2183868

[22] S. Mirmohammad Sadeghi, Vaezi M., Kazemzadeh A., Jamjah R., J. Appl. Polym. Sci.v, 135, (2018); <u>https://doi.org/10.1002/app.46337</u>

[23] M.S. de Urquijo-Ventura, Rao M.G.S., Meraz-Davila S., Ochoa J.A.T., Quevedo-Lopez

M.A., Ramirez-Bon R., Polymer, 191, (2020); https://doi.org/10.1016/j.polymer.2020.122261

[24] H. Chen, Zhao L., Xiang Y., He Y., Song G., Wang X., Liang F., Desalination Water Treat., 57, 9660 (2015); <u>https://doi.org/10.1080/19443994.2015.1035339</u>

[25] C. Diaz-Uribe, Vallejo W.,Ramos W., Appl. Surf. Sci., 319, 121 (2014), https://doi.org/10.1016/j.apsusc.2014.06.157

[26] F. Güzelçimen, Tanören B., Çetinkaya Ç., Kaya M.D., Efkere H.İ., Özen Y., Bingöl D.,

Sirkeci M., Kınacı B., Ünlü M.B.,Özçelik S., Vacuum, 182, (2020), https://doi.org/10.1016/j.vacuum.2020.109766

[27] M. Pisarek, Krawczyk M., Holdynski M., Lisowski W., ACS Omega, 5, 8647 (2020); https://doi.org/10.1021/acsomega.0c00094

[28] S.A. Abdullah, Sahdan M.Z., Nayan N., Embong Z., Hak C.R.C., Adriyanto F., Mater. Lett., 263, (2020), <u>https://doi.org/10.1016/j.matlet.2019.127143</u>

[29] L. Wang, Qi Y., Li H., Guan R., Zhang F., Zhou Q., Wu D., Zhao Z., Zhou G., Sun Z., Sci. China Mater., 65, 974 (2021); <u>https://doi.org/10.1007/s40843-021-1833-1</u>

[30] L. Wang, Zhou G., Tian Y., Yan L., Deng M., Yang B., Kang Z., Sun H., Appl. Catal. B, 244, 262 (2019), <u>https://doi.org/10.1016/j.apcatb.2018.11.054</u>

[31] J. Chen, Gao J., Liu X., Wang P., Yu X., Zhao F., Sun Y., Feng W., Wang Q., Nanomaterials (Basel), 12, (2022), <u>https://doi.org/10.3390/nano12173019</u>

[32] R. Brüninghoff, Wenderich K., Korterik J.P., Mei B.T., Mul G., Huijser A., J. Phys. Chem. C, 123, 26653 (2019); <u>https://doi.org/10.1021/acs.jpcc.9b06890</u>