

Efficacy comparison on photocatalytic activity of pure and doped ZnO nanoparticles at different pH values

T.S. Vijayapreetha¹, S. Otchadevan¹, P.Kokila^{1*}, M.Umayavalli²

¹Department of Physics, A.P.A. College of arts and Culture, Palani-624601, Tamilnadu, India

²Department of Chemistry, A.P.A. College of arts and Culture, Palani-624601, Tamilnadu, India

Abstract: In this study pure and Ni doped ZnO nanoparticles were fabricated by using sol-gel method. The morphology and the microstructure of the pure and doped samples have been characterized by X-ray diffraction (XRD), scanning electron microscope (SEM). The results revealed that the samples were crystalline hexagonal wurzite structure and the absorption spectra were observed under the UV- visible spectroscopy. The effect of pH on the rate of degradation is important and it has to be considered. In order to investigate the effect of pH on pure and doped ZnO nanoparticles photocatalytic activity of the water degradation of methyl orange was also studied with different pH values and it is observed that the absorption of the dye on ZnO and Nickel doped ZnO nanoparticles surface is strongly dependent on the pH of the solution and which plays an important role in photocatalytic degradation also the dopant studies shows a greater efficacy value under pH 6.

Keywords: Zinc Oxide; Nickel dopant; photodegradation; pH variations

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I. Introduction

ZnO is an multifunctional II-VI group semiconductor which creating centre for core of attention to researches because of its fascinating properties such as wide band gap of 3.37eV at room temperature high optical transparency, high surface stability and strong excitonic emission etc., Therefore it is desirable to tune the band gap of ZnO with the purpose of enhancing the solar cells performance, such tunability in the band gap and consequently the optical absorption shift of ZnO are achievable by doping with transition metals such as Cu, Fe, Ni and Mn. It is necessary to achieve ZnO materials with lower band gap and this depends on the dopant type and synthesis technique among transition metal sources for doping ZnO and Ni doping is that to shift the optical band gap towards the red wavelength. There are many reports for Ni doped ZnO nanoparticles deposition and characterization, such as by spincoating, sol-gel immersion, magnetron sputtering, and spray pyrolysis technique. In recent years, Ni-doped ZnO nanoparticle shows versatile properties with enhanced photocatalytic activity by recombining with photo-generated charge carriers and increasing the number of surface hydroxyl groups¹⁻⁴. Zinc oxide is generally transparent to visible light but strongly absorbs ultra violet light below 365.5 nm many papers show its optical properties. The absorption in ZnO is stronger than other white pigments. In the region of visible wavelengths, regular zinc oxide appears white, but, rutile and anatase titanium dioxide have a higher refractive index and thus has a superior opacity. The band gap energy (between valence and conducting bands) is 3.2eV. Under ultra violet light zinc oxide is photoconductive. The combination of optical and semiconductor properties of doped Zinc oxide make a contender for new generations of devices. Among transition metal sources for doping ZnO, Ni doping in ZnO could shift the optical band gap towards the red wavelengths. The chemical stability of Ni²⁺ while occupying Zn²⁺ sites makes it unique and make it identified as one of the most efficient doping elements as it enhances ZnO with optical and electrical properties. The effects of doping Ni in ZnO are dramatically dependent on the growth technique used. Here we use zinc nickel oxide (Ni-doped ZnO) grown by sol-gel method at different pH levels^{5,6}.

II. Materials and Methods

First we have to weigh the starting material according to their molarities in the solution. ZnSO₄·7H₂O and NiSO₄·6H₂O were dissolved in 30 ml of distilled water under stirring at room temperature for 30 min both solutions were prepared separately. Then these solutions are mixed during continuously stirring, an aqueous solution of NaOH was slowly added to the mixture under constant stirring until the pH of the solution reached to 10. During adding of NaOH solution, precipitation was start. The final solution was then stirred for 20 hours at room temperature, so that homogeneity can be maintained. The reaction mixture was centrifuged to get the precipitate out, before the washing of sample pH was above 10, then sample was washed several times until the pH was treated to 6, 8 and 10. After washing we have dried the sample and obtain in the powder form to make fine particles we have grinded it and then it was calcined at 400 °C and 500°C for 4 hours in the muffle furnace.

III. Results and Discussion

X-ray diffraction

Fig.1 and 2 shows the X-ray diffraction (XRD) patterns of Ni-doped ZnO nanoparticles, annealed at 400 and 500°C with different pH values of (6, 8 and 10). The peaks at 31.86, 36.87 and 66.38 with corresponding diffraction from planes (100), (111) and (200) respectively, confirms hexagonal wurtzite Ni-doped ZnO nanoparticles and also matched with JCPDS 897102, 750273.

Ni-doped ZnO nanoparticles annealed at 400°C with pH value 10 shows poor crystallinity with amorphous nature whereas, pH values 6 and 8 show good crystalline nature. But in case of Ni-doped ZnO nanoparticles annealed at 500 °C shows amorphous nature for all the three pH values^{7,8}.

Utilizing the X-ray diffraction data, the average particle/ grain size in ZnO nanoparticles was estimated by Scherer's equation,

$$D = \frac{0.94 \lambda}{\beta \cos \theta} \quad (1)$$

Where D is grain size, β the full width at half maxima and λ the wavelength of X-ray used (1.54 Å). The particle of Ni-doped ZnO nanoparticles at 400°C is calculated as 20 nm. Whereas, the particle size get increased to 23 nm when the temperature get's increase to 500°C whose pH value 6.

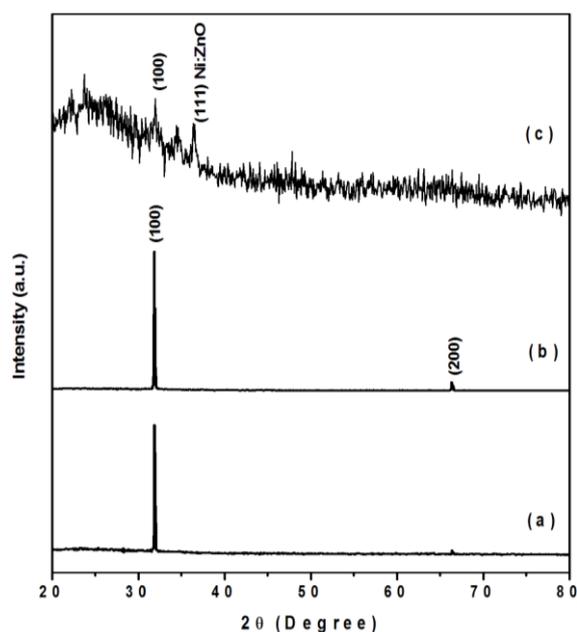


Fig. 1 XRD patterns of Ni-doped ZnO nanoparticles annealed at 400 °C and different pH values of a) pH = 6, b) pH = 8 and c) pH=1

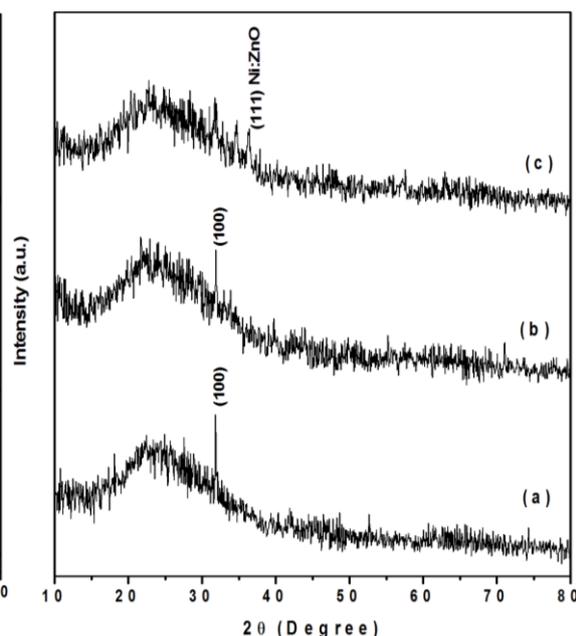


Fig. 2 XRD patterns of Ni-doped Zn nanoparticles annealed at 500°C and different pH values of a) pH = 6, b) pH = 8 and c) pH=10

Scanning electron microscopy

It is observed that role of pH is not only the formation of structure but also the smoothness enhancement of ZnO nanoparticles. The shape control was performed under acidic range of pH shown in Fig. 3a and 4a. Scanning electron microscope magnification of Ni-doped ZnO nanoparticles deposited for different pH values of (6, 8, and 10). When pH value in 6 the surface of uniform spherical grains without cracks or pinholes and well cohered. Fig 3c shows fine hexagonal shaped grains for pH 8 the average particle size of micro crystallite was calculated from the intercept method and size determined from SEM in the range of 80 nm to 120 nm⁹⁻¹². SEM sample annealed at 500°C with different pH values of (6, 8 and 10) with different magnifications are shown in fig 4. It is clear that the surface morphology was modified with doping. Fig. 4a shows uniform distribution of spherical grains over total coverage of the substrate with compact morphology. Agglomeration observed in Fig. 4c smooth background that may correspond to some amorphous phase of Ni-doped ZnO nanoparticles. For the precise morphological control of oxide particles, pH control is another key factor, since the adsorption of the shape controllers is strongly affected by pH.

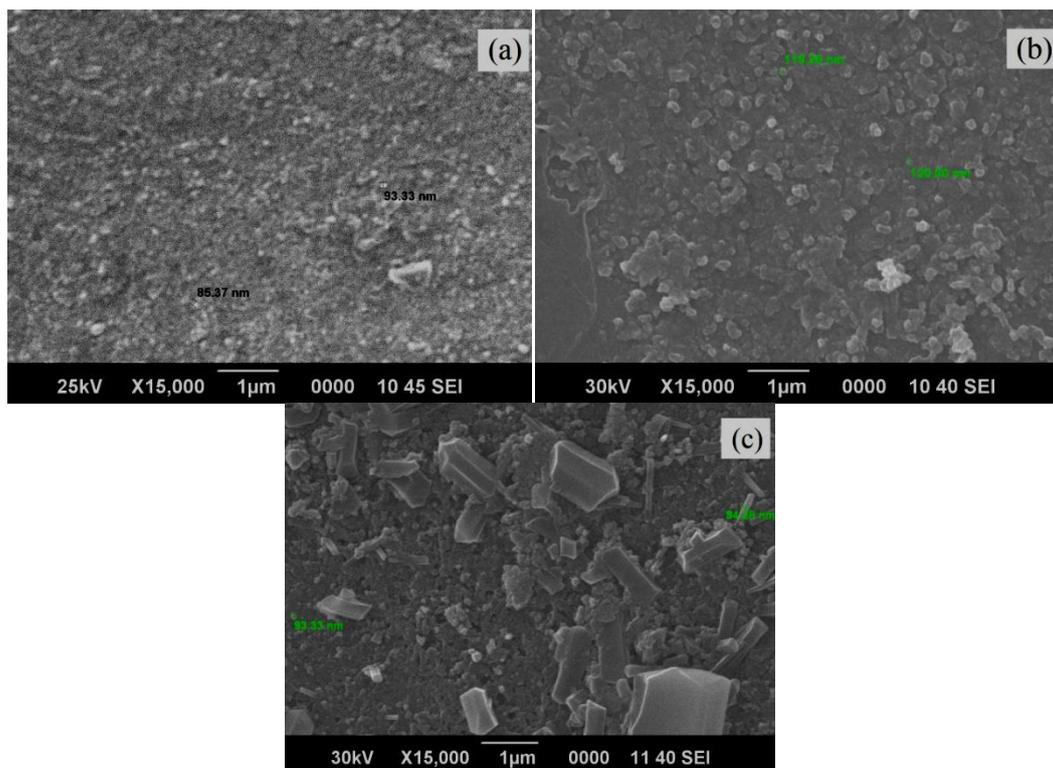


Fig. 3 SEM images of Ni - ZnO nanoparticles annealed at 400°C for a) pH=6 b) pH= 8 and c) pH=10

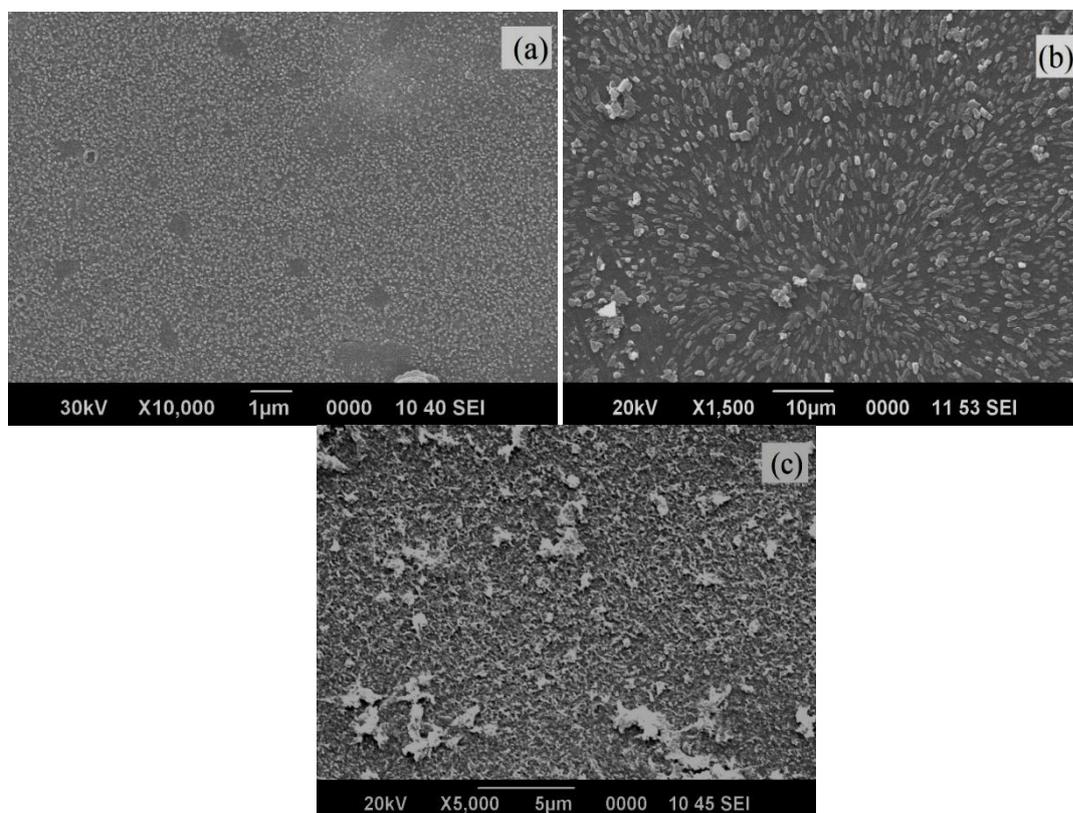


Fig. 4 SEM images of Ni doped ZnO nanoparticles annealed at 400 °C for pH a) pH=6 b) pH= 8 and c) pH=10

Optical Analysis

The absorption spectra of Ni-doped ZnO nanoparticles were investigated by UV-visible spectrophotometer¹³⁻¹⁵. The spectra of Ni-doped ZnO nanoparticles at different pH values (6, 8 & 10) were annealed at 400⁰ C and 500⁰ C shown at fig 5 & 6. The optical bandgap energies are calculated as 3.25, 2.95 and

2.90 eV for Ni-doped ZnO nanoparticles annealed at 400⁰ C and shown in Fig.7. Similarly Fig. 8 shows band gap energies of Ni-doped ZnO nanoparticles annealed at 500⁰ C as 3.2eV, 3.25eV and 3.16eV respectively. The calculated optical bandgap values were found to be in the range from 3.25 eV, 2.9 eV and 2.90 eV. The bandgap values decreases with the increase pH Values.

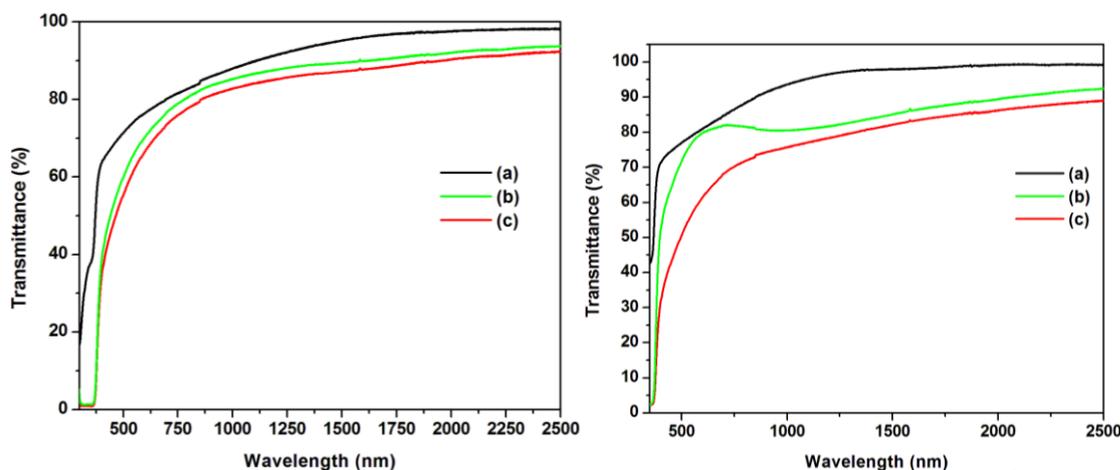


Fig. 5 & 6 Transmittance spectrum of Ni doped ZnO nanoparticles annealed at 400⁰C 500⁰ C for different pH values of a) pH=6, b) pH=8 and c) pH=10.

Photocatalytic activity

The interpretation of influence of pH on photocatalytic reactions was highly difficult it plays multiple roles such as electrostatic interactions between semiconductor surface, solvent molecules, substrate and charged radicals formed during the course of reaction. The ionization state of the surface of the photocatalyst can be protonated or deprotonated in acidic and alkaline conditions¹⁶⁻¹⁷. Hence, the pH is optimized to 4 for further analysis. The effect of pH on the removal of methylene blue is shown in Fig. 9.

At lower pH values (pH=6) Ni doped ZnO nanocrystals (0.04%) shows enhanced % of decolourization whereas at pH values the samples shows the reduced % of decolourization. It is also evident that the photocatalytic activity of Ni doped ZnO is strongly dependent on the dopant concentration. Doping of small concentrations of Ni increases the lifetime of excited charge carriers, which may results the enhanced photocatalytic activity. When the doping concentration becomes too

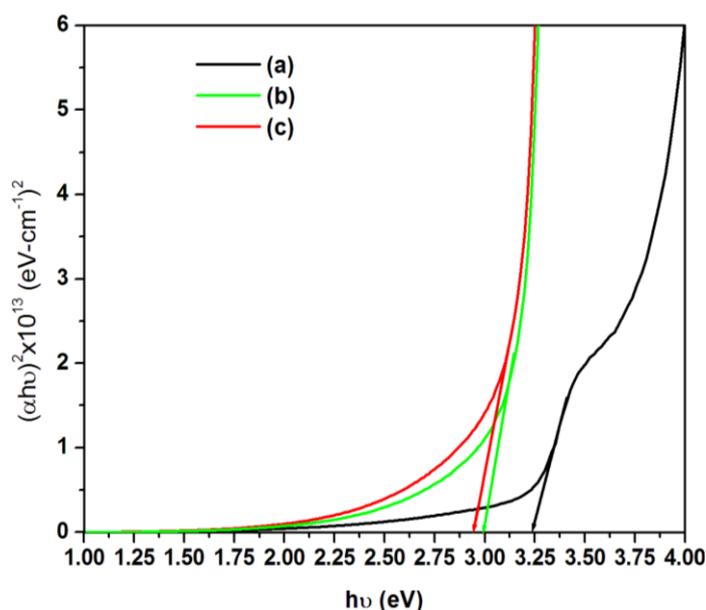


Fig. 7 The plots of $(\alpha hv)^2$ versus $h\nu$ for Ni doped ZnO nanoparticles annealed at 400⁰ C for different pH values of a) pH=6, b) pH=8 and c) pH=10.

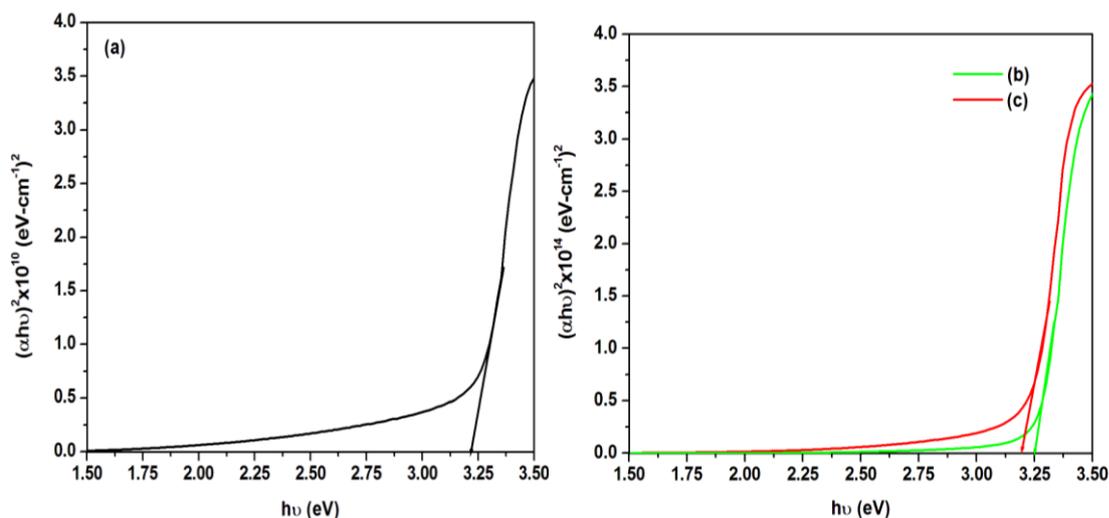


Fig. 8 The plots of $(\alpha h\nu)^2$ versus $h\nu$ for Ni doped ZnO nanoparticles annealed at 500 °C for different pH values of a) pH= 6 ,b) pH=8 and c) pH=10.

high, many crystal defects may induce and it may serve as recombination centres to reduce the photocatalytic activity. After 90 min of testing, the percentage degradation was 30 % (pH=10) 32% (pH=8) and 65% (pH=6) photocatalytic activity with pH=6 of Ni doping is related to shift in optical absorption of the catalyst in visible region. ZnO absorbs only UV energy (below 400nm) whereas doped catalyst absorbs UV and portion of visible energy hence there is increase in photo-catalytic activity. The presence of metal ions on the surface of the photocatalyst particles improves the rate of electron transfer to beneficial effect on the photo-oxidation rate of organic species. The more number of pores increases the hydroxyl content. In heterogeneous photocatalysis, the illumination of semiconductor produces electrons holes (h^+). The holes (h^+) are combining with OH there is formation of hydroxyl radical. These surface hydroxyl radicals formed on the surface of the photocatalyst are oxidizing species which ultimately affects the photocatalytic activity. This suggests that the increase in hydroxyl content of the film increases the photo activity. Also stated that these dopant exists only as the recombination centre for the electron / holes, thus having no noticeable effect on the reaction rate but the pH plays a major role in degradation¹⁸⁻²⁰.

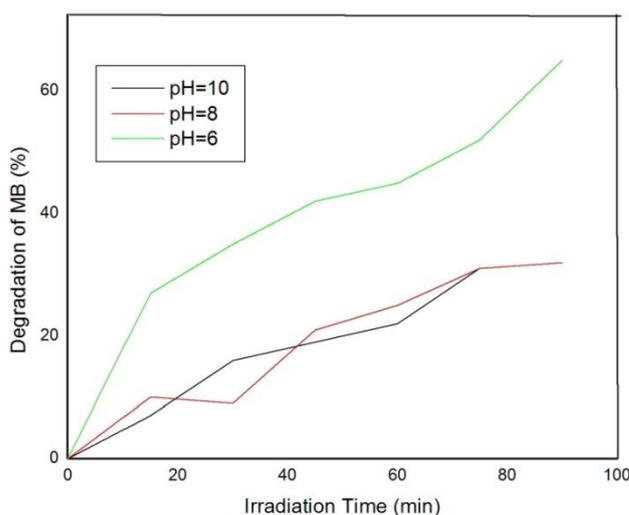


Fig.9. Degradation of ethylene blue solution for different pH values.

IV. Conclusion

The enhancement of photocatalytic activity is due to their large surface area. Ni – doped ZnO nanoparticles for different pH values shows at ph=6 the establishment is well incorporated with good crystallinity and degradation of contaminants compared to the pH 8 and 10. Also the Ni doped ZnO

nanoparticles will prove higher efficacy in future while dope with organic dopants leads to environmental remediation.

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