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Invisible Ink from ZnO Waste Batteries Susilo Sudarman Desa¹, Hasri², and Suriati Eka Putri³ ¹Student of Chemistry department, Faculty of Mathematics and Natural Sciences, Universitas Negeri Makassar, Parangtambung, Makassar, Indonesia. ²Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Makassar, Parangtambung, Makassar, Indonesia ³Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Makassar, Parangtambung, Makassar, Indonesia ¹susilosd32@gmail.com, ²hasriu@unm.ac.id

Abstract.

Zn metal is the base on ZnO making as I invisible ink. Zn metal can be obtained from battery waste and become the target of this research. Synthesis of nanoparticles through several stages is the determination of stirring time, characterization and application of ZnO as invisible ink. Colonized white ZnO colloidal nanoparticles, optimum agitation time of 60 minutes, particle size 10.03-46.24 nm, gap energy of 3.5 eV.

The wurtzite hexagonal crystalline lattice system. The ZnO nanoparticle colloid application provides a purple glow on yellow filter paper and luminescence for HVS paper, cardboard, and bill ¹. Introduction Battery is a tool that can convert chemical energy into electrical energy in electronic equipment such as mobile phones, clocks, laptops, flashlights and so on. There are two kinds of batteries that are known namely primary battery (disposable) and secondary battery (refill) [1].

Primary batteries that have been used are generally disposed of as waste, but in the battery there are heavy metals and corrosive compounds that can cause pollution and harm to natural resources. The main components in the primary battery are the carbon

rods as the cathode, the zinc as the anode and the conducting electrolyte [2].

Zinc content in the battery can be utilized as a raw material for ZnO manufacture which is semiconductor crystalline material having properties such as; Transparent, high electron mobility, wide band gap, strong luminescence at room temperature [3]. Thus ZnO has the potential as a transparent electrode in solar cell technology, electroluminescence devices and devices for ultraviolet transmitters.

Engineering of ZnO particle size into nanoscale, will give different performance results with bulk size. The nanometer size will change the properties of materials such as changes in boiling point, freezing point, chemical reactivity, emitted color change, transparency, mechanical strength, electrical conductivity and magnetization [4].

Semiconducting nanoparticles can emit luminescence rays when given energy corresponding to the UV-Vis range to excite electrons from the valence band to the conduction band. Emission generated in the form of luminescence rays. The wider the energy band gap, (the smaller the particle size), the greater the luminescence energy to be emitted [4].

This trait can be used as a safety ink of secret documents for its invisible state without being given excitation energy such as ultraviolet light. Various methods can be used to synthesize ZnO nanoparticles such as sonokimia, mechanochemical, chemical precipitation, hydrothermal [5], vacuum deposition (CVD, PVD), Pyrolysis Spray and Sol-Gel [6].

The short process sol gel method, carried out at low temperatures, can produce metal oxide in nano size and exhibit better characteristics than other methods. Therefore this research is one effort to improve the quality of battery waste using simple method and can be used as secret ink. 2. Method Of Experiment 2.1. Tools and materials The tools used in this research are glassware, oven, magnetic stirrer, hot plate, UV Vis spectrophotometer, Tanur, Mortar, X-Ray Diffraction (XRD). The materials used are battery anodes, pure Zn metal, 96% ethanol, Na₂CO₃, HCl pa, CH₃COOH pa, LiOH.H₂O, HVS paper, paperboard, filter paper and banknotes.

2.2. Preparation of Zinc Acetate A total of 10 grams of Zinc-Carbon battery anodes were dissolved in 10mL concentrated HCl. The solution is allowed to dissolve until the solvent anode dissolves. The filtrate was added with a 0.75M sodium carbonate solution of 200 mL. The suspension formed was filtered and dried at room temperature. The suspension is then added with 20 mL acetic acid.

The solution is heated to gel form and solidifies at room temperature. The solids are smoothed and stored in an airtight container. The same treatment is given for the original Zn solids. 2.3. ZnO Colloid Synthesis Weighed 2.20 grams of zinc acetate and dissolved in 100 mL of 96% ethanol, further distilled to residue left behind about 60% (zinc acetate solution). Then weighed 1.46 grams of lithium hydroxide monohydrate and dissolved with 100 mL of 96% ethanol, (lithium hydroxide solution).

A total of 60 ml of zinc acetate solution mixed with 40 mL of lithium hydroxide solution at low temperature and stirred with stirrer for 1, 2, 3, 4 hours. The ZnO colloid formed as a invisible / safety ink on HVS paper, filter paper, paperboard, and banknote and characterized by UV-Vis and X-Ray Diffraction (XRD) spectrophotometers. 3. Results And Discussion ZnO powder produced from zinc acetate precursor, the precursor to function in controlling the process of hydrolysis and polymerization.

The growth of ZnO particles from zinc acetate precursors by sol gel method undergoes four stages: salvation, hydrolysis, polymerization and transformation into ZnO. Zn ions will be hydrolyzed to produce Zn(OH)₂ then polymerized to convert the sol to gel. The polymerization bonding Zn-O-Zn thus transformed into ZnO (Rani, 2008). The mechanism is as follows: Based on the reaction stage shows that ZnO crystals has been formed, according to PDF data (Powder Data File) entry number # 96-230-0113 for stirring time 2, 3 and 4 hours. Entry number # 96-320-0116 for 1 hour time of stiring and entery number # 96-900-4180 as ZnO comparison.

The 3 three data are known that the resulting ZnO has a hexagonal lattice system and a crystal phase that is wrutzite The presence of impurities causes unwanted noise. Figure 1. ZnO Diffractogram Based on the length of time of stirring, (a) 1 hour, (b) 2 hour, (c) 3 hour, (d) 4 hour Table 1. Determination of ZnO size and content

Stirring (hour)	Approximately size (nm)	Content of ZnO (%)
1	10,03 – 46,25	17,5
2	40,88 – 90,20	5,8
3	44,86 – 214,21	7,6
4	72,48 – 277,52	23,2

Reference 53,27 – 71,51 81,5 Based on the data of Table 1 the longer the stirring the greater particle size produced Due to the more Zn(OH)₂ is formed so that the distribution of the crystals more quickly and can form a larger ZnO particles. Table 2. Results of energy gap determination No.

ZnO with the variation of stirring (hour)	Gap Energy (eV)
1	3.47
2	3.43
3	3.43
4	3.48

reference 3.47 The stirring process one to three hours, the energy gap decreased with increasing particle size, but stirring four hours, the particle size increases, but the energy gap also increased, it is not in line with 4 the theory. The energy gap will widen if the particle size is small, otherwise the gap energy will narrow if the particle size is large [6].

This is thought to be due to the greatest ZnO concentration occurring in a four-hour stirring time of 23.2%. Thus the doping agent is less so that its gap energy is greater. This is in line with Ilham and Astuti [7] which states that the greater value of doping agent the gap energy value will decrease; otherwise the less doping the gap energy will be greater. Table 3.

Color of luminescence Stirring (jam) Color of luminescence HVS Cardboard Filter Paper Banknote 1 Yellow Yellow Purple Yellow 2 Yellow Yellow Purple Yellow 3 Yellow Yellow Purple Yellow 4 Yellow Yellow Purple Yellow Reference Yellow Yellow Purple Yellow Yellow color indicates on HVS paper, paperboard, and paper money while filter paper produces purple glow.

In general, the luminescence for all variations does not give a significant difference, in accordance with the amount of energy gap obtained is not much different. High cellulose content on HVS paper, paperboard and filter paper can produce blue luminescence [8]. On filter paper shows purple color intensity, it is due to the high content of cellulose and the ability of filter paper to absorb the particles so that the intensity on the filter paper to purple. Banknotes show low luminescence intensity. Banknotes made of cotton fibers have a high absorbency and visible luminescence of photoluminescence.

4. Conclusion ZnO colloid nanoparticles have been successfully synthesized by sol-gel methods that can be applied to HVS paper, paperboard and banknotes by producing yellow sparkle, while for filter paper it produces a purple glow.

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