

Removal of Mercury (II) in Aqueous Solution by Using ZnO and ZnO/CdS Nanoparticles as Photocatalysts

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ABSTRACT

Zinc oxide (ZnO) and ZnO/CdS nanoparticles have been synthesized. The samples were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and scanning electron microscopy (SEM). Photocatalytic reduction of toxic Hg (II) in aqueous solutions by suspension ZnO_{NPs} and ZnO/CdS_{NPs} has been studied under an oxygen atmosphere. Flame atomic absorption (FAAS) has been used to determine the concentration of Hg (II) in aqueous solutions. Photocatalytic reduction of Hg (II) was carried out with various ZnO nanoparticles (ZnO_{NPs}) concentrations. The optimum concentration of ZnO NPs was obtained at 0.24 mg/L. The highest photo reduction rate was obtained at 0.24 mg/ZnO/CdS_{NPs} concentration. According to the experimental results, the reaction mechanism of ZnO_{NPs} and ZnO/CdS_{NPs} illumination to produce oxidizing species and the effect of these species on the Hg (II) in aqueous solution has been suggested.

Keywords: Nanocomposites, semiconductors, environmental treatments, ZnO nanoparticle.

1. Introduction

Semiconductor nanoparticles exhibit interesting size-tunable photocatalytic properties due to the confinement of the electronic wave functions [1]. Zinc oxide (ZnO) semiconductor is one of the most important photocatalysts because of its stability, non-toxic, low cost and high photoreactivity [2,3]. The band gap energy of ZnO is approximately 3.2 eV [4]; therefore ZnO promotes photocatalysis upon illumination with 387 nm [5]. Coupling ZnO particles with narrow band gap semiconductors such as (CdS, In₂S₃, BiO₃) [6] can be utilized band gap ZnO to visible light. Coupled semiconductors can be shown in Fig. 1.

Hg(II) in industrial waste waters is one of the most dangerous pollutants due to its toxic and bio-accumulative properties [7]. Exposure to inorganic mercury compounds can cause severe renal and gastrointestinal damage [8]. The removal of Hg (II) in

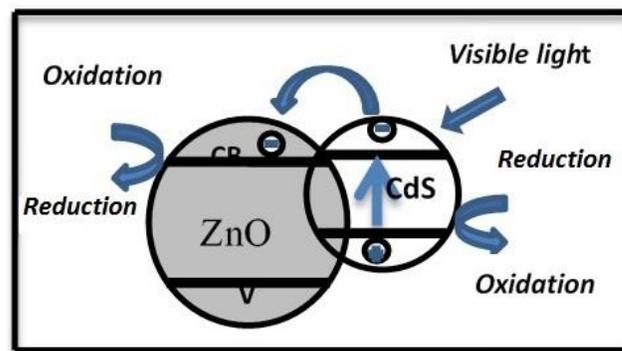


Fig. 1 Schematic formation of ZnO/CdS composites and the transferring routes of photo generated electron.

aqueous solutions has been studied by using several methods such as carbon adsorption, ion exchange, precipitation and photocatalytic reduction [9]. Heterogeneous photocatalysis is a most effective process applied for purification of water from organic [10,11] and inorganic pollutants. The photocatalytic reduction appears to be most promising because of their high efficiency and simplicity of operation [12]. The present work reports a preparation of ZnO_{NPs} and ZnO/CdS_{NPs} and an investigation of the photocatalytic

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reduction of toxic Hg (II) in aqueous solution on these nanoparticles.

2. Experimental

2.1. Materials and Methods

Mercury chloride (HgCl_2) was purchased from G.P.R. Thioacetamide and cadmium nitrate were supplied from HANNOVER. Zinc acetate dehydrate, oxalic acid and toluene were purchased from china. Olic acid was supplied from Germany and O-xylene was purchased from Washington.

2.2. Preparation of ZnO_{NPs} and Modification with CdS_{NPs}

Using zinc acetate 2g; triton-100, and NH_3 solution as the following procedure: dissolving 2g from zinc acetate with 25 ml distilled water in room temperature and then added 10 ml of Triton-100 after that mixing in stirrer for 3 hours, after one an hour of mixing, NH_3 has been added solution to precipitate the nanoparticles, to be filtered and washing with distilled water three times. Lastly dries the thick recipe at $353\text{ }^\circ\text{C}$ for 1 hour following that calculation at $673\text{ }^\circ\text{C}$ to obtain Nano powder ZnO [13]. Modification process, including adding of Olic acid, O-xylene and washing the results with toluene to get finally surface area modified non agglomerate nanoparticles.

The modification process of ZnO with CdS_{NPs} was prepared by immersing ZnO_{NPs} into the clear reactant solution containing $\text{Cd}(\text{NO}_3)_2(0.01\text{M})$, thioacetamide $\text{C}_2\text{H}_5\text{NS}$ (0.01M) at room temperature for 15 min. CdS growth was observed by the emergence of a yellow color on the surface of the sample. A yellow sample was filtrated and washed with deionized water to remove the surface residue and finally dried $90\text{ }^\circ\text{C}$ [14].

2.3. Photocatalytic Reduction Experiment

The aqueous Hg^{+2} solution was prepared by dissolving certain quantities of HgCl_2 in distilled water and add 0.3 g/ml of ZnO or ZnO/CdS nanoparticles. The reaction mixture was carried out by using 500 ml, Pyrex glass reservoir placed in the laboratory temperature ($25\text{ }^\circ\text{C}$) and kept homogeneously by stirring on the magnetic stirrer. The light source was focused directly on the solution vertically without the use of the lens.

2.4. Measurement

Hg^{+2} concentration solutions was measured by using flame atomic absorption.

2.5. Photo degradation Experiments

All Photo degradation experiments were carried out by irradiation the aqueous solution of Hg (II) (60ppm) by UV-visible light emitted from 360nm in the reaction beaker (250 ml) with continuous stirring of the suspensions were irradiated for 50min. A small quantity (1ml) of suspension was taken and centrifuged to remove NPs.

3. Results and Discussion

3.1. Scanning Electron Microscopy (SEM)

Fig. 2 shows different magnifications of ZnO naked and modified NPs surface. The results of this analysis showed the highly aggregation of ZnO_{NPs} because it has a high surface energy that tends to clump together in large particles and this agrees with the results of the recent research [15]. It was found that the surface modified ZnO_{NPs} by oleic acid has reduced the agglomeration by reducing the energy of the surface by isolating each particles from others, after modification the results showed that the ZnO_{NPs} were dispersed homogeneously as shown in figure A and B, while in **Fig. 2** (C, D) the particle size is increased because adhering of CdS_{NPs} to the surface of ZnO_{NPs} , the larger particles were the aggregates of smaller CdS_{NPs} when a multilayer of CdS_{NPs} was formed on the surface ZnO_{NPs} , the loading of CdS_{NPs} was raised and could significantly enhance the photo electrochemical property of ZnO_{NPs} with Hg treatment.

3.2. Atomic Force Microscopy

The Atomic force microscopy was done to identify the topological appearance and the size range was found out around 87.2 nm rendering 3D profile. The (AFM) images were also used for roughness, porosity and fractal dimension.

Fig. 3 shows the AFM (2-D) images of naked ZnO_{NPs} and ZnO modified NPs. AFM images prove that the grains are distributed homogeneously within the selected scanning area (1518×1514) nm. The average diameter of naked and modified synthesized ZnO is measured from AFM analysis using software and is found to be around (47.69-85.62) nm depending on the preparation conditions. The surface morphology of the ZnO unmodified NPs obtained from the AFM analysis in **Fig. 3A**, **Fig. 3B** shows the AFM images of ZnO modified NPs, the average roughness of modified ZnO is 6.45 nm while in the case of naked ZnO the average roughness is 21.09nm. This result agrees with [16]. **Fig. 4** shows that the high ratio nanoparticles within the range (50-60) nm.

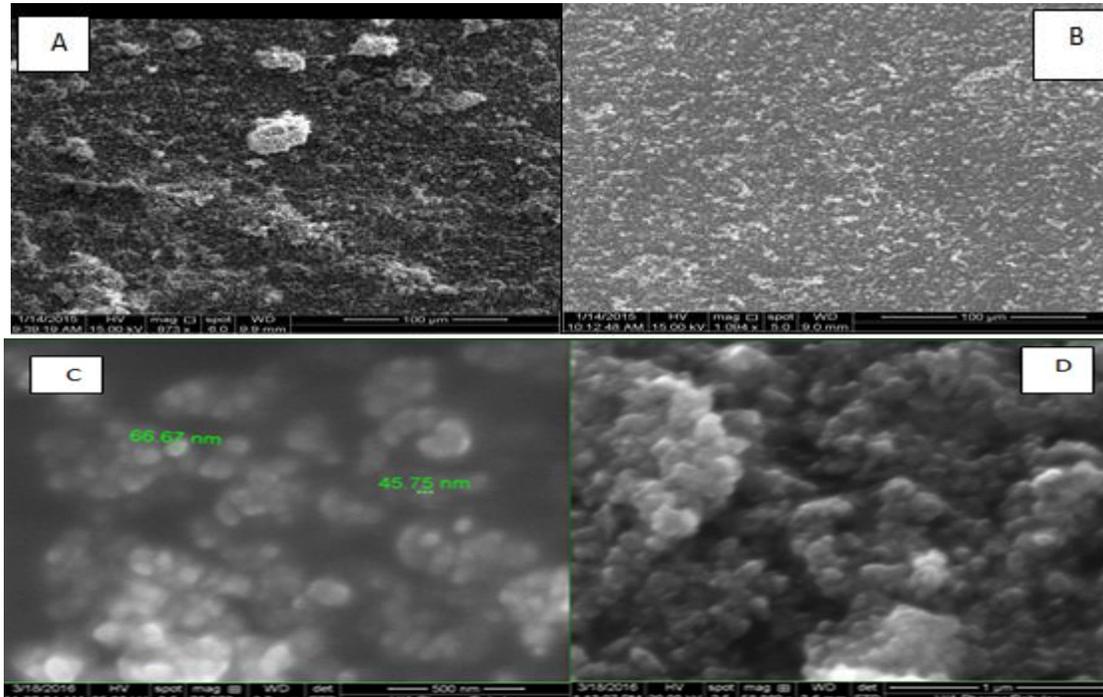


Fig. 2. (A, B) The same magnified images of SEM of naked ZnONPs, and (C, D) different magnified images of SEM of modified surface area ZnO/CdSNPs

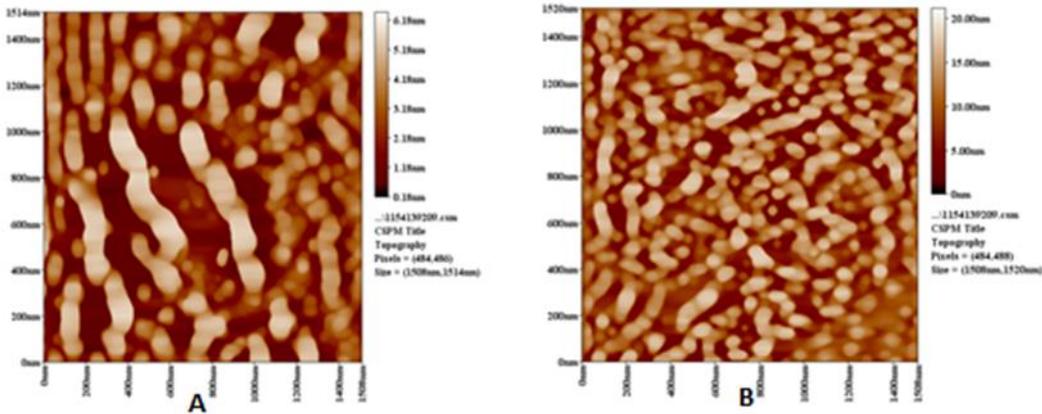


Fig. 3. AFM image of the (a) naked ZnONPs and (b) Surface area Modified ZnONPs

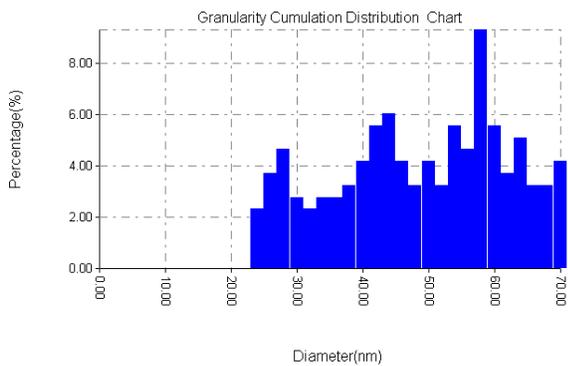


Fig. 4. The Distribution of Different Diameter modified ZnO Nanoparticles

3.3. X-ray Diffraction Analysis (XRD)

From the X-ray test **Fig. 5** of ZnO naked and modified NPs at a diffracted angle (30° to 70°), a crystalline peak appeared which indicate crystalline structure at ($2\theta = 34$). Also, a peak for modified ZnO at ($2\theta = 36.569$). This indicates that crystalline material is prepared which agrees with the results of the Zhang and Hong [17,18].

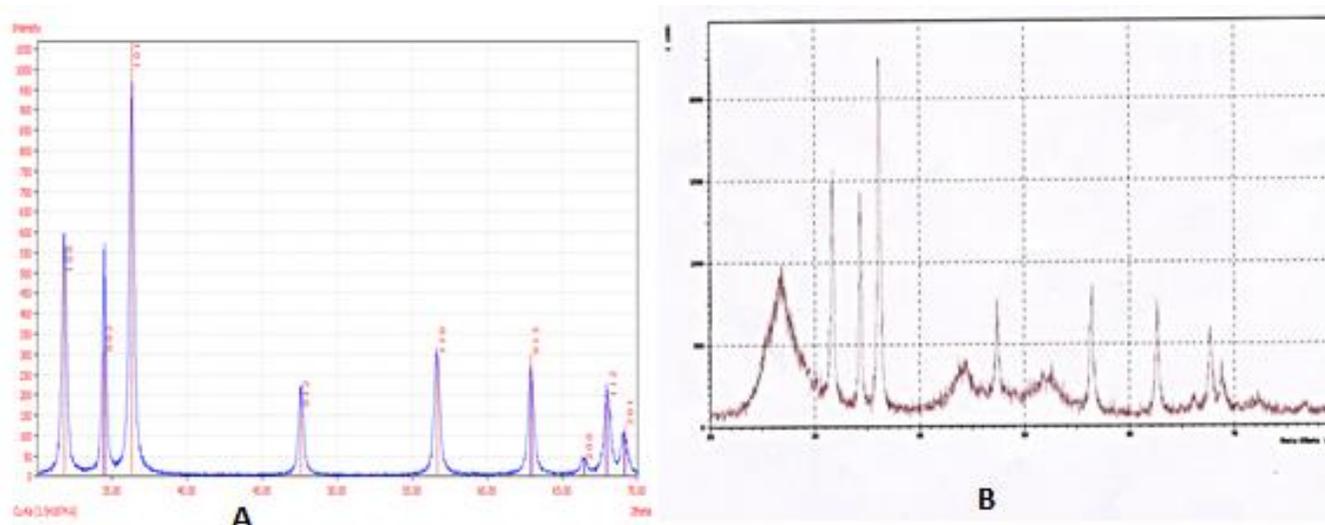


Fig. 5. A: Analysis of X-ray Diffraction for Surface Area Modified ZnONPs and B: for ZnO/CdS NPs.

3.4. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectrum of crystalline ZnO showed in **Fig. 6** in which indicated these several transmission bands. The spectrum is matched with the standard spectrum of crystalline ZnO and in a good agreement with Kahn⁽¹⁹⁾. **Fig. 6** shows the FTIR spectra of ZnO modified NPs a broad peak at 3419 cm⁻¹ for ZnO modified NPs due to the vibrations of the (-OH group) to the surface of ZnONPs, and a high intensity broad band around 559.79 cm⁻¹ for modified due to the vibration mode of zinc and oxygen bond[20].

3.4. Photocatalytic Results

A series of primary experiments to determine the optimum conditions of the photo-degradation rate has been done.

Fig. 7 was observed that there is no photo-degradation rate in the presence of light and air without using ZnONPs and ZnO/CdSNPs. The same results were obtained by using ZnONPs and air under dark conditions. This means that the presence of light, O₂ and photo catalyst are very essential for removal of Hg⁺² in aqueous solution [9].

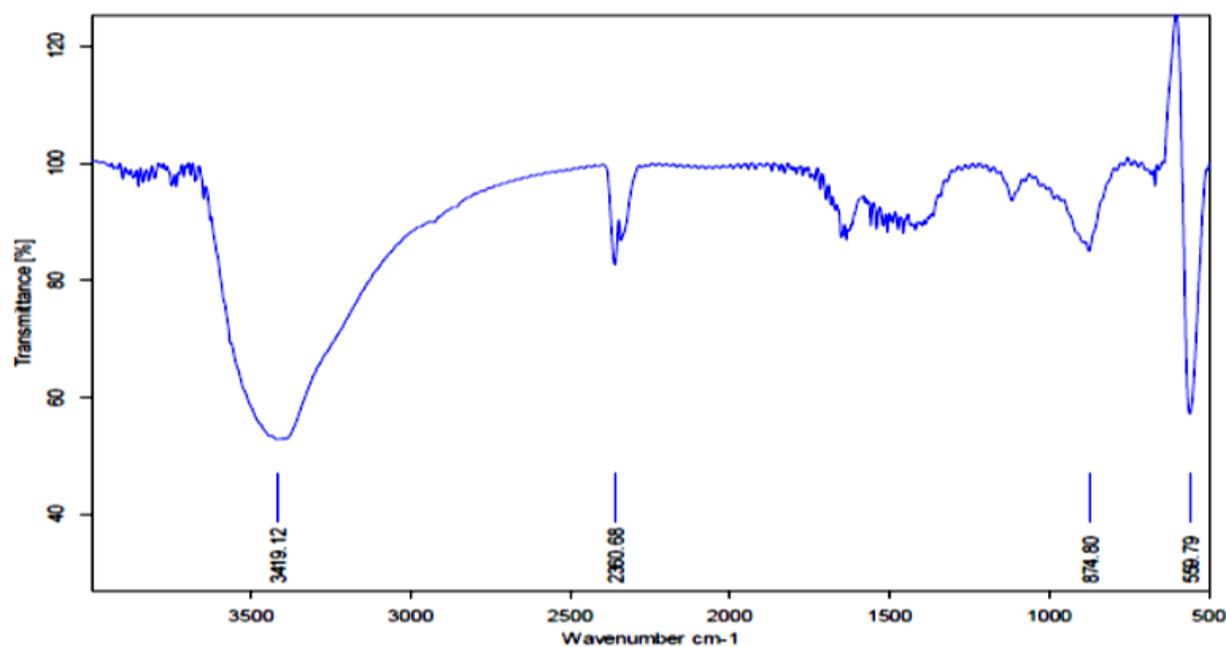


Fig. 6. FTIR spectrum of ZnONPs

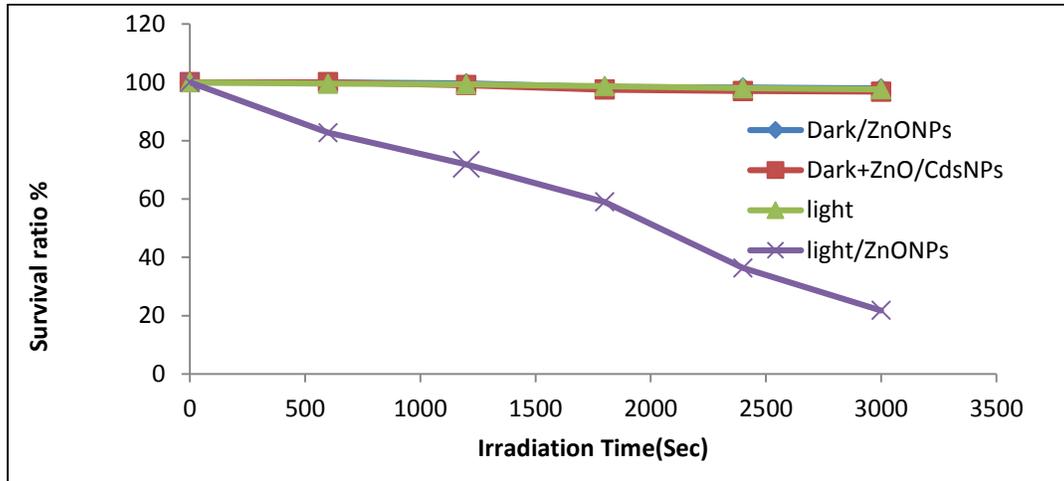


Fig. 7. Survival ratio of Hg⁺² reduction in aqueous solution with various conditions at 25C°.

3.5. Effect of ZnONPs Concentration

A series of experiments to determine the ideal amount of ZnONPs has been carried out. The maximum rate of photocatalytic degradation was obtained at (0.24) mg/ml of ZnONPs of the solution. So that this amount will be chosen to study the effect of ZnONPs and ZnO/CdSNPs on the photocatalytic degradation process. Fig. 8 illustrates that the rate of photocatalytic degradation increases with the increasing of ZnONPs loading. The increasing in the amount of photo catalyst increases the number of active of the ZnONPs surface that in turn increases the number of O₂ and OH radicals [21]. However the addition of the high amount of catalyst (0.3,0.4 GM/l) decreases the light penetration by the photo catalyst suspension as shown in Fig. 9.

3.6. Photocatalytic degradation of Hg⁺² by using coupled ZnO/CdSNPs:

The rate of photocatalytic reduction reaction of Hg⁺² was increased by using 0.24 gm/ml coupled ZnO/CdSNPs instead of naked ZnONPs. This observation can be explained that the band gap of CdS equal (2.5 eV) [5], it mean CdS absorbs visible light to generate excited negative electrons and positive holes. These excited electrons are injected into the conduction band of ZnONPs to produce oxidizing radical species [22]. These oxidizing agents were reduced Hg⁺² in aqueous solutions as shown in Fig. 10.

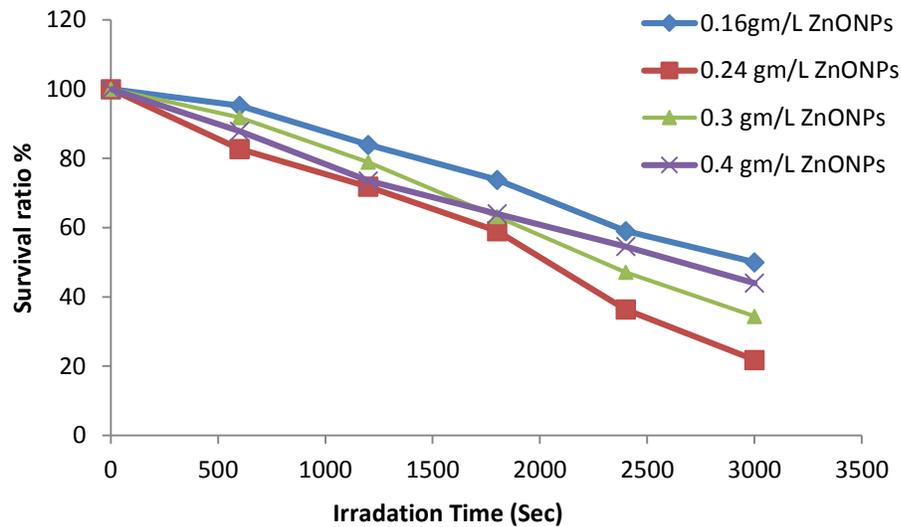


Fig. 8. Survival ratio of Hg⁺² reduction in aqueous solution with various concentrations of ZnO NPs at 25C°.

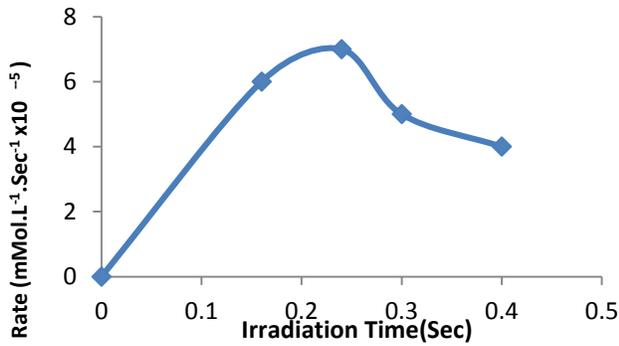


Fig. 9. The relationship between the rate of photocatalytic reduction of Hg⁺² in aqueous solution and TiO₂ concentrations at 25 C°.

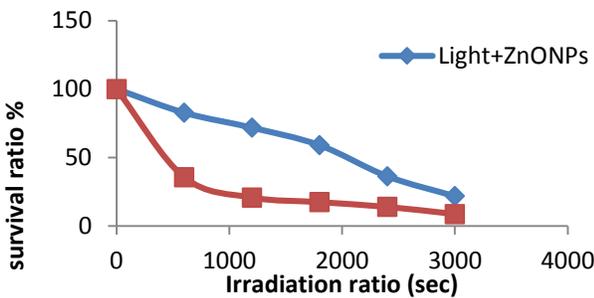
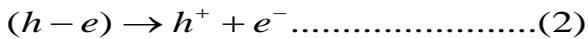
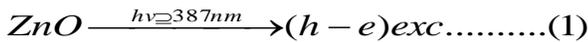


Fig. 10. Compression of survival ratio of photo reduction reaction of Hg⁺² in aqueous solution under various conditions at 25 C°.

3.7. Mechanism of Photocatalytic:

Reduction of Hg⁺² When ZnO NPs irradiated with light of energy (3.2 eV) [4], the photon energy generates an electron hole pair on the nanoparticle surface [22].



The electron in the conduction band can reduce Hg⁺² to produce a black precipitate of Hg⁰ [8] according to the following equation

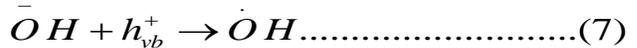
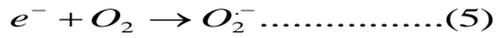


Hg⁺² were then produced and could deposit on the surface of solid nanoparticle to decrease photo catalyst activity.

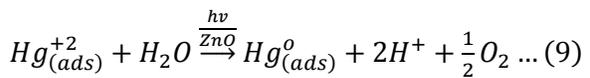
Hg⁺² can become trapped on the surface [4] according to the following equation.



Also, these existed electrons was reacted with atmospheric oxygen and water to yield reactive oxygen species such as super oxide O₂⁻ hydroxyl radical OH and hydrogen dioxide (H₂O₂) [22] according to the following equations



HO₂ and H₂O₂ can be reacted with Hg⁺² to produce a black precipitate of Hg⁰. The net photocatalytic reduction reaction is



4. Conclusions

Light, oxygen and semiconductors are very essential for photocatalytic activity. The highest photocatalytic reduction of Hg⁺² was obtained at 0.24 mg/l ZnO concentration. Nanoparticles coupled is an effective method to realize the transformation of UV active transition metal oxide to visible- light responsive photo catalyst. So that photo reduction efficiency of Hg⁺² was increased by using coupled ZnO/CdS NPs instead of ZnO NPs as a photo catalyst.

References

- [1] B. Dai, C. Chao, X. Lu, Q. Xia, J. Han, F. Mao, J. Yang, D. Sun, Preparation of ZnO/CdS/BC photocatalyst hybrid fiber and research of its photocatalytic properties, Journal of Nanotechnology, 2015 (2015) 1-8.
- [2] S. Naghizadeh-Alamdari, A. Habibi-Yangjeh, M. Pirhashemi, One-pot ultrasonic-assisted method for preparation of Ag/AgCl sensitized ZnO nanostructures as visible-light-driven photocatalysts, Solid state sciences, 40 (2015) 111-120.
- [3] J. Zhou, S. Zhang, X. Qiao, L. Wu, ‘Controlled Growth of One-Dimensional Oxide Nanomaterials, Polym. Sci. A: Polym. Chem, 44 (2006) 3202.
- [4] M. Seyed-Dorraj, N. Daneshvar, S. Aber, Influence of inorganic oxidants and metal ions on photocatalytic activity of prepared zinc oxide nanocrystals, Global Nest J, 11 (2009) 535-545.
- [5] P. Calza, C. Minero, E. Pelizzetti, Photocatalytic transformations of chlorinated methanes in the presence of

- electron and hole scavengers, *Journal of the Chemical Society, Faraday Transactions*, 93 (1997) 3765-3771.
- [6] J. Wang, X. Sun, Y. Yang, H. Huang, Y. Lee, O. Tan, L. Vayssieres, Hydrothermally grown oriented ZnO nanorod arrays for gas sensing applications, *Nanotechnology*, 17 (2006) 4995.
- [7] R. Herrero, P. Lodeiro, C. Rey-Castro, T. Vilariño, M.E.S. De Vicente, Removal of inorganic mercury from aqueous solutions by biomass of the marine macroalga *Cystoseira baccata*, *Water research*, 39 (2005) 3199-3210.
- [8] G. McKay, Y. Ho, The sorption of lead (II) on peat, *Water Res*, 33 (1999) 578-584.
- [9] Y. Li, C.-Y. Wu, Role of moisture in adsorption, photocatalytic oxidation, and reemission of elemental mercury on a SiO₂-TiO₂ nanocomposite, *Environmental science & technology*, 40 (2006) 6444-6448.
- [10] F.F. Al-Qaim, Photocatalytic Removal of Methyl Orange in aqueous solution by TiO₂ using solar irradiation process, *National Journal of Chemistry*, 34 (2009) 355-362.
- [11] F.A.-Z.G. Gassim, A.N. Alkhateeb, F.H. Hussein, Photocatalytic oxidation of benzyl alcohol using pure and sensitized anatase, *Desalination*, 209 (2007) 342-349.
- [12] C.A. Gouvêa, F. Wypych, S.G. Moraes, N. Durán, P. Peralta-Zamora, Semiconductor-assisted photodegradation of lignin, dye, and kraft effluent by Ag-doped ZnO, *Chemosphere*, 40 (2000) 427-432.
- [13] B. Dindar, S. Içli, Unusual photoreactivity of zinc oxide irradiated by concentrated sunlight, *Journal of Photochemistry and Photobiology A: Chemistry*, 140 (2001) 263-268.
- [14] A. Chica, G. Gatti, B. Moden, L. Marchese, E. Iglesia, Selective Catalytic Oxidation of Organosulfur Compounds with tert-Butyl Hydroperoxide, *Chemistry-A European Journal*, 12 (2006) 1960-1967.
- [15] S.Y. Yeo, H.J. Lee, S.H. Jeong, Preparation of nanocomposite fibers for permanent antibacterial effect, *Journal of Materials Science*, 38 (2003) 2143-2147.
- [16] R. Spolenak, W. Ludwig, J. Buffiere, J. Michler, In situ elastic strain measurements—diffraction and spectroscopy, *MRS bulletin*, 35 (2010) 368-374.
- [17] F. Zhang, J. Yang, Preparation of nano-ZnO and its application to the textile on antistatic finishing, *International Journal of Chemistry*, 1 (2009) 18.
- [18] R. Hong, T. Pan, J. Qian, H. Li, Synthesis and surface modification of ZnO nanoparticles, *Chemical Engineering Journal*, 119 (2006) 71-81.
- [19] M.L. Kahn, M. Monge, V. Collière, F. Senocq, A. Maisonnat, B. Chaudret, Size- and shape-control of crystalline Zinc Oxide nanoparticles: A new organometallic synthetic method, *Advanced Functional Materials*, 15 (2005) 458-468.
- [20] Y. Wu, Y. Dai, S. Jiang, C. Ma, Y. Lin, D. Du, Y. Wu, H. Ding, Q. Zhang, N. Pan, Interfacially Al-doped ZnO nanowires: greatly enhanced near band edge emission through suppressed electron-phonon coupling and confined optical field, *Physical Chemistry Chemical Physics*, 19 (2017) 9537-9544.
- [21] H. Chen, L. Wang, Nanostructure sensitization of transition metal oxides for visible-light photocatalysis, *Beilstein journal of nanotechnology*, 5 (2014) 696.
- [22] F. Al-Zahra, G. Gassim, R.A. AL-Anbaeki, N.Y. Fairouz, Application of the photocatalytic reaction of TiO₂ to disinfection and the killing of *Escherichia coli* bacteria.