



## **DIVERSITY OF ZINC OXIDE NANOPARTICLES: APPLICATIONS**

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### **Abstract**

Photophysical and photochemical studies of anticancer drug functionalized nanoparticles are of great importance. Now days, these nanoconjugates have greater application towards the field of novel photo-based nanodevices for photocatalysis and drug delivery. Nanoscale systems are forecast to be a means of integrating desirable attributes of molecular and bulk regimes into easily processed materials. During light-matter interactions, the electronic excited-states, excitons are produced in nanostructured materials. It is interesting to know all kinds of excitons and study a diverse range of materials to see how electronic excited-states are formed and evolve on femto/nanosecond time scales. Moreover, it is exciting to learn the mechanisms for photo-initiated processes like solar energy conversion using ultrafast lasers to find out new photonic and biphotonic applications. Hundred of “chromophores” (light absorbing molecules) are used to harvest sunlight and direct the excitation energy to nature’s solar cells-proteins called reaction centers.

### **1. Introduction**

Nanomaterials composed of metal oxides have received enormous attention due to their current and potential commercial importance. Specially, ZnO is an excellent candidate for application as photocatalyst, photodetector and biomedicine. To date, a variety of strategies have been utilized to improve the photocatalytic performance of ZnO (to reduce the recombination of photogenerated electrons and holes). ZnO NPs has attracted much attention due to its high photosensitivity, thermal stability, low cost, low toxicity and good biocompatibility, which evoke great interest and desire for exploration in photocatalytic and biological applications [1]. Yuan et. al. used ZnO

quantum dots (QDs) combined with biodegradable chitosan for tumor-targeted drug delivery [1] where ZnO QDs were coated with folate-conjugated chitosan via electrostatic interaction that was loaded with doxorubicin (DOX), a widely used chemotherapy drug at 75% efficiency. Liu et. al. reported a pH-responsive drug delivery system based on the ZnO NP loaded with anticancer drug, DOX [2]. Moreover, there are number of literature reports where noble metal/zinc oxide hybrid nanostructures exhibited enhanced photocatalytic and antibacterial activity which in turn have great potential for use in water purification and as well as in different pathogenic applications [2-6]. ZnO nanostructured materials are comparatively insoluble in a physiological environment, although it can dissolve in an acidic environment such as the late endosome and lysosome of tumor cells, as nontoxic ions [7-10] as well as in strong basic condition if the surface is in direct contact with the solution [11]. Therefore, based on the enviable properties, ZnO NPs have achieved enormous significance as multifunctional nanocarriers to facilitate the release process [12]. Moreover, ZnO NPs can acts as efficient drug carriers in photodynamic therapies (PDT) which avoid non-significant accumulation of the drug at the target site [13].

## 2. Methodology

TEM images were taken by using a JEOL-TEM 2100 transmission electron microscope with an operating voltage 200 KV. The crystal structures of the samples were determined by X-ray diffractometer (Seifert 3000P) using CuK $\alpha$  radiation ( $\lambda=1.54178\text{\AA}$ ). The XPS measurements were carried out using Omicron Nanotechnology instrument. The DLS and zeta potential were measured by zetasizer nanosystem (Malvern instruments Ltd.). Room temperature optical absorption spectra were recorded by UV-vis spectrophotometer (SHIMADZU). The PL spectra were recorded using Fluoromax-P (HORIBA JOBIN YVON) photoluminescence spectrophotometer. For the time-correlated single-photon counting (TCSPC) measurement, the samples were excited at different wavelengths using a picosecond NANO-LED IBH 370L. Photocurrent measurement was performed with a 300 W Newport Solar Simulator (power supply Newport model 69911) under 1 sun (AM 1.5 G) illumination at 100 mW cm $^{-2}$ .

### Synthesis of ZnO nanoparticles

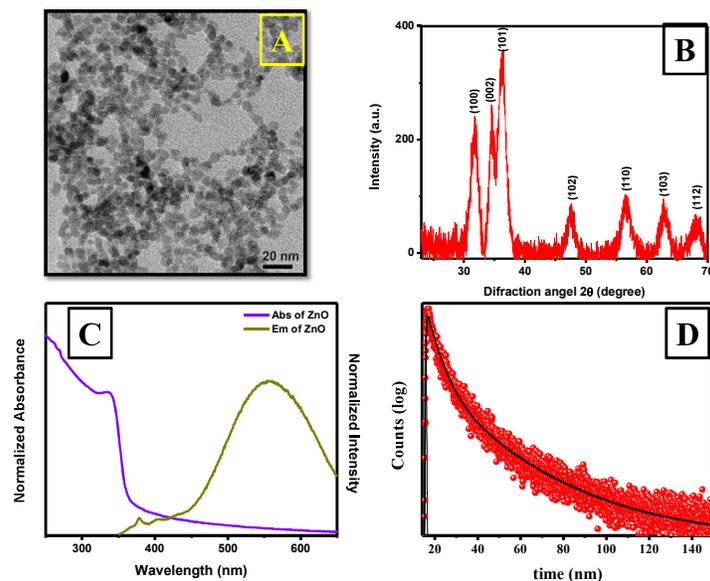
ZnO nanoparticles (ZnO NPs) were synthesized using previously reported method. Zinc acetate dihydrate (0.22 g) was dissolved in 80 ml of absolute ethanol. Upon complete dissolution of zinc acetate, the temperature of the solution was raised to 100°C. After that, 3ml solution of tetramethyl ammonium hydroxide (TMOH, 0.86 g in methanol) was added drop wise to the boiling ethanolic solution of zinc acetate under vigorous stirring at 100 °C. The solution then allowed boiling for another 30 minutes. The solution color turns colorless to white and it was cooled to room temperature under stirring condition. The obtained ethanolic solution of ZnO NP was centrifuged at 10000 rpm for 10 minutes and the precipitate was further dissolved in ethanol and centrifuged. The procedure was performed several times to wash out the excess precursor. Finally, we obtained the ZnO NP for further use. [14, 15]

### 3. Results and Discussion

A series of characterization techniques such as transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy are being employed to establish the formation of nano conjugation.

#### Zinc oxide nanoparticles

Figure 1A represents the TEM image of ZnO nanoparticles. The particles size distribution of ZnO NPs shows mono-dispersed nature with the particle size  $\sim 6 \pm 0.5$  nm. Figure 1B shows the XRD pattern of ZnO NPs. The XRD analysis confirms that as synthesized nanoparticles correspond to the pure phase of ZnO wurtzite structure with hexagonal crystal phase. The XPS spectrum shows two peaks at 1020.5 eV and 1043.9 eV are due to Zn2p<sub>3/2</sub> and Zn2p<sub>1/2</sub>. The UV-Vis spectrum of ZnO NP exhibits a band at 334 nm (Figure 1C). A sharp absorption peak also depicts the narrow size distribution of ZnO NP. The ZnO NP shows an intense yellow emission at 557 nm (Figure 1C) dominated by oxygen vacancy defect in ZnO. Time resolved decay of ZnO NP is depicted in Figure 1D, measured at the defect emission centered at 557 nm. The decay follows the bi-exponential kinetics. The lifetimes of the faster and the slower components are 7.69 ns and 42.99 ns with the contribution of 55% and 45%, respectively and the average lifetime is found to be 23.74 ns. The visible emissions are still subject of controversies and several explanations have been proposed. It is said that the photoluminescence lifetime determines the concentration of defects. Such an emission originates due to recombination of a shallow trapped electron with a deeply trapped hole. In our system, the longer lifetime component (43.0 ns) arises due to such recombination through surface defects of O<sup>2-</sup>/O<sup>-</sup>. The faster lifetime component of  $\sim 7.7$  ns originates due the band gap related exciton recombination.



**Figure 1:** (A) TEM image, (B) XRD pattern, (C) absorption and emission spectra and (D) Time resolved decay curve of zinc oxide nanoparticles. [14, 15]

Several attempts have been made to mimic natural light harvesting systems using self-assembled molecules, especially DNA conjugated system and supra-molecular organization of conjugated molecules/fluorophores, dendrimers, organo gel etc. Another alternative approach for light harvesting device fabrication is to incorporate fluorophore molecules inside confined matrix for better stability, functionality and aggregation free molecular arrangement. However, in case of both donor-acceptor incorporated host material based light harvesting device fabrication, several limitations are found, i.e., (i) aggregation based emission quenching may be possible inside microchannel, (ii) both donor and acceptor molecules sometime have to possess similar molecular structure etc. To avoid such inconveniences, distinct arrangement of donor-acceptor moieties can be plausible. For this purpose, dye doped organic/polymer fluorescent nanoparticles may be suitable as an acceptor system. Further, in search of a light absorbing material, it is now well established that inorganic nanocrystals or quantum dots (QDs) are very useful for enhancing the light harvesting process, as they can absorb light over a wide spectral window. Particularly, variable sized quantum dots with tunable band gap energies have received significant attention for efficient solar light energy harvesting system because visible light is effectively absorbed by QDs.

To the best of our knowledge, rotational relaxation of photoactive molecules inside the polymer nanoparticle, which are convenient means of probing the microenvironment of the polymer nanoparticles, are not available in the literature till date. Time-resolved anisotropy study is essential to unravel the origin of the rotational relaxation behavior of the dye inside polymer nanosphere. The rotational motion of the dye molecule will be restricted due to encapsulation of the dye in polymer nanoparticles. The anisotropy decay of the dye molecule in the polymer nanoparticles have been adequately described by reorientation times which is coupled to the wobbling motion and the lateral diffusion of the dye in the nanoparticles.

## **Conclusion**

Now days, the designing of artificial light harvesting system using nanomaterials is a challenging task. A detailed understanding of photophysical properties and the carrier relaxation dynamics of photoexcited nanocrystals (NCs) is of major importance for both fundamental research and technological applications. The photophysical properties of semiconductor NCs are significantly different from those of bulk materials because of quantum confinement effect and an enhanced surface-to-volume ratio. The detailed understanding of the carrier relaxation dynamics is essential because it dictates the overall efficiency in various optoelectronics, photovoltaic, photocatalysis, light-harvesting and sensing applications.

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## References

- [1] Q. Yuan, S. Hein, and R. D. K. Misra, “ New generation of Chitosan-encapsulated ZnO quantum dots loaded with drug: Synthesis, Characterization and in vitro drug delivery response,” *Acta Biomaterialia*, 6, 2732-2739 (2010).
- [2] J. Liu, X. Ma, S. Jin, X. Xue, C. Zhang, T. Wei, W. Guo, and X.-J. Liang, “ Zinc Oxide Nanoparticles as Adjuvant To Facilitate Doxorubicin Intracellular Accumulation and Visualize pH-Responsive Release for Overcoming Drug Resistance”, *Mol. Pharmaceutics*, 13, 1723-1730 (2016).
- [3] W. He, H-K. Kim, W. G. Wamer, D. Melka, J. H. Callahan and J-J. Yin, “ Photogenerated Charge Carriers and Reactive Oxygen Species in ZnO/Au Hybrid Nanostructures with Enhanced Photocatalytic and Antibacterial Activity”, *J. Am. Chem. Soc.*, 136, 750–757 (2014).
- [4] J. Hu, Z. Zhong, F. Zhang, W. Xing, W. Jin, and N. Xu, “High-efficiency, Synergistic ZnO-Coated SiC Photocatalytic Filter with Antibacterial Properties”, *Ind. Eng. Chem. Res.*, 55, 6661–6670 (2016).
- [5] R. Kumar, S. Anandan, K. Hembram, and T. N. Rao, T. N. “Efficient ZnO-Based Visible-Light-Driven Photocatalyst for Antibacterial Applications”, *ACS Appl. Mater. Interfaces*, 6, 13138–13148 (2014).
- [6] C. Mao, Y. Xiang, X. Liu, Z. Cui, X. Yang, K.W. K. Yeung, H. Pan, X. Wang, P. K. Chu, and S. Wu, “Photo-Inspired Antibacterial Activity and Wound Healing Acceleration by Hydrogel Embedded with Ag/Ag@AgCl/ZnO Nanostructures”, *ACS Nano*, 11, 9010–9021 (2017).
- [7] Y-W.Wang, A. Cao, Y. Jiang, X. Zhang, J-H. Liu and Y. Liu, “ Superior Antibacterial Activity of Zinc Oxide/Graphene Oxide Composites Originating from High Zinc Concentration Localized around Bacteria”, *ACS Appl. Mater. Interfaces*, 6, 2791–2798 (2014).
- [8] H. M. Xiong, “ ZnO nanoparticles applied bioimaging and drug delivery”, *Adv. Mater.*, 25 (37), 5329-5335 (2013).
- [9] N.-H.Cho, T.-C.Cheong, J. H. Min, J. H.Wu, S. J. Lee, D. Kim, J.-S.Yang, S. Kim, Y. K. Kim and Y. K. S.-Y. Seong, “A multifunctional core-shell nanoparticle for dendritic cell-based cancer immunotherapy”, *Nat. Nanotechnol.*, 6 (10), 675-682 (2011).
- [10] F. Muhammad, M. Guo, W. Qi, F. Sun, A. Wang, Y. Guo and G. Zhu, “ pH-Triggered controlled drug release from mesoporous silica nanoparticles via intracellular dissolution of ZnO nanolids”, *J. Am. Chem. Soc.*, 133 (23), 8778-8781 (2011).
- [11] A. M. Abdelmonem, B. Pelaz, K. Kantner, N. C. Bigall, P. del Pino and W. J. Parak, “Charge and agglomeration dependent in vitro uptake and cytotoxicity of zinc oxide nanoparticles”, *J. Inorg. Biochem.*, 153, 334-338 (2015).

[12] J. Zhou, N. S. Xu and Z. L. Wang, Dissolving Behavior and Stability of ZnO Wires in Biofluids: A Study on Biodegradability and Biocompatibility of ZnO Nanostructures. *Adv Mater*; 18: 2432-5 (2006).

[13] Z. Y. Zhang, Y. D. Xu, Y. Y. Ma, L. L. Qiu, Y. Wang, J. L. Kong and H. M. Xiong, “Biodegradable ZnO@ polymer Core-Shell Nanocarriers: pH-Triggered Release of Doxorubicin In Vitro”, *Angew. Chem., Int. Ed.*, 52 (15), 4127-4131 (2013).

[14] M. K. Barman, P. Mitra, R. Bera, S. Das, A. Pramanik and A. Patra, “An Efficient Charge Separation and Photocurrent Generation in the Carbon dot-Zinc Oxide Nanoparticles Composite”, *Nanoscale* 9, 6791–6799 (2017).

[15] P. Mitra, M. K. Barman, S. Basu, S. Das, A. Pramanik and A. Patra, “Interfacial Charge Transfer between Zinc Oxide Nanoparticles and Methyl Viologen: Influence of Size”, *Chem. Select*, 2, 9869-9877 (2017).