



A Systematic Study of ZnO/CuO Core/Shell Nanostructures Pegylated by Microwave Assistant Reverse Micelles (RM) Method

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Received: 28 April 2018 / Published online: 25 June 2018
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Abstract

In this work we synthesized ZnO/CuO nanostructures pegylated by simple and fast microwave method assistant reverse micelles, Reverse micelles protocol creates many advantages in stability, particle size control, morphology, density, loading level, distribution, uniformity, charge and purification. Based on the statistical results ZnO/CuO nanostructures placed in the hydrophilic substrate. The effect of microwave and concentration of surfactant on the surface area, pore diameter and pore volume of the final product was systematically studied using Taguchi technique. ZnO/CuO core/shell pegylated nanostructures, indicating a ZnO as core and CuO as shell and continuous micelles chains around this structures. Products were characterized by UV–Vis spectra, X-ray diffraction, scanning electron microscopy, Dynamic light scattering, Energy-dispersive X-ray spectroscopy, transmission electron microscopy and nitrogen adsorption (i.e. Brunauer–Emmett–Teller surface area analysis).

Keywords ZnO/CuO · Reverse micelles · Core/shell nanostructures · Pegylation

Introduction

Recently nanoparticles delivery system has been proposed as colloidal drug carriers. Nanoparticles (NP) are a type of colloidal drug delivery system comprising particles with a size range from 10 to 1000 nm in diameter [1]. Today, to reduce complications and increase the efficiency of chemotherapy agents nanotechnology and nanomaterials are being used in the medical field [2]. PEG is a non-biodegradable polymer and PEGylation can impart several significant pharmacological advantages over the unmodified form, such as improved drug solubility, reduced dosage frequency, without diminished efficacy with potentially reduced toxicity, extended circulating life, increased drug stability, and enhanced protection from proteolytic degradation; pegylated forms may also be

eligible for patent protection [3]. Micelles like structures such as niosomes have a bilayer structure and are formed by self-assembly of nonionic surfactants in an aqueous phase, due to their non-ionic nature, they are highly adapted to biological systems and have very low toxicity [4]. The use of nanoparticles and core–shell structures in pharmaceutical sciences improves the stability [5] and pharmacokinetics of the drug [6] and, consequently, increases the therapeutic effects and reduces the side effects of the drug [7]. As research in the field of nanotechnology is expanding, mixed metal-oxide nanoparticles have many application in drug delivery systems (DDS) [8], antimicrobial drugs [9], diagnostic [10], photodynamic therapy for cancer [11], biosensors [12], toxicology [13], there are many methods for the preparation mixed metal-oxide core/shell nanostructures such as co-precipitation method [14], solid-state reaction of oxides [15] chemical vapor deposition [16], sol–gel method [17], citrate precursor method [18], wet impregnation method [19] and thermal decomposition method [20]. Micellization conjugation techniques had some advantages effects on the enhances the therapeutic efficacy of the drugs and increasing the circulation solubility without affecting activity [21]. In core–shell compounds, core or shell should

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include a metal compound or asymmetric supercapacitors, core-shell structures such as CdTe/CdS, CdSe/ZnS, CdSe/CdS, CuO, Au-TiO₂ binary nanocomposites have wide applications in bio-imaging, sensors, delivery systems (DDS), drug carrier systems and biosensors [22–25]. Summary of the formation ZnO/CuO core/shell pegylated suspension is shown in Scheme 1. In this study for the first time, ZnO/CuO core/shell pegylated synthesis by reverse micelle method being reported, nanoparticles have been synthesized in the core of reverse micelles then the performance of nanocomposite was studied by UV-Vis spectroscopy, X-ray, SEM, DLS, EDS, TEM, FT-IR, BET analysis.

Experimental

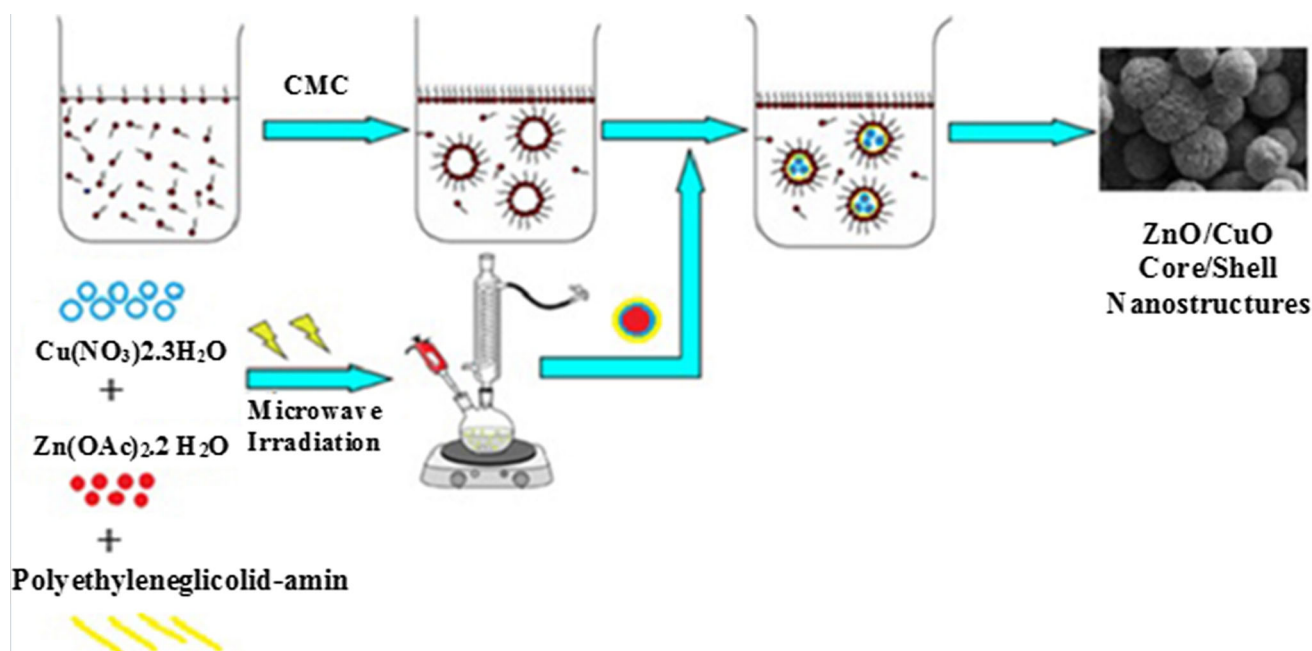
Materials and Instrumentations

All chemicals had the highest purity and there was no need to purify methods, copper(II) nitrate trihydrate (MW: 241.60 g/mol, 99.90%), zinc acetate dihydrate (MW: 219.50 g/mol, 99.80%) and Polyethyleneglycol-amine (PEGdiamine MW: 2000) were purchased from Sigma Aldrich (St. Louis, MO, USA). Sorbitan monostearate; Span 60; (MW: 430.626 g/mol, 99.99%) and NaOH (d: 2.13 g/ml, MW: 39.9971 g/mol, 99.99%) were purchased from Merck (Darmstadt, Germany). All materials used in this study were used as received, without further purification. XRD patterns were recorded by a Rigaku D-max C

III, X-ray diffractometer using Ni-filtered Cu K α radiation. Microscopic morphology of products was visualized by SEM (LEO 1455VP). The energy dispersive spectrometry (EDS) analysis was studied by XL30. Transmission electron microscopy (TEM) images were obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 200 kV. Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. TGA and DSC were turned from room temperature to 800 °C with a heating rate of 10 °C/min under an argon atmosphere using SCINCO thermal gravimeter S-100 (Seoul, Korea) and Netzsch QMS403C (Selb, Germany), respectively. UV-Vis diffuse reflectance spectroscopy analysis was carried out using Shimadzu UV-2600 UV-Vis spectrophotometer with an integrating sphere attachment and BaSO₄ was used as the reference.

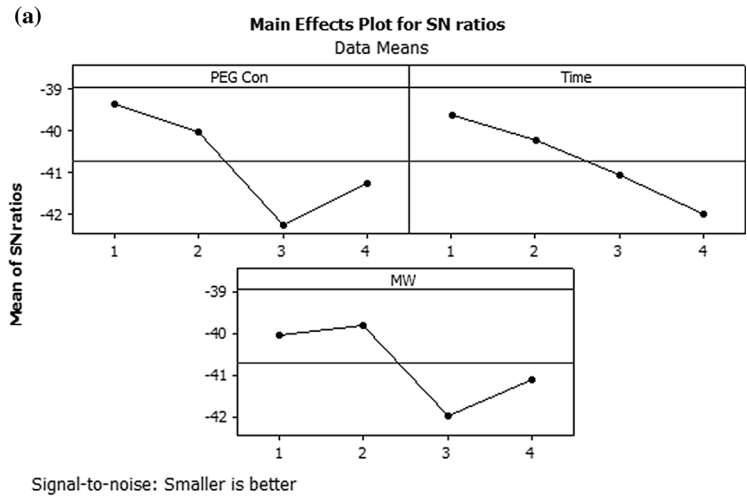
Taguchi Technique

A well planned set of experiments, in which all parameters of interest are varied over a specified range, is a much better approach to obtain systematic data. In this work simulation calculations were done by Taguchi technique for systematic optimizing of the parameter on the size distribution of ZnO/CuO core/shell pegylated nanostructures. Based on the information obtained (Fig. 1a, b) from Taguchi method, irradiation Time, microwave power and PEG concentration all three cases showed a significant

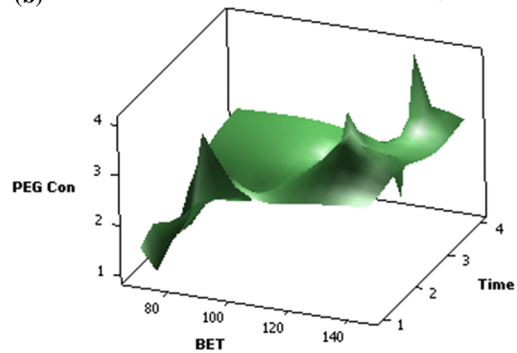


Scheme.1 Summary of the formation ZnO/CuO core/shell pegylated nanostructures

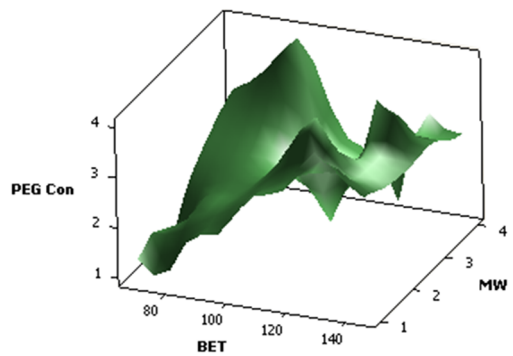
Fig. 1 a Data of surfactant, microwave power and irradiation time on BET parameter with Taguchi technique, **b** 3D surface plot between time, microwave irradiation, PEG concentration on BET as the response



(b) **Surface Plot of PEG Con vs Time; BET**



Surface Plot of PEG Con vs MW; BET



Surface Plot of Time vs MW; BET

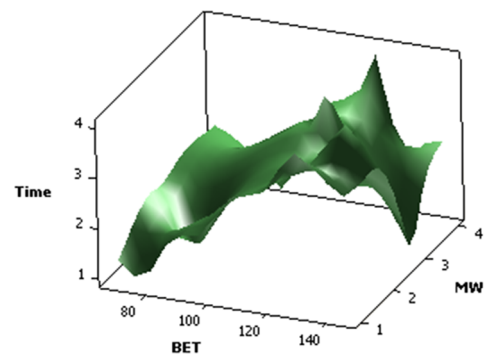


Fig. 2 XRD pattern of ZnO/CuO core/shell pegylated nanostructures by microwave assistant reverse micelles (RM)

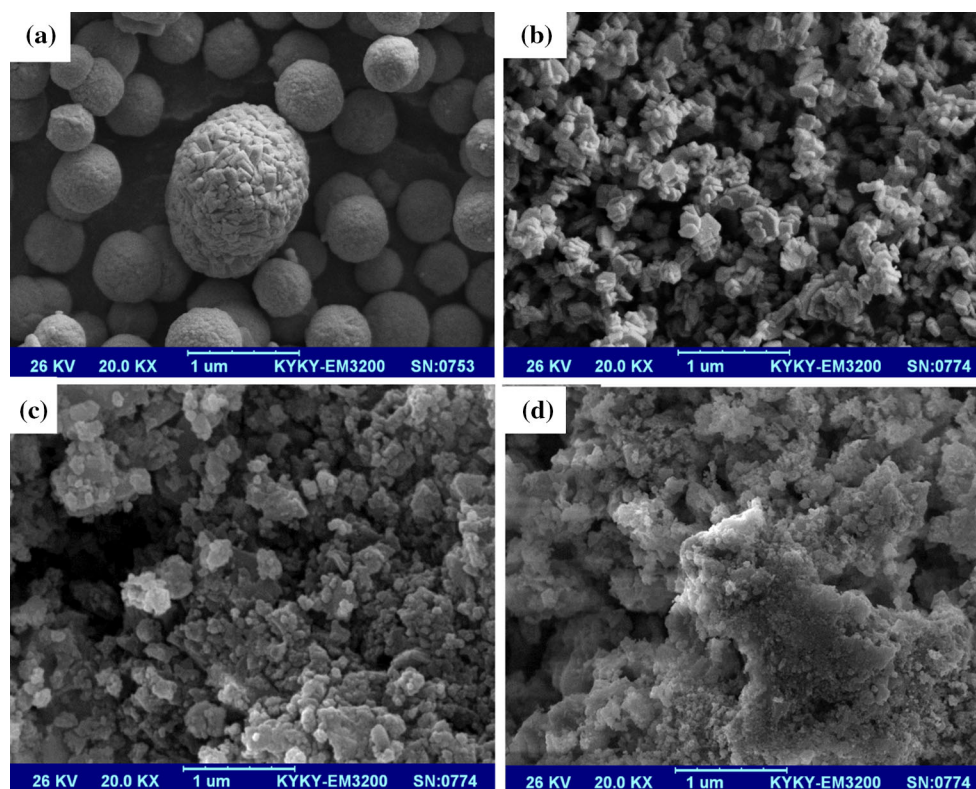
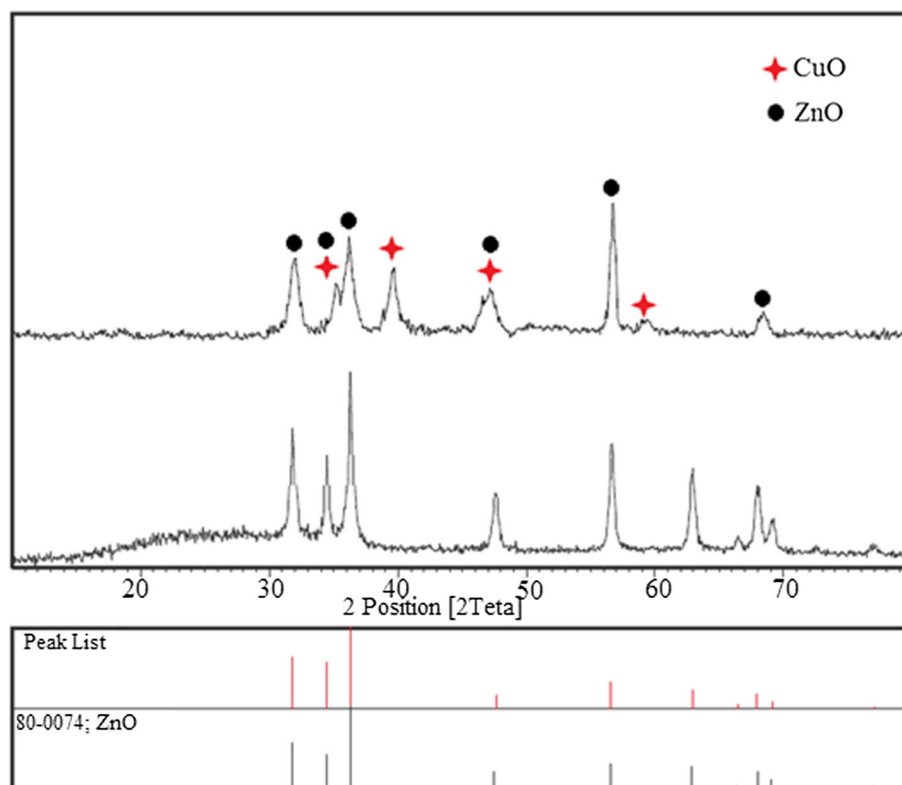


Fig. 3 SEM images of the ZnO/CuO Core/Shell pegylated nanostructures in different PEG concentrations **a** 1 mg, **b** 1.5 mg, **c** 2 mg and **d** 2.5 mg

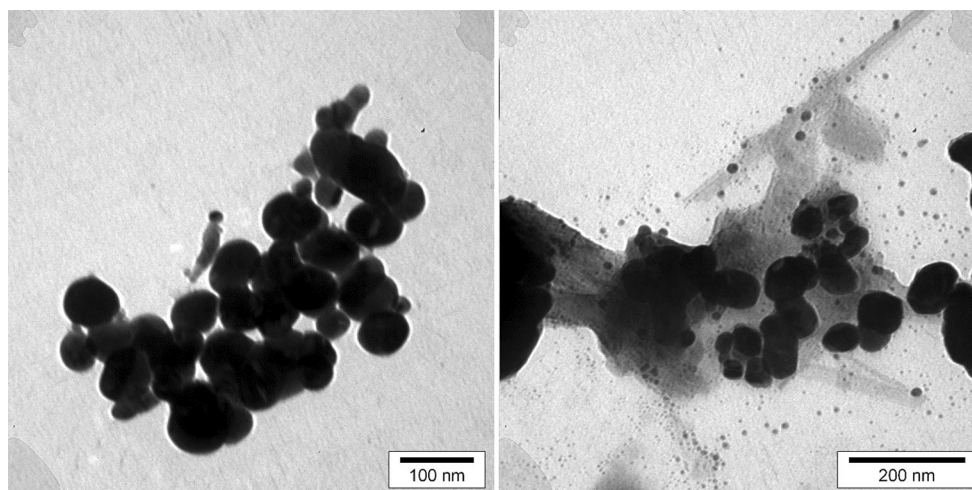


Fig. 4 TEM image of the ZnO/CuO core/shell pegylated nanostructures in 1 mg PEG concentrations

influence on the BET parameters as the response because the signal to noise (SN) varies with the level changes.

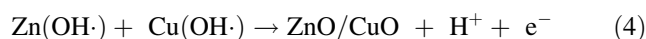
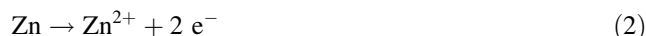
Preparation of ZnO/CuO Core/Shell Pegylated Nanostructures

Micellization occurs through the penetration of monomer micelles into the aqueous phase. After micellization, the suspension of the nanoparticles is neutralized by sodium hydroxide and temperature. The synthesis of ZnO/CuO core/shell pegylated nanostructures was performed by two steps inclusive (a) microwave method and (b) reverse micellization. For this study at first, 0.081 g of Span 60 (C₂₄H₄₆O₆) was dissolved in 20 mL of deionized water and then, by adding the surfactant concentration, critical point (CMC) was achieved. In the second step, 0.017 g of Cu(NO₃)₂·3H₂O dissolved in 5 mL of deionized water under vigorous stirring at 60 °C temperature for 120 min. In another beaker, 0.032 g of Zn(O₂CCH₃)₂(H₂O)₂ and 2 mg polyethyleneglycol-amine were dissolved in 3 mL ethanol and add to the above solution subsequently. Then prepared solution put in reflux system, 1 M NaOH solution has been added dropwise to the reflux system, it is suggested the mechanism of ZnO/CuO core/shell nanostructures involves the reaction of Cu²⁺ ions with Zn²⁺ ions to form seed (nucleation). After 120 min two solutions were mixed together as in situ monomer micelles act as the nanoreactor for production of ZnO/CuO core/shell pegylated nanostructures, in final products were obtained through the thermal degradation of the surfactant phase. Figure 1 shows the experimental schematic for the synthesis core/shell nanostructures. In this study irradiation time (60, 120, 180 and 240 min), microwave power (180, 300, 600 and 900 W) and PEG concentration (1, 1.5, 2 and 2.5 mg) were main parameters, the as-prepared products by

microwave method assistant reverse micelles were characterized by UV–Vis spectroscopy, X-ray, SEM, DLS, TEM and BET analysis.

Result and Discussion

Interaction performance of radicals such as [Zn(OH·), Cu(OH·)] leads to produced ZnO/CuO core/shell nanostructures by water oxidation via reaction (Eqs. 1–4) [26].



X-ray powder diffraction (XRD) used for phase identification of a crystalline material and can provide information on unit cell dimensions, from XRD data, the crystallite diameter (D_c) of ZnO/CuO core/shell nanostructures obtained was calculated 85 nm. The average size of the particles is calculated with the Debay–Scherer Eq. (5):

$$D_c = K\lambda / \beta \cos\theta \quad (5)$$

where D_c is the thickness of the crystals (in Å), K the shape factor, X-ray wavelength is given by k and Bragg angle by θ . The line broadening, B is measured from the extra peak width. XRD pattern of ZnO/CuO core/shell nanostructures in Fig. 2 shows both crystalline structures of ZnO and CuO included in crystalline networks. The existence of diffraction peaks of CuO in the ZnO structures establishing new structures of ZnO/CuO core/shell nanostructures. The sharp peaks shows the large size of the nanostructures. These peaks can be indexed at (32°), (35°), (36°), (39°),

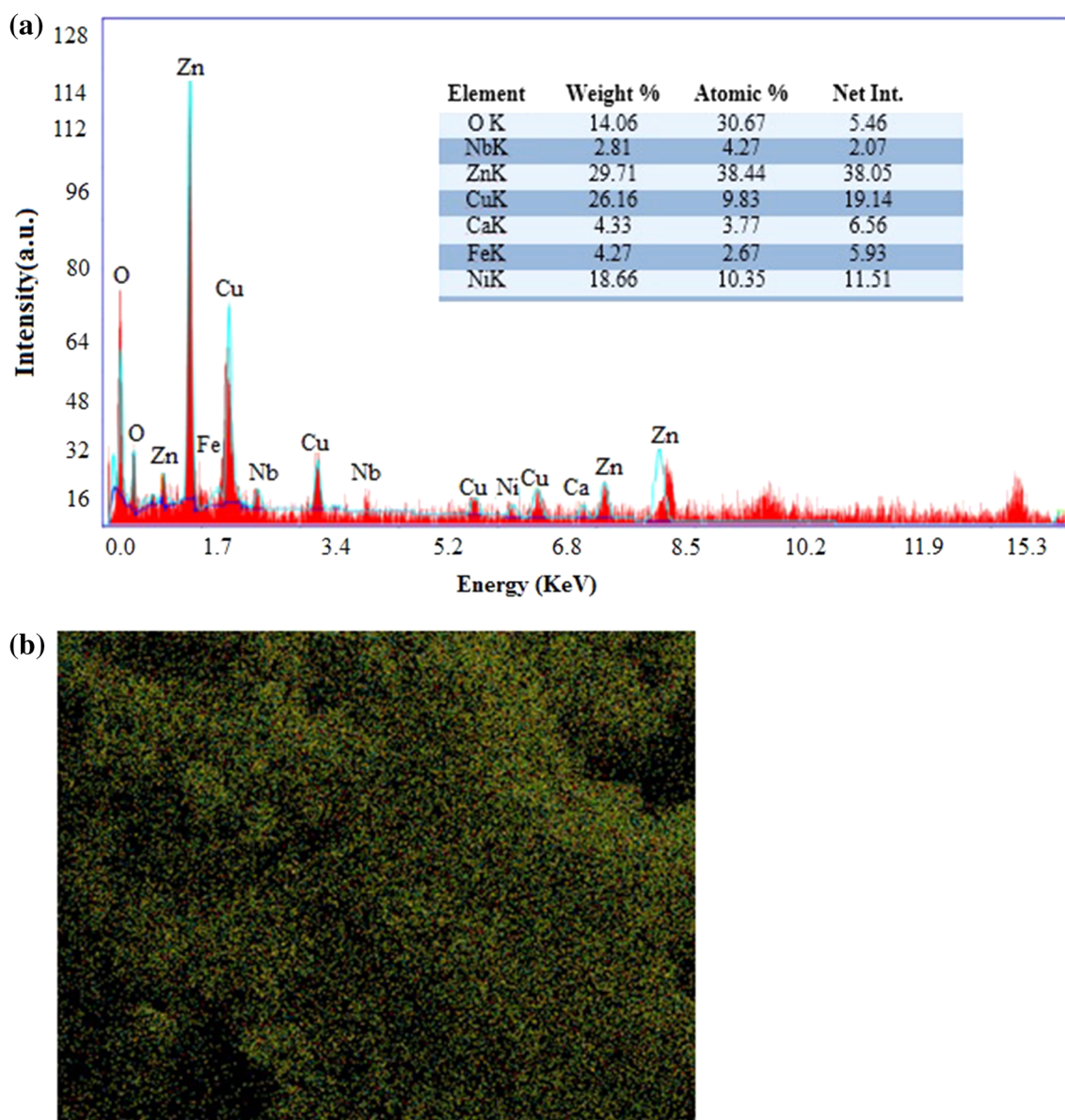


Fig. 5 EDS spectrum, element table (a) and EDS mapping (b) of the ZnO/CuO core/shell pegylated nanostructures

(48°), (57°), (59°) and (67°) diffraction lines, SEM such as a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons, SEM images of ZnO/CuO core/shell nanostructures show that morphology of all samples is spherical like and distribution is very uniform. Figure 3a–d illustrates SEM images of ZnO/CuO core/shell nanostructures in different PEG concentrations 1, 1.5, 2 and 2.5 mg PEG. As can be seen the increase in PEG concentrations for the synthesis of ZnO/CuO core/shell nanostructures causes agglomeration nanoparticles, this is due to an increase in the ratio of surface to volume in fine particles, therefore sample 1 is optimized sample because distribution, morphology and dispersion are more suitable. For further

interpretation of SEM images, we took TEM image from the samples, to study the growth of layers, analyze the quality, shape, size and density of quantum wells, wires and dots. TEM images of ZnO/CuO core/shell nanostructures (sample 1) in scales 100 and 200 nm are shown in Fig. 4. SEM and TEM images analysis confirm each other. Energy dispersive X-ray spectroscopy (EDS or EDX) as a chemical microanalysis technique used in conjunction with scanning electron microscopy (SEM). EDS analysis was employed to investigate the chemical composition and purity of the synthesized ZnO/CuO core/shell nanostructures. The EDX spectrum, element table (a) and EDS mapping (b) of the synthesized ZnO/CuO core/shell nanostructures are shown in Fig. 5. Impurities related to

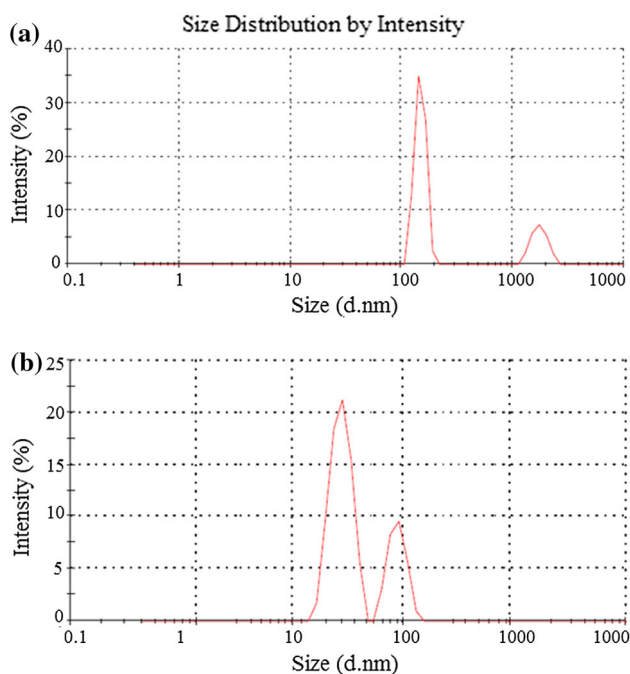


Fig. 6 DLS data image of **a** ZnO/CuO core/shell pegylated and **b** ZnO/CuO core/shell pegylated nanostructures

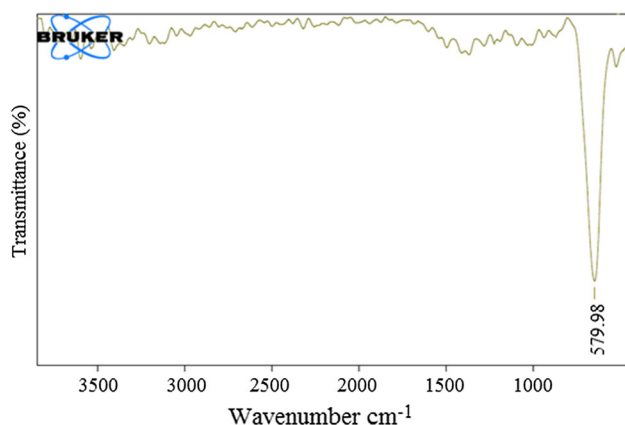


Fig. 7 FT-IR spectrum of the achieved ZnO/CuO core/shell pegylated nanostructures

elements such as Nb, Ca, Fe, Ni relates to elements that have absorbed the sample from the air or unpredictable factors. DLS is used to characterize the size of various particles including proteins, polymers, micelles, vesicles. All measurements were carried out at 25 °C, DLS data image of ZnO/CuO core/shell pegylated and ZnO/CuO core/shell pegylated nanostructures respectively showed in Fig. 6a, b. As seen from the graphs, with micellization and pegylation the particles size becomes smaller and the distribution is appropriate in the medium. FT-IR is a method of obtaining infrared spectra by first collecting an interferogram of a sample signal using an interferometer, and then performing a Fourier transform

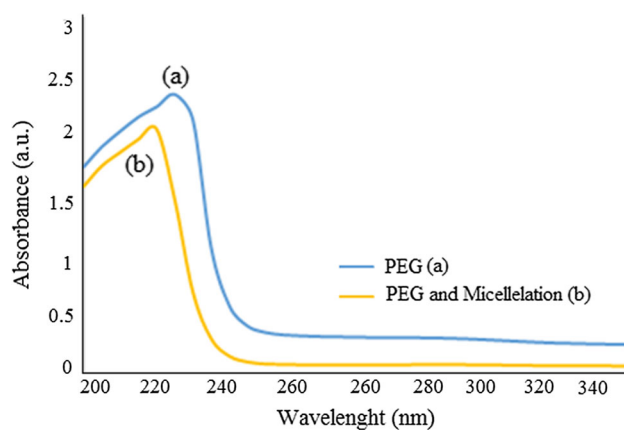


Fig. 8 UV-Vis absorption spectra of **a** ZnO/CuO core/shell pegylated and **b** ZnO/CuO core/shell pegylated nanostructures

(FT) on the interferogram to obtain the spectrum. Figure 7 shows FT-IR spectra of the synthesized samples in the range 400–4000 cm. The vibration assigned to the Zn–O–Cu bond in ZnO and CuO is observed at 579.98 cm^{-1} . UV-Vis spectroscopy is also used in the semiconductor industry to measure the thickness and optical properties of thin films on a wafer. To study optical properties we took UV-Vis absorption of ZnO/CuO core/shell pegylated and ZnO/CuO core/shell pegylated nanostructures are shown in respectively Fig. 8a, b. Graphs show, with micellization and smaller particle size we see the blue shift to fewer wavelengths, this event could be due to more defects in ZnO/CuO core/shell pegylated nanostructures because of the presence of micelles.

Conclusion

In this research work ZnO/CuO pegylated synthesized by simple and fast microwave method then ZnO/CuO nanostructures pegylated prepared with assistance reverse micelles assistant, studying the effect of parameters on the BET properties of the final product evaluated with the Taguchi technique, results of SEM images show ZnO/CuO core/shell pegylated nanostructures synthesized by emulsion method are smaller than ZnO/CuO core/shell pegylated synthesized by microwave method, this event prove plays micelles as nanoreactors.

Acknowledgements Authors are grateful to council of Pharmaceutics Research Center, Institute of Neuropharmacology, Kerman University of Medical Sciences, Kerman, Iran.

Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interests.

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