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Synthesis of ZnO/Zn nano photocatalyst using modified polysaccharides for photodegradation of dyes

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ABSTRACT

A complete set of experiments in two aspects of studies combining the various factors affecting both the preparation and photocatalytic activity of ZnO/Zn nanocomposite obtained using corn starch and cellulose (native and modified) as chelating agents for the photodegradation of methylene blue, and congo red was carried out and discussed. The resulting ZnO/Zn nanoparticles obtained using modified polysaccharides exhibited super catalytic capability. The ZnO/Zn nanoparticles possessed favored surface area (11.8443–15.7100 m^2/g) and pore size (12.3473–13.7453 nm). The photocatalytic degradation of nano ZnO/Zn was directly proportional to the surface area of nano ZnO/Zn. Regardless of the dye pollutants, nano ZnO/Zn obtained using modified corn starch showed enhanced catalytic activity than that of cellulose and methylene blue had comparatively faster degradation rate. Our findings shed light on the optimization of both preparation conditions of photocatalysts and their photocatalytic experimental conditions.

1. Introduction

Wastewaters contaminated with residual dyes from textile, paper and other industries are a source of environmental problems (Height, Pratsinis, Mekasuwandumrong, & Praserthdam, 2006). Conventional treatment of such wastewater usually involves either adsorption or chemical coagulation. These methods, however, simply transfer dyes from the liquid to the solid phase, entailing further treatment and causing secondary pollution (Tanaka, Padermpole, & Hisanaga, 2000). Oxidation is an alternative treatment strategy that can be applied to dyes and many other organics in wastewater and industrial effluents. In particular, semiconductor mediated photocatalytic oxidation can be conveniently applied toward the degradation of dye pollutants. The degradation of organic pollutants by photocatalysis, using semiconductors, such as TiO_2 and ZnO, has attracted widespread attention during recent years (Hoffmann, Martin, Choi, & Bahnemann, 1995). Such semiconductors can degrade most kinds of persistent organic pollutants, such as detergents, dyes, pesticides and volatile organic compounds, under UV-light irradiation (Cun et al., 2002). In particular, ZnO has engrossed much attention with respect to the degradation of various pollutants due to its high photosensitivity, stability and wide band gap (Akyol, Yatmaz, & Bayramoglu, 2004; Daneshvar, Salari, & Khataee, 2004; Kavitha, Meghani, & Jayaram, 2007; Khodja, Sehili, Pilichowski, & Boule, 2001; Poulios & Tsachpinis, 1999). It is of great interest to improve the photocatalytic activity of semiconductors for the degradation of organic compounds. For semiconductor photocatalysts, particle size is an important parameter for controlling surface area and electronic structure (Mekasuwandumrong, Pawinrat, Praserthdam, & Panpranot, 2010). Thus, it is clearly shown that the efficiency of photocatalytic process can be altered by optimizing the particle size of ZnO photocatalysts. It has been demonstrated that the structural and morphological characters such as the size, shape, crystalline form, photocatalytic activity and some relevant properties of ZnO can be significantly affected by different synthesis methods (Yu, Li, Gao, & Wu, 2005). Various methods have been developed to prepare ZnO photocatalyst, which mainly include template method, precipitation, gas-phase reaction, hydrothermal synthesis and microwave heating (Colón et al., 2008; Siddiquey, Furusawa, Sato, & Suzuki, 2008; Wang et al., 2007). It has been reported that ZnO could be successfully synthesized by chelation method using zinc metal salts and polysaccharides as starting materials (Baskoutas et al., 2007). It has also been realized (Tang & Hon, 2001) that the mechanism of complex formation of metals with polysaccharides is manifold and probably dominated by different processes taking place simultaneously, such as adsorption, ion-exchange and chelation, under different conditions. However, the use of metal-organic supramolecular compounds as precursors for the preparation of inorganic nanomaterials such as ZnO has not yet been thoroughly investigated (Ahmadzadi, Marandi, & Morsali,

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2009; Khanjani & Morsali, 2009a, 2009b; Ranjbar & Morsali, 2009). Fabrication of efficient nanomaterials has been a focus of an ever increasing number of researchers, mainly because of their unusual properties. These materials find a wide range of applications in fabrication of new materials such as ceramics, composites, etc. Semiconductor–metal composite nanoparticles have been extensively studied for their attractive capability in improvement of catalytic properties.

Natural polysaccharides and their derivatives have a wide range of industrial and medical applications because of their unique structure, distinctive properties, safety, and biodegradability. Among the derivatives, cellulose and starch are the most utilized and the cheapest polysaccharides that are used as both chelating and stabilizing agents because of their excellent biocompatibility (Chen, Wang, Liu, & Park, 2002). Generally polysaccharides contain hydroxyl, carboxyl and amino functional groups which can form chelation with Zn metals by chemical adsorption and finally calcination resulted into the cleavage of Zn-polysaccharides chelate to form nano ZnO. The synthesis of metal coordination polymers is often directed by the quest to understand how molecules can be organized and how their functions can be achieved. To enhance the degree of complexation of Zn metal and polysaccharides, necessary surface modifications have been carried out in this study. The chemical modification of polysaccharides is the most important route to modify the properties of the naturally occurring biopolymers and to use this renewable resource in the context of sustainable development. Carboxymethylation of polysaccharides is a widely studied conversion since it is simple and leads to products with a variety of promising properties. Carboxymethyl derivatives are usually polyelectrolyte with better aqueous solubility and this approach has been employed to synthesize high performance macromolecular materials. It is well known that the effective swelling of water soluble carboxymethylated polysaccharides require a chemically crosslinked network that can be obtained by different paths (Benke, Takacs, Wojnarovits, & Borsa, 2007) and these modified polysaccharides have many potential industrial applications ranging from the manufacture of synthetic resins and biodegradable polymers to the production of intermediates for chemical syntheses (Akar, Altınışık, & Sekib, 2012). Carboxymethylation of polysaccharides is based on the William synthesis (Silva et al., 2004) in which the polysaccharide alkoxide is reacted with monochloroacetic acid and the primary and secondary alcohol groups are substituted by carboxymethyl group.

The aim of this study was to present a simple method for the formation of nano ZnO/Zn based on the calcination (thermal decomposition) of zinc-polysaccharide complex formed by the interaction of polysaccharides with zinc metal salts. In this study, various nano ZnO/Zn with different surface characteristics were prepared, characterized and compared for the photodegradation efficiency of dyes such as methylene blue and congo red. Few reports (Baskoutas et al., 2007) on synthesis of ZnO using polysaccharides are available; however detailed studies regarding surface modification of polysaccharides, characterization of zinc-polysaccharide organic polymer intermediate, the morphology of obtained ZnO, effect of preparation conditions, and application of final ZnO are still to be addressed. Also, in this present work interestingly the modified polysaccharides resulted into the formation of nano ZnO/Zn. Hence, the present methodology is very significant and also it is a chemically simple, economic, toxic free, time saving and clean synthesis technique that is performed at ambient temperature and involves sustainable treatment. The influences of size, morphology and preparation method on the photocatalytic property of nano ZnO/Zn were studied. A ZnO/Zn assisted photocatalytic degradation study of these different dyes under UV-365 nm light irradiation has been sparse and hence this research focuses on understanding the mechanistic details of the photodegradation of dyes under UV light. Hereby, we believe that it is possible to obtain the metal oxide/metal composite nanoparticles by using crosslinking carboxymethyl starch and carboxymethyl cellulose and we have successfully prepared ZnO/Zn nanoparticles and reported in this present work.

2. Materials and methods

2.1. Chemicals

Deionized water was used to prepare all solutions. Zinc nitrate hexahydrate [$Zn(NO_3)_2{\cdot}6H_2O$] was obtained from J. T. Baker. Corn starch and cellulose were commercially obtained from Aldrich. Dyes methylene blue ($C_{16}H_{18}N_3ClS$) and congo red ($C_{32}H_{22}N_6Na_2O_6S_2$) were obtained from Merck. All other chemicals and reagents used in this study were of analytical grade and used without any further purification.

2.2. Chemical modification of corn starch (crosslinked carboxymethyl corn starch)

Crosslinked carboxymethyl corn starch was prepared according to the modified method (Kim & Lim, 1999). Corn starch (50 g) was dispersed in distilled water (150 ml) and the slurry was adjusted to pH 11.0 with 1 N NaOH solution. The cross-linking agent, $POCl_3$ (1% and 1.5%, v/w based on corn starch) was added dropwise over 10 min, while maintaining the pH at 11.0 with the NaOH solution. The starch dispersion was stirred for 1 h at room temperature, and then filtered. The filtered starch cake was dispersed in isobutyl ketone (150 ml), and a 50% NaOH solution (20 ml) was slowly added. Sodium chloroacetate (15 g) was added in the starch-isobutyl ketone dispersion, and the mixture was stirred for 2 h at 45 °C. After the reaction, the starch slurry was filtered, washed three times with distilled water and then dried at 40 °C overnight in an oven. Crosslinked carboxymethyl corn starch prepared using 1% $POCl_3$ was referred to CCMS-1 and crosslinked carboxymethyl corn starch prepared using 1.5% $POCl_3$ was referred to CCMS-1.5.

2.3. Chemical modification of cellulose (carboxymethyl cellulose)

Carboxymethyl cellulose was prepared according to the literature method (Toğrul & Arslan, 2003). Four gram (4 g) of cellulose, 100 ml of solvent (ethanol, isopropyl alcohol and isobutyl alcohol) and 20 ml of 30% NaOH were mechanically stirred for 2 h at 28 °C. Then different sodium chloroacetate concentrations (0.65, 1 and 1.5 M in respective solvents) are added and stirred at temperatures of 60 and 70 °C for 3 h. After the time of reaction was over, the mixture was neutralized with 90% acetic acid and filtered. The obtained cake was purified by washing with 70% methanol to remove undesired salts, filtered and then dried at 70 °C to obtain different carboxymethyl cellulose as shown in Table S1 (see Table S1).

2.4. Synthesis of ZnO/Zn using native and surface modified polysaccharides

Three gram (3 g) of zinc nitrate hexahydrate [$Zn(NO_3)_2{\cdot}6H_2O$] was dissolved in 100 ml water in a standard flask. To this zinc nitrate aqueous solution, three gram (3 g) of polysaccharides (native and modified) was added and the reaction mixture was stirred constantly at 28 °C for 6 h. Then the reaction mixture was filtered and the solid collected was dried in an oven at 50 °C to obtain zinc-chitosan organic polymers. Finally this zinc-chitosan

organic polymer was calcined at 450 °C to obtain different nano ZnO/Zn.

2.5. Photocatalytic experiments and analyses

By measuring the photodegradation efficiency of different dyes in aqueous solution under the illumination of UV, the photocatalytic activity of different nano ZnO was evaluated reliably. All the experiments were carried out in a Pyrex batch photoreactor. The radiation source was a UV lamp (λ_{max} = 365 nm, purchased from the Black-Ray), which was placed above a Pyrex reactor. Dye solutions were prepared by dissolving the respective dye in deionized water at different concentrations in the 30–70 ppm range. The pH of solutions was adjusted in the range 6–8 with 1 N H_2SO_4 or 1 N NaOH 1 M, after the addition of the catalyst. For the photocatalytic degradation of dyes, a solution containing known concentration of the dye and ZnO was prepared and allowed to equilibrate for 30 min in the darkness, then 200 ml of the prepared suspension was transferred into the reactor, then the lamp was switched on to initiate the reaction. During irradiation, the glass reactor mounted on a magnetic stirrer to keep the suspension homogenous and at every 15 min reaction intervals, 10 ml of sample was withdrawn, centrifuged, and the dye concentration was analyzed with a UV–vis spectrophotometer approximately at 664 nm and 497 nm for methylene blue and congo red respectively. A calibration plot based on Beer-Lambert's law was established by relating the absorbance to the concentration. The changes in the absorption spectra of dyes at different irradiation times were recorded on a UV–vis spectrophotometer (Hitachi U-2800 A) in the wavelength range from 190 to 690 nm. The degradation percentage can be obtained by the following formula:

$$\text{Degradation efficiency}\,(\%) = (C_0 - C/C_0) \times 100,$$

$$\text{The remaining dye}\,(\%) = [1 - (C_0 - C/C_0)] \times 100$$

C_0 is initial dye concentration (mg/L) and C is dye concentration at time t (mg/L).

2.6. Characterization techniques

The average pore diameter and specific surface area (BET surface and pore volume) were measured on a Quantochrome NOVA 1000. X-ray diffraction (XRD) patterns were obtained at room temperature using a Bruker KAPPA APEX II instrument. SEM was carried out on an HITACHI-S-800, field emission scanning electron microscope. TEM was carried out on a transmission electron microscope (JEM-2100 type). FT-IR spectra were obtained on a Neclit 6700 model, Fourier transform infrared spectrometer (FTIR).

3. Results and discussion

In this work detailed studies including the chemical modification of polysaccharides, preparation of nano ZnO/Zn, and photocatalytic degradation of dyes were carried out and discussed in the light of various factors.

3.1. FT-IR, SEM and BET characterization of polysaccharides

The FT-IR characterization revealed the nature of functional groups present both in unmodified and modified polysaccharides. Fig. 1 shows the FT-IR spectra of polysaccharides before and after modification. The peak at 3300–3400 cm^{-1} is due to ν(O—H), the peak around 2800 cm^{-1} is due to $\nu(CH_3, CH_2$ and CH), the peak around 1620–1660 cm^{-1} is due to ν(C=C) and ν(C=O) and the peak at (1050–1300) cm^{-1} is due to ν(C—O). Surface modification of polysaccharides was confirmed by FT-IR spectra and upon surface modification the peak intensities and peak position (some cases) of functional groups are definitely altered due to the carboxymethylation. from Fig. 1, the changes in the peak intensities at 3300–3400 cm^{-1} due to ν(O—H), at 2800 cm^{-1} due to $\nu(CH_3, CH_2$ and CH), at 1620–1660 cm^{-1} due to ν(C=C) and ν(C=O) clearly evidenced the successful surface modification of polysaccharides. The effect of sodium chloroacetate on surface modification could be understood by observing the changes in carboxyl group peak. For the modified polysaccharides, the peak at 1620 cm^{-1} indicates the presence of carboxyl groups. Also from Fig. 1, it is noted that increase in sodium chloroacetate concentration increases the intensity of C=O peak due to the enhanced availability of carboxyl groups.

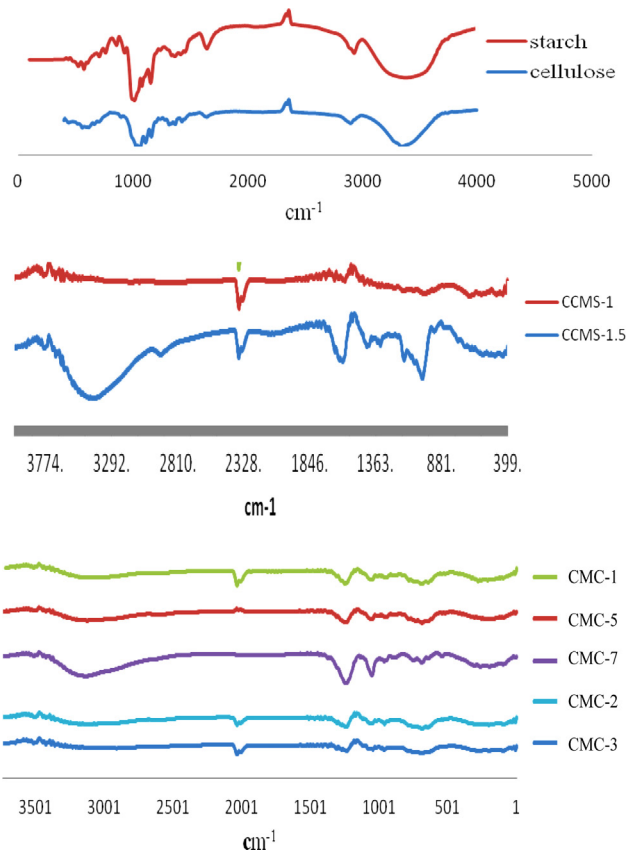

Fig. 1. FT-IR spectra of unmodified and modified polysaccharides.

Table 1
Surface area, pore size and adsorption capacity of different polysaccharide precursors.

Precursors	BET surface area (m^2/g)	Pore size (nm)	The maximum adsorption of zinc (mg/kg)
Starch	3.0	11.32	85.42
Cellulose	0.9	6.1	67.11
CCMS-1	1.2	5.23	4675
CCMS-1.5	0.3	3.60	3635
CMC-1	0.8	5.44	3708
CMC-2	0.4	5.16	3294
CMC-3	0.9	4.17	3155
CMC-4	0.8	5.38	3607
CMC-5	0.4	2.55	341
CMC-6	0.6	5.23	273
CMC-7	0.4	6.48	509
CMC-8	0.2	7.36	433

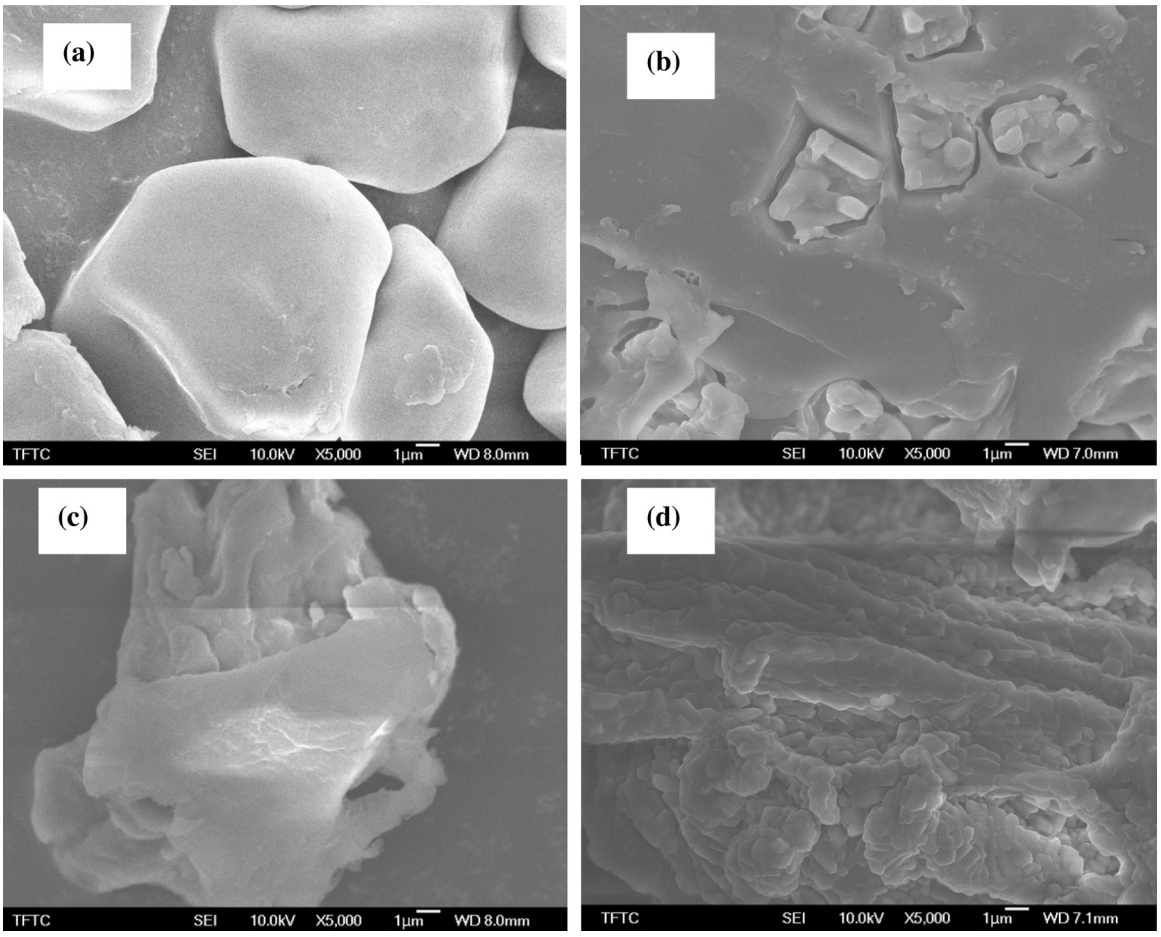

Fig. 2. SEM of (a) starch; (b) CCMS-1; (c) cellulose; (d) CMC-1.

Based on the FT-IR results it is well understood that chemical modification (carboxymethylation) of hydroxyl functional groups was achieved successfully for the enhanced interaction between polysaccharides and zinc metal salts. BET surface area and pore size of modified and unmodified polysaccharides are given in Table 1.

From Table 1, it is clearly seen that for both starch and celluloses, the modified polysaccharides possessed smaller surface area and pore size compared to that of unmodified polysaccharides. Thus, the decrease in surface area and pore size favored the effective interaction of these modified polysaccharides with zinc metal salts and ultimately eases the effective formation of nano ZnO/Zn. The BJH pore distribution revealed the effective pore size engineering. The narrow uniform pore size distribution is accumulated for modified polysaccharides due to smaller pore sizes. The SEM morphology studies of the polysaccharides as shown in Fig. 2 confirmed that the unmodified polysaccharides possessed larger holes due to the larger particle size whereas the modified polysaccharides possessed uniformly distributed well defined smaller holes and in some cases even smooth surface also. The detailed study of SEM reports that different experimental conditions necessarily affected the pore dimensions of the modified polysaccharides. The results obtained from above experimental studies clearly revealed the effect of sodium chloroacetate and temperature during surface modification of the polysaccharides. Based on these studies, it is very clear that the required surface modification is necessary for the effective interaction of these polysaccharides with zinc metal which really favored the formation of effective nano ZnO/Zn.

3.2. Zn^{2+} adsorption studies

In order to evaluate the interaction of both native and modified polysaccharides (starch and cellulose) with zinc metal ions, adsorption studies were carried out using polysaccharides as adsorbents prior to the preparation of nano ZnO/Zn. The adsorption behavior of these polysaccharides clearly explained the effective formation of zinc-polysaccharide organic polymers and thus will definitely affect the formation of nano ZnO/Zn obtained upon cleavage of zinc-polysaccharides organic polymers. The presence of OH functional groups and also the presence of intermolecular hydrogen bonding in both polysaccharides facilitated the adsorption of zinc metal ions. Langmuir isotherms as compared to another models showed the best fitting value for the kinetics of Zn^{2+} on polysaccharides and the adsorption process is chemical adsorption. Langmuir adsorption isotherms of different polysaccharides for Zn^{2+} ion are shown in Fig. 3a and Table 1 includes the maximum adsorption of zinc ions for different systems.

Due to the water swelling effect, the carboxymethylation of cellulose was carried out in non aqueous medium, whereas crosslinked carboxymethylation of corn starch was carried out using water as solvent. For surface modified polysaccharides, the degree of carboxymethylation plays (Pushpamalar, Langford, Ahmad, Hashim, & Lim, 2013) a vital role on the adsorption phenomenon and the presence of water content of polysaccharides also definitely altered the adsorption capacity of modified polysaccharides. The experimental results clearly revealed that unmodified polysaccharides generally showed lower affinity toward Zn^{2+} than that of modified starch indicating that hydroxyl function groups

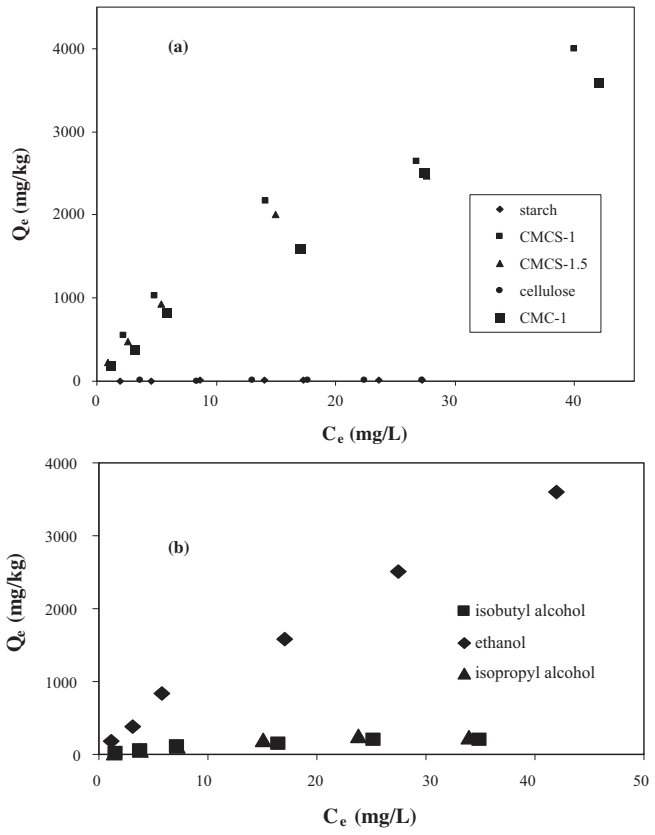

Fig. 3. Adsorption of Zn^{2+} ions (a) for unmodified and modified polysaccharides; (b) for modified cellulose in different solvent systems (60 °C).

did not favor the complexation of Zn^{2+} with polysaccharides where as carboxyl functional groups favored the effective complexation of Zn^{2+} with polysaccharides. Thus, it is confirmed that due to surface modification, the affinity of polysaccharides toward Zn^{2+} is enhanced owing to the presence of COOH groups. In the case of starch, the order of adsorption capacity can be arranged as CCMS-1 > CCMS-1.5 > corn starch. In the case of modified cellulose, the smaller sodium chloroacetate concentration favored the increased adsorption of zinc than that of larger sodium chloroacetate concentration. Among modified cellulose, regardless of the solvents (ethanol, isopropyl alcohol and isobutyl alcohol) low etherification temperature (60 °C) facilitated the adsorption of Zn^{2+} ions. In general, in raising the temperature, the probability of collision between molecules increases and there by reaction rate would also increase. But, when the etherification temperature increases (70 °C), it makes the system more heterogeneous due to cellulose gelatinization (too viscous). Thus, low etherification temperature (60 °C) enhances the carboxymethylation due to low viscosity (Toğrul & Arslan, 2003) and prevents the hydrolysis reaction during surface modification by increasing the utilization of sodium chloroacetate. Based on the results on comparison of different solvents used for carboxymethylation of cellulose, it is concluded that the ethanol system showed the best adsorption compared than that of isopropyl alcohol and isobutyl alcohol as shown in Fig. 3b. Moreover isopropyl alcohol and isobutyl alcohol systems almost showed the identical adsorption of zinc. This is due to the reason that in the case of ethanol, cellulose was uniformly distributed in the system whereas in the case of remaining solvents, the cellulose viscosity increased substantially and thus the utilization of sodium chloroacetate was reduced. Also ethanol is a good solvent (Olaru, Olaru, Stoleriu, & Timpu, 1998) for sodium chloroacetate than that of others and hence in the case of ethanol system, the best carboxymethylation was achieved easily. Among all modified cellulose, cellulose obtained using ethanol at 60 °C (CMC-1), showed the enhanced adsorption of zinc.

Based on the above results, it can be noted that both the concentration of sodium chloroacetate and crosslinking agent are the major factors that control the adsorption process upon surface modification. The fundamental results indicated that smaller the sodium chloroacetate concentration and crosslinking agent the greater the Zn^{2+} affinity. If sodium chloroacetate concentration is increased, instead of Zn^{2+} complexation with carboxyl groups, Na^{+} complexation is dominated and thus availability of free COOH is less for Zn^{2+} interaction. Similarly during crosslinked carboxymethylation, different forms of oxygen atoms may be present as follows: (1) oxygen atoms may react with phosphorus to form O═P, (2) carboxymethylation process to form O—CH_2COOH (Na) by carboxyl group of C═O, (3) unmodified OH group. In the case of (1) and (2), it is the presence of organic oxygen with double bond whereas in the case of (3) it is not organic oxygen. The data suggested that with the increase in the degree of crosslinking, the ability of adsorption of zinc was declined due to the formation of phosphorus diester and thus it is confirmed that effective adsorption was achieved using low degree of crosslinking. Thus, it is well understood that crosslinked carboxymethyl starch (CCMS-1) obtained using 1% crosslinking agent and carboxymethyl cellulose (CMC-1) obtained using 0.65 M sodium chloroacetate in ethanol at 60 °C could be considered as optimum precursors for the preparation of nano ZnO/Zn. Hence, nano ZnO/Zn obtained using CCMS-1 and CMC-1 was chosen to be discussed in this work.

3.3. Characterization of nano ZnO/Zn

In this study ZnO/Zn obtained using modified cellulose (CMC-1) and starch (CCMS-1) are represented as (ZnO/Zn)-C and (ZnO/Zn)-S respectively. Various techniques including XRD, SEM, TEM, BET, and zeta potential analysis were used to better under the characteristics of nano ZnO/Zn. The XRD patterns of nano ZnO/Zn are given in Fig. 4. The samples exhibited strong diffraction peaks from ZnO and weak one from Zn (Zeng, Cai, Li, Hu, & Liu, 2005). The diffraction peaks indicated the nanocrystalline nature and identical to the hexagonal phase with Wurtzite structure. The peaks around angles (2θ) 31°, 35°, 37°, 48°, 56°, 62°, 67°, 68°, and 69° correspond to the reflection from 1 0 0, 0 0 2, 1 0 1, 1 0 2, 1 1 0, 1 0 3, 2 0 0, 1 1 2, and 2 0 1 crystal planes, respectively (Gu et al., 2004). The peak at (2θ) 46° indicated the existence of interstitial zinc in ZnO lattices (Zeng et al., 2005). Thus, the XRD results clearly revealed the feasible formation of ZnO/Zn. From Fig. 4, it is observed that the intensity of Zn peak at (2θ) 46° is comparatively larger in the case of (ZnO/Zn)-S when compared to that of (ZnO/Zn)-C. Thus, Fig. 4 also explained the component evolution of the products associated with the nature of the modified polysaccharides. The increase in Zn peak intensity indicated that in the case of (ZnO/Zn)-S, the relative formation of Zn also increased. Thus, it is confirmed that among the polysaccharides, modified starch enhanced the relative formation of ZnO/Zn composite. Interestingly encouraging result such as formation of nano ZnO/Zn was obtained via chelation method in this study when crosslinked carboxymethyl starch and carboxymethyl cellulose were used as precursors. In our earlier report (Thirumavalavan, Huang, & Lee, 2013) we have obtained only nano ZnO using modified starch and sodium alginate and not ZnO/Zn nanocomposite. Thus, it is clear evidence that the significant modification of polysaccharides definitely alters the formation of nanomaterials. The existence of a small amount of metal zinc in the final product is due to the presence of larger zinc-polysaccharide polymer particles formed in the intermediate step, leading to ZnO/Zn shell/core structured composite nanoparticles upon thermal cleavage. This is also an indication that the

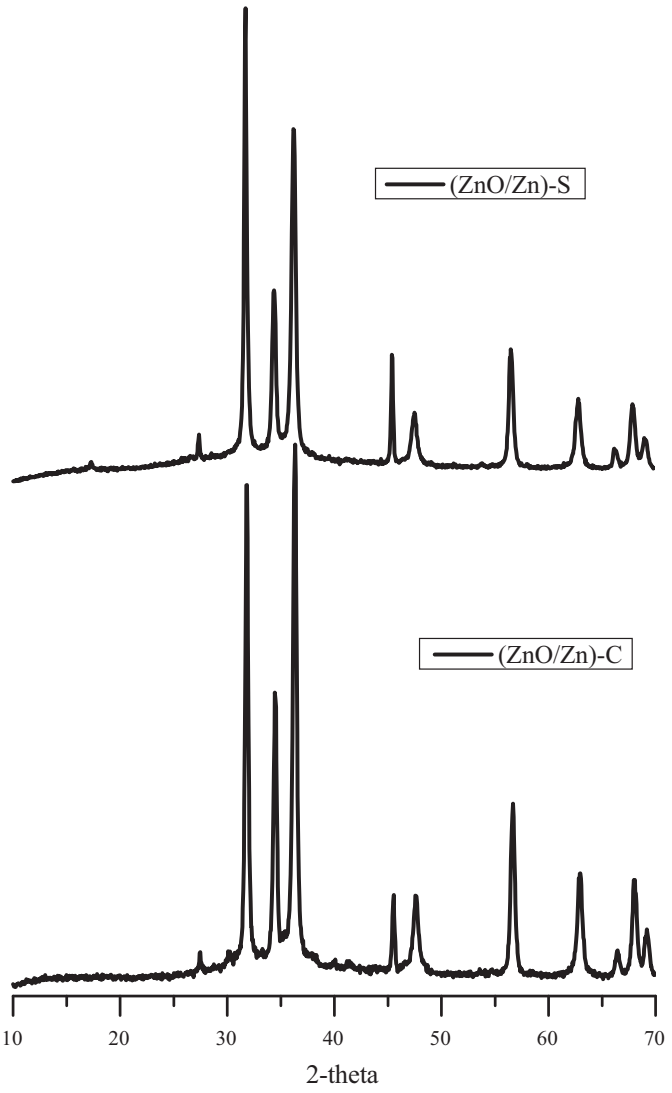

Fig. 4. XRD patterns of various ZnO/Zn samples.

modified polysaccharides in this work possessed typically large enough particle size to yield even ZnO/Zn shell/core structure.

On the basis of our experimental results, the formation of ZnO/Zn composite nanoparticles could be described as illustrated in Fig. 5. With the polysaccharides, the formed zinc-polysaccharides polymer encounter the solvent in the solution, which induces some chemical reactions and the final structure and morphology of the particles are dependent on the cleavage (oxidation) of zinc-polysaccharides polymer.

The SEM of ZnO/Zn various nanocrystalline particles obtained is shown in Fig. 6. As seen in Fig. 6, in the case of (ZnO/Zn)-C almost single phase primary granular particle with smaller size (20–100 nm) in spherical shape with irregular distribution was

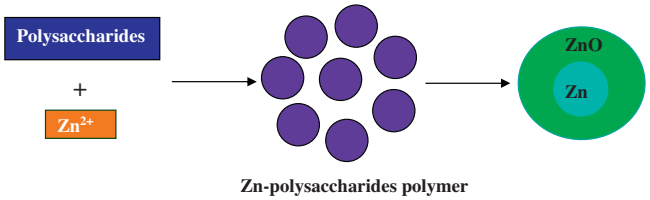

Fig. 5. Schematic representation of the formation of ZnO/Zn nanocomposite.

obtained however a small number of particles with size larger than 100 nm were also obtained. As seen in Fig. 6, almost single phase primary particle with smaller size (20–60 nm) in spherical shape with uneven distribution was obtained for (ZnO/Zn)-S. This clearly explained that nano ZnO/Zn with same crystal type but different particle size can be obtained (Wang, Zhang, Bi, & Luo, 2010). Moreover, it can be noticed that, extensive networks of pores exist on the surfaces of nano ZnO/Zn. The size and morphology of ZnO/Zn particles analyzed by TEM is represented in Fig. 6 and this also revealed the uniform shape and irregular size distribution of nano ZnO/Zn. As shown in Fig. 6, homogeneous spherical pores distributed among nano-particulates of several nanometers in diameter can be observed within whole particles for all the samples. During the calcination of zinc-polysaccharides organic polymer, the primary nano-particulates are generated along with the loss and decomposition of polysaccharides and then they stacked together to form their inter-particulate pores.

Further, results indicated that (ZnO/Zn)-C possessed relatively larger particle size than that of (ZnO/Zn)-S. The BET experimental data as shown in Table 3 indicated that different polysaccharides significantly affected the specific surface area and pore size distribution of nano ZnO/Zn.

In order to evaluate the surface charged property of the ZnO/Zn, zeta potential pH of the medium was measured as shown in shown in Table S2 (see Table S2). The zeta potential indicates the degree of repulsion between adjacent, similarly charged particles in dispersion. For molecules and particles that are small enough, a high zeta potential will confer stability, that is, the solution or dispersion will resist aggregation. When the potential is low, attraction exceeds repulsion and the dispersion will break and flocculate. From Table S2, it is clear that the pH value of obtained ZnO/Zn at isoelectric point is almost neutral. Thus, under alkaline conditions, nano ZnO/Zn is negatively charged and will facilitate the adsorption of positively charged dye contaminant on ZnO/Zn particle surface. Under acidic conditions, nano ZnO/Zn is positively charged and thus facilitates the adsorption of negatively charged dye contaminant on ZnO/Zn particles.

3.4. Photocatalytic degradation of dyes

The molecular structures and UV–visible absorption spectra of methylene blue, and congo red are represented as shown in Fig. S1 (see Fig. S1). The studies on the adsorption of the dyes from aqueous solution onto photocatalysts are relevant and important because the photocatalytic degradation of dyes occurs predominantly on the surface of photocatalysts. To assess and confirm the role of nano ZnO/Zn as photocatalysts, two sets of experiments were performed to compare dyes degradation rates. One set was performed with dyes exposed to only photocatalysts and the second set was performed by exposing dyes to both photocatalysts and UV light (the photocatalysis condition).

The experimental results clearly revealed the relative adsorption of dyes onto nano ZnO/Zn obtained from different polysaccharides. As can be seen from Table S3, different dyes showed different adsorption capacities toward nano ZnO/Zn. For example (ZnO/Zn)-S showed enhanced adsorption toward congo red when compared to methylene blue where as (ZnO/Zn)-C showed increased adsorption of methylene blue than that of congo red. The possible reason could be attributed to this may be the difference in pH values at isoelectric point as seen in Table S2 [(ZnO/Zn)-C is slightly acidic (pH 6.55) compared to (ZnO/Zn)-S (pH 7.58)]. Thus, the difference in pH values at isoelectric point also causes for the discrepancy in the adsorption behavior of nano ZnO/Zn. It can be observed that whatever the dye, the steady state of adsorption is reached within 30 min. Therefore, this time has been selected for the initial period in the dark previous to UV irradiation at time $t_{UV} = 0$ to make sure

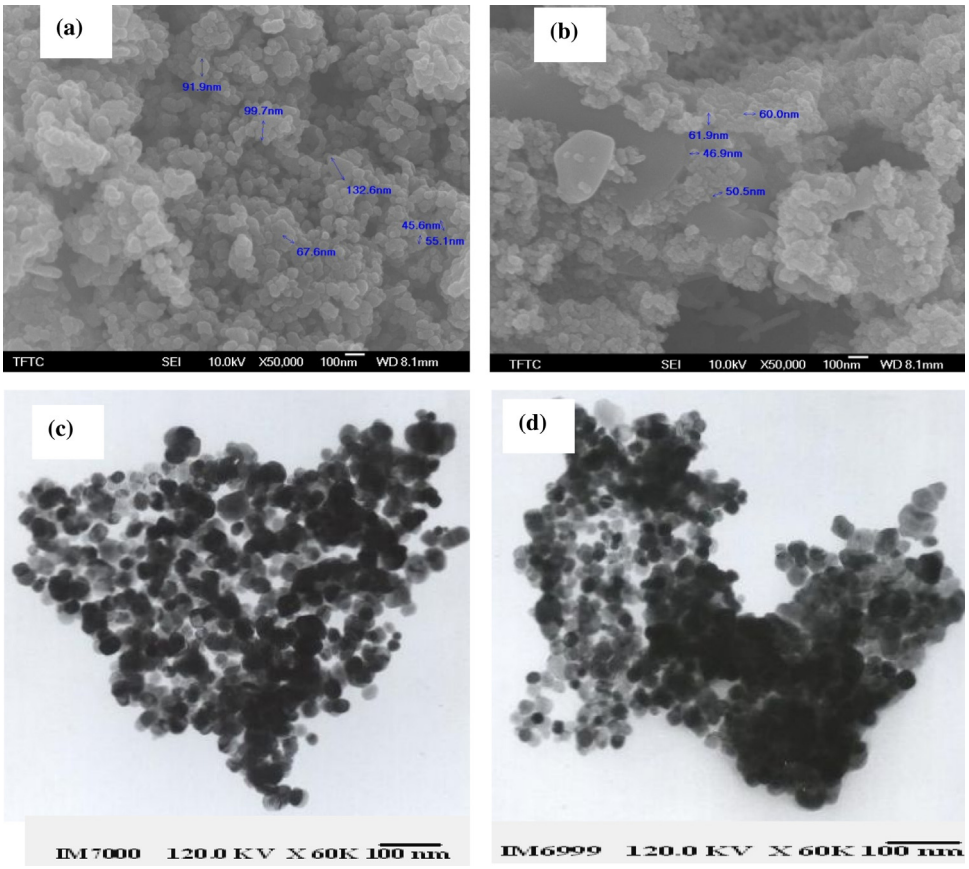

Fig. 6. (a) SEM of (ZnO/Zn)-C; (b) SEM of (ZnO/Zn)-S; (c) TEM of (ZnO/Zn)-C; (d) TEM of (ZnO/Zn)-S.

that the initial degradation initiates at the equilibrium of adsorption.

This study mainly focused on the evaluation of photocatalytic efficacy of nano ZnO/Zn toward different dyes and hence, the photocatalytic degradation of these dyes was carried out as shown in Fig. 7 using the nano ZnO/Zn. It can be observed that in the presence of UV light gradual photodegradation occurred effectively and the monitoring of the presence of residual dyes in the solution both in the case of adsorption and photodegradation experiments clearly conveyed that in the case of adsorption experiment it is simple adsorption but not degradation where as in the case of photodegradation the degradation is actual degradation due to the formation of free radicals. The results of photodegradation of dyes are displayed in Table S4. Though the adsorption capacity of (ZnO/Zn)-C and (ZnO/Zn)-S is different for congo red and methylene blue, (ZnO/Zn)-S invariably showed enhanced photodegradation of both congo red and methylene blue than that of (ZnO/Zn)-C.

From Table S4, it is also obvious that the photodegradation efficiency of methylene blue is greater than that of congo red and almost complete degradation (92 and 98%) of methylene blue by both nano ZnO/Zn is witnessed in this study. The smallest rate constant of congo red can be explained by the steric hindrance of a large aromatic molecule which leads to a smaller number of congo red molecule adsorbed on ZnO/Zn. Another explanation could also be their ability to be adsorbed on ZnO/Zn. This hypothesis agrees with a reaction occurring at the surface of the photocatalysts and not in the solution, close to the surface. The mineralization of hetero atoms such as N and S present in the dyes may also affect the degradation of dyes (Guillard et al., 2003).

The kinetics study clearly showed that the equilibrium constant value (k) for (ZnO/Zn)-S obtained from ln C_e vs time is greater than that of (ZnO/Zn)-C regardless of the dyes as shown in Table

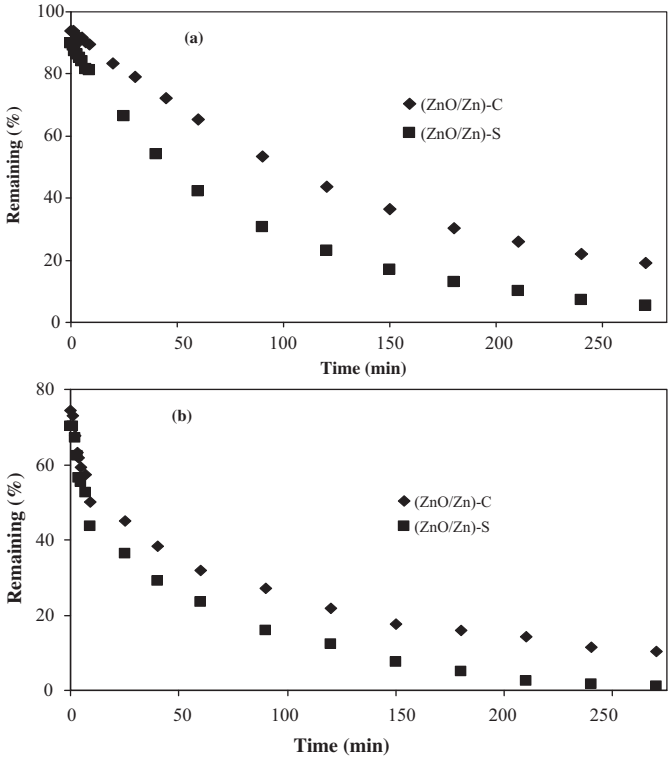

Fig. 7. Photocatalytic degradation of (a) congo red; (b) methylene blue by nano ZnO/Zn.

S4. The larger k value of (ZnO/Zn)-S designated the ease attainment of reaction equilibrium in the case of (ZnO/Zn)-S and hence enhanced photocatalytic activity of (ZnO/Zn)-S. The experimental results also indicated that the photodegradation rates are quite agreed proportionally with the surface area of nano ZnO/Zn. As the surface area increased, the photodegradation efficiency also increased. This result in fact emphasized the significance of effective crosslinking carboxymethylation (surface modification) and it can be finalized that the effective crosslinking of polysaccharides resulted into nano ZnO/Zn that can act as robust photocatalyst for degradation of different dyes. It is important to study the dependence of removal efficiency on the initial concentration of the dye. It was observed that the degradation decreases with increasing the initial concentration of the dyes. This is due to the possible competence between dye and OH^- ion adsorption on the surface of catalyst. If the initial concentration of the dye is increased, the hydroxyl concentration on surface of catalyst remains constant for all dye molecules and the formation of hydroxyl radicals is also constant. The higher concentration of the pollutants induced the degree of increased light source, i.e. once the concentration of the pollutants is increased, it also causes the dye molecules to absorb more light and photons that never reach the photocatalyst surface, and thus the photodegradation efficiency decreases (Daneshvar, Rabbani, Modirshahla, & Behnajady, 2005; Peternel, Koprivanac, Božić, & Kušić, 2007; Sakthivel et al., 2003). It is noteworthy to say that the initial concentration of photocatalyst will also affect the photocatalytic efficiency. The increase in the amount of catalyst increased the number of active sites on the photocatalyst surface, which in turn increased the number of hydroxyl radicals (Joseph, Destaillats, Hung, & Hoffmann, 2000). However, when the concentration of ZnO/Zn catalyst was increased above the limiting value, the degradation rate may be decreased in some cases due to an increase in the turbidity of the suspension and a decrease in UV light penetration as a result of increased scattering effect. The duration of light irradiation also determined the efficiency of photodegradation. At longer exposure time to light, the photodegradation efficiency was enhanced as shown in Table S4.

4. Conclusion

We demonstrated the feasibility of synthesis of ZnO/Zn composite nanoparticles. The utilization of nano ZnO/Zn as photocatalysts obtained using both modified and unmodified polysaccharides (corn starch and cellulose) for the degradation of methylene blue and congo red in the light of various possible factors was investigated. A complete set of experiments in two aspects of studies (synthesis and application of nano ZnO/Zn) indicated that surface modification of polysaccharides for the preparation of nano ZnO/Zn affected the final photocatalytic studies along with photocatalytic experimental conditions. Thus a combined study of preparation conditions as well as photocatalytic experimental conditions was studied extensively in a single work which is the highlight of this task. Various factors such as crosslinking agent, degree of carboxymethylation, temperature and solvent affected the synthesis of nano ZnO/Zn. When the degree of crosslinking and concentration of sodium chloroacetate increased, the efficiency of formation of nano ZnO/Zn dropped and thus the optimum precursors selected for the preparation of nano ZnO/Zn were CCMS-1 and CMC-1. It is suggested that crosslinking coupling technique was used to obtain nano ZnO/Zn which would definitely enhance the efficiency of photodegradation of pollutants, since ZnO possess wide band gap. The obtained results could confirm that regardless of the dyes, (ZnO/Zn)-S displayed enhanced photocatalytic ability among the photocatalysts discussed in this work. In conclusion, among two dyes methylene blue exhibited comparatively faster degradation rate. Nano ZnO/Zn obtained in this work displayed promising super photocatalytic degradation aptitude for different organic dyes. We believe that crosslinking carboxymethyl starch and carboxymethyl cellulose are appropriate chelates to synthesize a series of metal oxide semiconductor–metal composite nanoparticles with controlled composition and size, which is of importance to study the catalysis, sensitivity, and energy conversion of metal–semiconductor nanocomposites.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.01.017.

References

Ahmadzadi, H., Marandi, F., & Morsali, A. (2009). Structural and X-ray powder diffraction studies of nano-structured lead(II) coordination polymer with η^2 Pb...C interactions. *Journal of Organometallic Chemistry*, *694*, 3565–3569.

Akar, E., Altınışık, A., & Sekib, Y. (2012). Preparation of pH- and ionic-strength responsive biodegradable fumaric acid crosslinked carboxymethyl cellulose. *Carbohydrate Polymers*, *90*, 1634–1641.

Akyol, A., Yatmaz, H. C., & Bayramoglu, M. (2004). Photocatalytic decolorization of Remazol Red RR in aqueous ZnO suspensions. *Applied Catalysis B: Environmental*, *54*, 19–24.

Baskoutas, S., Giabouranis, P., Yannopoulos, S. N., Dracopoulos, V., Toth, L., Chrissanthopoulos, A., et al. (2007). Preparation of ZnO nanoparticles by thermal decomposition of zinc alginate. *Thin Solid Films*, *515*, 8461–8464.

Benke, N., Takacs, E., Wojnarovits, O. L., & Borsa, J. (2007). Pre-irradiation grafting of cellulose and slightly carboxymethylated cellulose (CMC) fibres. *Radiation Physics and Chemistry*, *76*, 1355–1359.

Chen, X. G., Wang, Z., Liu, W. S., & Park, H. J. (2002). The effect of carboxymethylchitosan on proliferation and collagen secretion of normal and keloid skin fibroblasts. *Biomaterials*, *23*, 4609–4614.

Colón, G., Hidalgo, M. C., Navío, J. A., Melián, E. P., González Díaz, O., & Doña Rodríguez, J. M. (2008). Highly photoactive ZnO by amine capping-assisted hydrothermal treatment. *Applied Catalysis B: Environmental*, *83*, 30–38.

Cun, W., Jincai, Z., Xinming, W., Bixian, M., Guoying, S., Ping'an, P., et al. (2002). Preparation, characterization and photocatalytic activity of nano-sized ZnO/SnO_2 coupled photocatalysts. *Applied Catalysis B: Environmental*, *39*, 269–279.

Daneshvar, N., Rabbani, M., Modirshahla, N., & Behnajady, M. A. (2005). Photooxidative degradation of Acid Red 27 in a tubular continuous-flow photoreactor: Influence of operational parameters and mineralization products. *Journal of Hazardous Materials*, *118*, 155–160.

Daneshvar, N., Salari, D., & Khataee, A. R. (2004). Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO_2. *Journal of Photochemistry and Photobiology A: Chemistry*, *162*, 317–322.

Gu, F., Wang, S. F., Lu, M. K., Zhou, G. J., Xu, D., & Yuan, D. R. (2004). Structure evaluation and highly enhanced luminescence of Dy^{3+}-doped ZnO nanocrystals by Li^+ doping via combustion method. *Langmuir*, *20*, 3528–3531.

Guillard, C., Lachheb, H., Houas, A., Ksibi, M., Elaloui, E., & Herrmann, J.-M. (2003). Influence of chemical structure of dyes, of pH and of inorganic salts on their photocatalytic degradation by TiO_2 comparison of the efficiency of powder and supported TiO_2. *Journal of Photochemistry and Photobiology A: Chemistry*, *158*, 27–36.

Height, M. J., Pratsinis, S. E., Mekasuwandumrong, O., & Praserthdam, V. (2006). Ag-ZnO catalysts for UV-photodegradation of methylene blue. *Applied Catalysis B: Environmental*, *63*, 305–312.

Hoffmann, M. R., Martin, S. T., Choi, W., & Bahnemann, D. W. (1995). Environmental applications of semiconductor photocatalysis. *Chemical Reviews*, *95*, 69–96.

Joseph, J. M., Destaillats, H., Hung, H.-M., & Hoffmann, M. R. (2000). The sonochemical degradation of azobenzene and related azo dyes: Rate enhancements via Fenton's reactions. *Journal of Physical Chemistry A*, *104*, 301–307.

Kavitha, R., Meghani, S., & Jayaram, V. (2007). Synthesis of titania films by combustion flame spray pyrolysis technique and its characterization for photocatalysis. *Materials Science and Engineering B*, *139*, 134–140.

Khanjani, S., & Morsali, A. (2009a). A new nano-particles LaIII compound as a precursor for preparation of $La_2O_2(SO_4)$ nano-particles. *Journal of Molecular Structure*, *935*, 27–31.

Khanjani, S., & Morsali, A. (2009b). New nano-particle La(III) supramolecular compound as a precursor for preparation of lanthanum oxybromide-, hydroxide-, and oxide nanostructures. *Journal of Coordination Chemistry*, *62*, 3343–3350.

Khodja, A. A., Sehili, T., Pilichowski, J. F., & Boule, P. (2001). Photocatalytic degradation of 2-phenylphenol on TiO_2 and ZnO in aqueous suspensions. *Journal of Photochemistry and Photobiology A: Chemistry*, *141*, 231–239.

Kim, B. S., & Lim, S.-T. (1999). Removal of heavy metal ions from water by cross-linked carboxymethyl corn starch. *Carbohydrate Polymers*, *39*, 217–223.

Mekasuwandumrong, O., Pawinrat, P., Praserthdam, P., & Panpranot, J. (2010). Effects of synthesis conditions and annealing post-treatment on the photocatalytic activities of ZnO nanoparticles in the degradation of methylene blue dye. *Chemical Engineering Journal*, *164*, 77–84.

Olaru, N., Olaru, L., Stoleriu, A., & Timpu, D. (1998). Carboxymethylcellulose synthesis in organic media containing ethanol and/or acetone. *Journal of Applied Polymer Science*, *67*, 481–486.

Peternel, I. T., Koprivanac, N., Božić, A. M. L., & Kušić, H. M. (2007). Comparative study of UV/TiO_2, UV/ZnO and photo-Fenton processes for the organic reactive dye degradation in aqueous solution. *Journal of Hazardous Materials*, *148*, 477–484.

Poulios, I., & Tsachpinis, I. (1999). Photodegradation of the textile dye Reactive Black 5 in the presence of semiconducting oxides. *Journal of Chemical Technology and Biotechnology*, *74*, 349–357.

Pushpamalar, V., Langford, S. J., Ahmad, M., Hashim, K., & Lim, Y. Y. (2013). Absorption characterization of Ca^{2+}, Na^{+}, and K^{+} on irradiation crosslinked carboxymethyl sago pulp hydrogel. *Journal of Applied Polymer Science*, *128*, 1828–1833.

Ranjbar, Z. R., & Morsali, A. (2009). Sonochemical syntheses of a new nano-sized porous lead(II) coordination polymer as precursor for preparation of lead(II) oxide nanoparticles. *Journal of Molecular Structure*, *936*, 206–212.

Sakthivel, S., Neppolian, B., Shankar, M. V., Arabindoo, B., Palanichamy, M., & Murugesan, V. (2003). Solar photocatalytic degradation of azo dye: Comparison of photocatalytic efficiency of ZnO and TiO_2. *Solar Energy Materials and Solar Cells*, *77*, 65–82.

Siddiquey, I. A., Furusawa, T., Sato, M., & Suzuki, N. (2008). Microwave-assisted silica coating and photocatalytic activities of ZnO nanoparticle. *Materials Research Bulletin*, *43*, 3416–3424.

Silva, D. A., Paula, C. M. R., de Feitosa, P. A. J., Brito, C. F. A., de Maciel, S. J., & Paula, C. B. H. (2004). Carboxymethylation of cashew tree exudates polysaccharide. *Carbohydrate Polymers*, *58*, 163–171.

Tanaka, K., Padermpole, K., & Hisanaga, T. (2000). Photocatalytic degradation of commercial azo dyes. *Water Research*, *34*, 327–333.

Tang, L.-G., & Hon, D. N.-S. (2001). Chelation of chitosan derivatives with zinc ions. II. Association complexes of Zn^{2+} onto O,N-carboxymethyl chitosan. *Journal of Applied Polymer Science*, *79*, 1476–1485.

Thirumavalavan, M., Huang, K.-L., & Lee, J.-F. (2013). Synthesis and properties of nano ZnO using polysaccharides as chelating agents: Effects of various parameters on surface modification of polysaccharides. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *417*, 154–160.

Toğrul, H., & Arslan, N. (2003). Production of carboxymethyl cellulose from sugar beet pulp cellulose and rheological behaviour of carboxymethyl cellulose. *Carbohydrate Polymers*, *54*, 73–82.

Wang, S. M., Yang, Z. S., Lu, M. K., Zhou, Y. Y., Zhou, G. J., Qiu, Z. F., et al. (2007). Coprecipitation synthesis of hollow Zn_2SnO_4 spheres. *Materials Letters*, *61*, 3005–3008.

Wang, Y., Zhang, C., Bi, S., & Luo, G. (2010). Preparation of ZnO nanoparticles using the direct precipitation method in a membrane dispersion micro-structured reactor. *Powder Technology*, *202*, 130–136.

Yu, W., Li, X., Gao, X., & Wu, F. (2005). Large-scale synthesis and microstructure of SnO_2 nanowires coated with quantum-sized ZnO nanocrystals on a mesh substrate. *Journal of Physical Chemistry B*, *109*, 17078–17081.

Zeng, H., Cai, W., Li, Y., Hu, J., & Liu, P. (2005). Composition/structural evolution and optical properties of ZnO/Zn nanoparticles by laser ablation in liquid media. *Journal of Physical Chemistry B*, *109*, 18260–18266.