

Article

Ruthenium Supported on Ionically Cross-linked Chitosan-Carrageenan Hybrid MnFe_2O_4 Catalysts for 4-Nitrophenol Reduction

Kin Hong Liew ¹, Tian Khoon Lee ^{2,*}, Mohd Ambar Yarmo ¹, Kee Shyuan Loh ²,
Andreia F. Peixoto ³, Cristina Freire ³ and Rahimi M. Yusop ^{1,4,*}

¹ School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, Bangi 43600 UKM, Selangor Darul Ehsan, Malaysia; edwin85_kh@yahoo.com.sg (K.H.L.); ambar@ukm.edu.my (M.A.Y.)

² Fuel cell Institute (FCI), Universiti Kebangsaan Malaysia, Bangi 43600 UKM, Selangor Darul Ehsan, Malaysia; ksloh@ukm.edu.my

³ REQUIMTE-LAQV, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal; andreia.peixoto@fc.up.pt (A.F.P.); acfreire@fc.up.pt (C.F.)

⁴ Kluster Perubatan Regeneratif, Institut Perubatan dan Pergigian Termaju, Universiti Sains Malaysia, Bertam Kepala Batas 13200, Pulau Pinang, Malaysia

* Correspondence: edison_tiankhoo@hotmail.com (T.K.L.); rahimi@ukm.edu.my (R.M.Y.); Tel.: +6012-7279286 (T.K.L.); +6010-2678586 (R.M.Y.)

Received: 23 January 2019; Accepted: 28 February 2019; Published: 12 March 2019



Abstract: Herein, we report a facile procedure to synthesize the hybrid magnetic catalyst (Ru@CS-CR@Mn) using ruthenium (Ru) supported on ionically cross-linked chitosan-carrageenan (CS-CR) and manganese ferrite (MnFe_2O_4) nanoparticles with excellent catalytic activity. The ionic gelation of CS-CR is acting as a protecting layer to promote the encapsulation of MnFe_2O_4 and Ru nanoparticles by electrostatic interactions. The presence of an active metal and a CS-CR layer on the as-prepared Ru@CS-CR@Mn catalyst was well determined by a series of physicochemical analyses. Subsequently, the catalytic performances of the Ru@CS-CR@Mn catalysts were further examined in the 4-nitrophenol (4-NP) reduction reaction in the presence of sodium borohydride (reducing agent) at ambient temperature. The Ru@CS-CR@Mn catalyst performed excellent catalytic activity in the 4-NP reduction, with a turnover frequency (TOF) values of 925 h^{-1} and rate constant (k) of 0.078 s^{-1} . It is worth to mentioning that the Ru@CS-CR@Mn catalyst can be recycled and reused up to at least ten consecutive cycles in the 4-NP reduction with consistency in catalytic performance. The Ru@CS-CR@Mn catalyst is particularly attractive as a catalyst due to its superior catalytic activity and superparamagnetic properties for easy separation. We foresee this catalyst having high potential to be extended in a wide range of chemistry applications.

Keywords: Ruthenium; chitosan; carrageenan; MnFe_2O_4 ; 4-nitrophenol reduction

1. Introduction

Phenols and nitrophenol derivatives are toxic organic wastes that are generated or released as wastewater during the manufacturing process of agriculture, dyes, and pharmaceuticals. [1]. Due to the environmental concerns related to water disposal, water scarcity and water pollution, there is a growing interest in the transformation of these harmful organic pollutants into non/less toxic composite in aqueous solutions under mild conditions [2]. Several techniques have been employed for nitrophenol degradation in polluted water, including membrane filtration, photodegradation, adsorption and chemical reduction [3–7]. Among these techniques, chemical reduction of nitrophenol is one of the

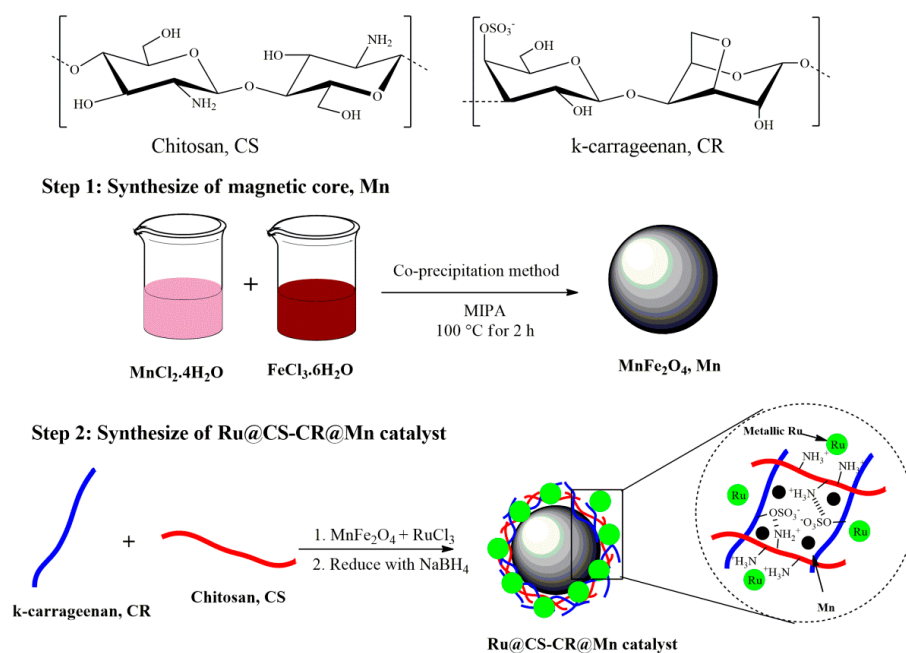
most popular techniques to address this issue due to its high efficiency [8]. The transformation of nitrophenol to aminophenol compounds is of great industrial importance. Aminophenol is an important intermediate compound in the chemical industry, especially for pharmaceuticals and bulk chemical production [8,9]. Hence, numerous studies have been carried out to develop an ideal catalytic reaction to convert nitrophenol compounds into valuable amine derivatives. Furthermore, conversion of nitrophenol to aminophenol using a reducing agent (e.g., NaBH_4 , H_2O_2 , NH_3NH_2) is presently considered as a benchmark reaction to evaluate the respective catalytic behavior for a newly-prepared catalyst [10].

Recently, the reduction of 4-NP to 4-aminophenol (4-AP) over metal catalysts has been broadly studied. Many literature studies have focused on the use of noble metal nanoparticles (NPs) such as Pd, Au, Pt, and Ru for the nitroarenes reductions [11–14]. For the nitrophenol reduction, Ru metal is one of the promising noble metals in this reaction, owing to its high efficiency. Different types of Ru catalysts have been successfully exploited for many chemical reactions. Although, the homogeneous Ru catalysts usually exhibited superior reaction rates towards the 4-NP reduction, it is difficult to recover and reuse in the next reaction. Furthermore, the performance of the catalyst degrades over time as a result of agglomeration and leaking during the reduction process [15,16]. To alleviate these problems, the development of a new heterogeneous supported catalyst with a larger surface area is needed. Thus, many studies have been conducted on Ru metals impregnated on various supports, which include metal oxide, activated carbon, and dendrimers [17–19].

The development of magnetic-supported catalyst that works on a wide range of application such as C–C coupling reaction, waste water treatment, and heavy metal removal has been extensively studied [20–22]. The magnetic-supported catalysts have a magnetic nature that allows for simple separation and recovery from the reaction medium by an external magnetic field [23]. Manganese(II) ferrite (MnFe_2O_4) is a magnetic material that showed high adsorption capacity, biocompatibility, exceptional chemical stability, and high magnetic susceptibility [24].

In the recent past, the coating of magnetic nanoparticles (MNPs) with polymer and other materials was explored rapidly. The coating process can act as a protecting layer to prevent the degradation of MNPs during the catalytic reactions [25]. The surface modification of MNPs can be easily to achieve through coating it by natural or synthetic polymers [26]. Chitosan (CS), is a natural polyaminosaccharide that has a good biocompatibility, low toxicity, and low pH sensitivity as well as containing amino and hydroxyl functional groups that could promote metal ion chelation [27]. Based on the literature, the introduction of MNPs into a CS network using a cross-linker, such as tripolyphosphate (TPP) and glutaraldehyde, allows the interaction of metal NPs with the cationic CS via electrostatic interactions [28]. Kappa carrageenan, denoted as CR, is another type of polysaccharide that can be found in red seaweeds. CR has a linear structure of sulfated polysaccharide of D-galactose and 3,6-anhydro-D-galactose [29]. The crosslinking of biopolymers, CS-CR can be formed via electrostatic interaction of $-\text{NH}_3^+$ cations on CS with sulfate groups ($-\text{OSO}_3^-$) on CR.

In this work, we fabricated a facile synthesis of Ru@CS-CR@Mn catalysts at ambient temperature by a simple wet-impregnation technique based on ionic gelation between CS and CR and the entrapped MnFe_2O_4 as the magnetic core for magnetic separation purpose (Scheme 1). The newly-prepared Ru@CS-CR@Mn catalysts exhibited magnetic properties of the MnFe_2O_4 together with the metal adsorption capabilities of CS that would promote the immobilization of Ru metal and magnetic core. This is the first article in the literature on the synthesis of Ru@CS-CR@Mn catalysts by entrapped of Ru metal onto MnFe_2O_4 with a CS-CR matrix by an ionic gelation method. The catalytic performance of the newly-prepared Ru@CS-CR@Mn catalysts was evaluated in 4-NP reduction in mild condition.



Scheme 1. Schematic illustration of preparation of the Ru@CS-CR@Mn catalysts.

2. Results

2.1. Characterization of Ru@CS-CR@Mn Catalyst

Figure 1 illustrated the Fourier transform infrared (FTIR) spectra of MnFe₂O₄ and Ru@CS-CR@Mn catalyst. In the FTIR spectra of MnFe₂O₄, the absorption band at 3328, 1626, 1576 and 1420 cm^{−1} are ascribed to O–H stretching vibration of hydroxyl group overlapped with the N–H stretching vibration, C=O stretching of amide I, C=O stretching of amide II and C–N bending of amide III, respectively of the protecting layer of isopropanolamine (MIPA) on the surface of MnFe₂O₄ [30]. After the formation of the Ru@CS-CR@Mn catalyst, the specific bands at 1655 and 1596 cm^{−1} that related to the CS materials were shifted to 1647 and 1534 cm^{−1} in the spectrum of Ru@CS-CR@Mn catalyst [31]. The absorption band at 1534 cm^{−1} is attributed to –NH₃⁺ groups formed during the fabrication process. Several identical bands of CR were observed in the FTIR spectra, which is including carbohydrate overtones of the –COH stretch at 2200–2000 cm^{−1}, sulfate groups at 1259 cm^{−1}, 3,6-anhydrogalactose at 930 cm^{−1}, and galactose-4-sulfate at 846 cm^{−1}. All the results indicated the formation of CS-CR complexes between –NH₃⁺ groups of CS and sulfates groups of CR [32–34].

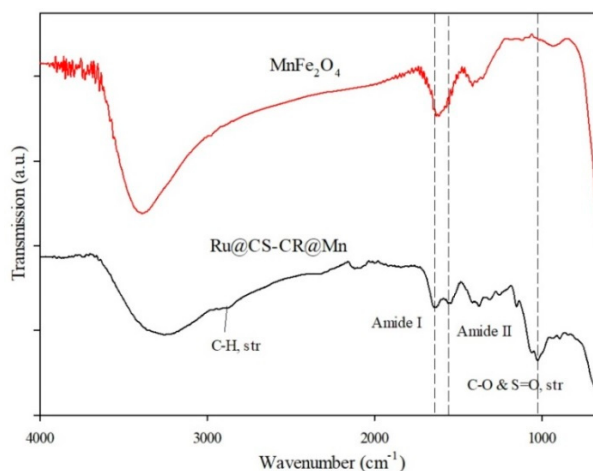


Figure 1. Fourier transform infrared (FTIR) spectra of MnFe₂O₄ and Ru@CS-CR@Mn catalyst.

The X-ray diffraction (XRD) patterns of MnFe_2O_4 and Ru@CS-CR@Mn catalyst are shown in Figure 2. The diffraction patterns for MnFe_2O_4 and Ru@CS-CR@Mn catalyst displayed a similar pattern with seven characteristic peaks at $2\theta = 18.3^\circ, 29.8^\circ, 35.3^\circ, 43.0^\circ, 53.1^\circ, 56.2^\circ$ and 62.1° , which corresponded to the (111), (220), (311), (400), (422), (511) and (440) planes of the face centered-cubic (fcc) close packing structure of the MnFe_2O_4 nanoparticles (JCPDS No. 88-1965), respectively [31]. These results suggested that the spinel structure of the MnFe_2O_4 magnetic core remains unchanged after the ionic gelation of CS-CR complex on the surface of magnetic core. Overall, the intensity of peaks of Ru@CS-CR@Mn catalyst was slightly lower than MnFe_2O_4 , which confirmed the protecting layer of CS-CR on the surface of MnFe_2O_4 . The diffraction peak of Ru metal was not observed in the XRD pattern of Ru@CS-CR@Mn and this may due to the Ru NPs were in an amorphous state and with very low abundance of Ru content [35]. The average crystal size of the MnFe_2O_4 in Ru@CS-CR@Mn was determined to be 12.2 nm (calculated by Scherrer formula) and this size is similar to the raw MnFe_2O_4 MNPs (~ 12.0 nm).

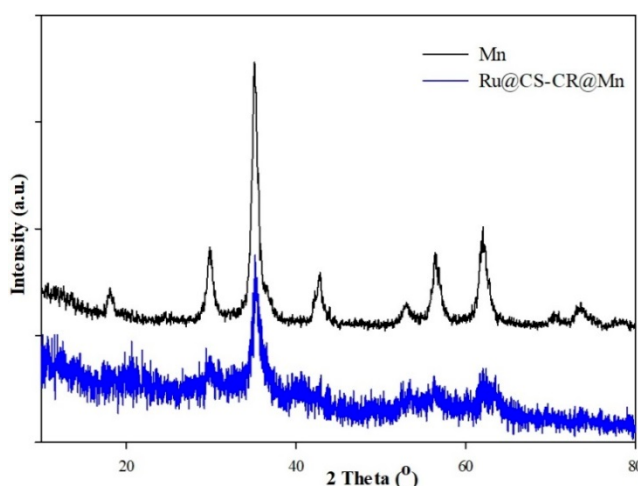


Figure 2. X-ray diffraction (XRD) patterns of MnFe_2O_4 and Ru@CS-CR@Mn catalyst.

The morphology of the Ru@CS-CR@Mn catalyst was carried out by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis and the micrographs of the catalyst are presented in Figure 3. The obtained SEM micrograph showed that the Ru@CS-CR@Mn catalyst is in nanosize and the chemical composition was identified by using energy-dispersive X-ray spectroscopy (EDX), which shows that it is constituted mainly elements of C, O, Mn, and Fe (Figure 3a). The existence of Ru peak in the EDX spectrum indicated the immobilization of Ru metal in the Ru@CS-CR@Mn catalyst. Additionally, the high resolution (HR)TEM image showed the average diameter of Ru@CS-CR@Mn catalyst was 15.6 ± 0.7 nm which is larger than the MnFe_2O_4 MNPs (~ 9.3 nm) that reported previously [30]. To identify the Ru content, ICP-MS was used. The ICP-MS analysis indicated that the Ru@CS-CR@Mn catalyst consists of 0.46 wt. % of Ru NPs.

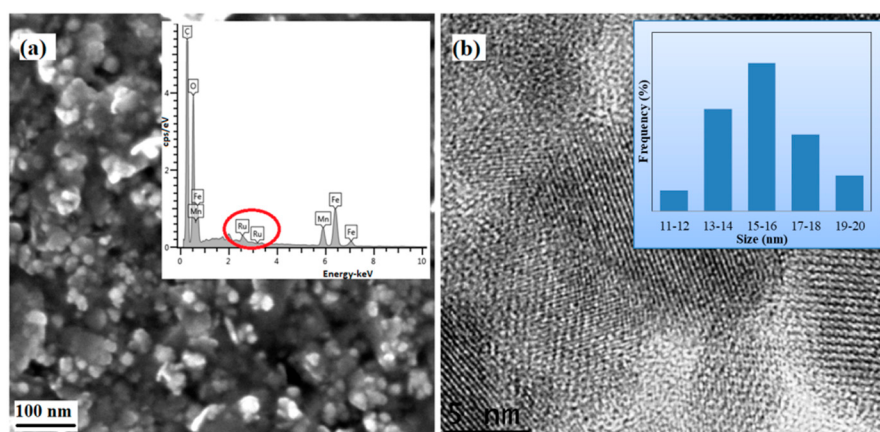


Figure 3. (a) Scanning electron microscopy (SEM) image (inset: energy-dispersive X-ray spectroscopy (EDX) spectrum) and (b) high resolution transmission electron microscopy (HRTEM) image of Ru@CS-CR@Mn catalyst.

The magnetic properties of MnFe_2O_4 and Ru@CS-CR@Mn catalyst were investigated further by using vibrating sample magnetometry (VSM) at room temperature. The magnetic field-dependent magnetization (M - H) curve of the samples at 300 K at a magnetic field up to $H = 30\,000$ Oe is shown in Figure 4, and the magnetic detail data is summarized in Table 1. The saturation magnetization (M_s) values obtained for MnFe_2O_4 and Ru@CS-CR@Mn catalyst were 63.3 and 38.7 emu/g, respectively. The M_s value of Ru@CS-CR@Mn was reduced compared to that of MnFe_2O_4 MNPs because of the coating layer of CS-CR complexes, which is a nonmagnetic material [36]. The coercivity (H_c) and remnant magnetization (M_r) values of MnFe_2O_4 are 15.0 Oe and 1.7 emu/g, respectively. By contrast, the H_c and M_r values for Ru@CS-CR@Mn are 15.9 Oe and 1.7 emu/g, respectively. Both of the samples showed a very low squareness ratio (M_r/M_s) (0.027 and 0.044 for MnFe_2O_4 and Ru@CS-CR@Mn, respectively) which confirms the superparamagnetic behavior of samples [37].

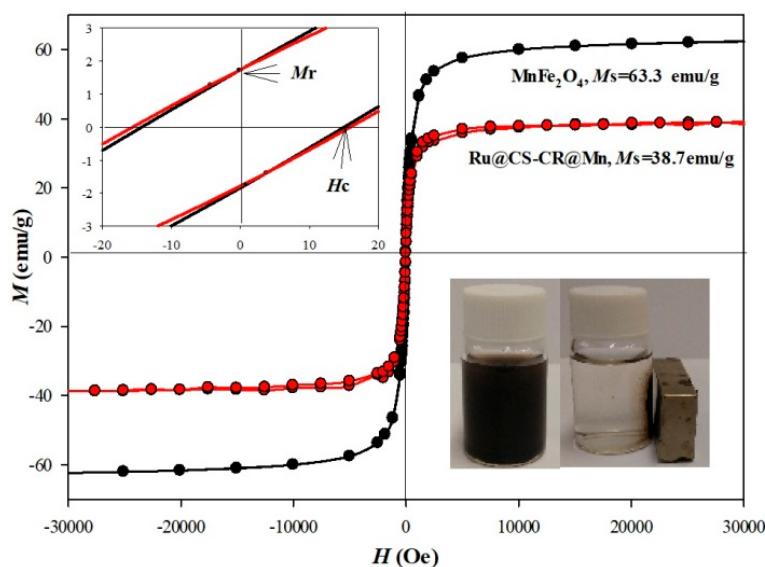


Figure 4. Applied magnetic field-dependent magnetization (M - H) curve of the samples at 300 K in the magnetic field range of $-30\,000$ to $30\,000$ Oe (insert image: separation and re-dispersion of Ru@CS-CR@Mn).

Table 1. Magnetic properties of samples.

Materials	$M_S^{300\text{ K}}$ (emu/g)	$M_r^{300\text{ K}}$ (emu/g)	H_c (Oe)	M_r/M_S Ratio
MnFe ₂ O ₄	63.3	1.7	15.0	0.027
Ru@CS-CR@Mn	38.5	1.7	15.9	0.047

2.2. Catalytic Performance Test of Ru@CS-CR@Mn Catalyst

The reduction of 4-NP to 4-AP is an ideal model catalytic reaction to determine the catalytic activity of metal nanoparticles in aqueous solution [10]. Thus, the catalytic activity of the as-prepared Ru@CS-CR@Mn catalyst was evaluated in the 4-NP reduction reaction in aqueous solution with NaBH₄ as a reducing agent. Because of the highly excess amount of NaBH₄ that was used, the reduction rate can be assumed to be independent of the concentration of NaBH₄ and thus, the reduction rate can be calculated based on pseudo-first-order kinetics [31]. The rate constant of the catalyst (k) was calculated from the slopes of the linear ranges of the $\ln(A_t/A_0) = -kt$ plots, where A_t and A_0 are refer to the 4-NP concentrations at time t and 0, respectively (Figure 5) [38]. For a better comparison, the turnover frequencies (TOF) value was also calculated from the rate constant, k according to the equation: $\text{TOF} = k n_{0\text{4-NP}}/n_{\text{Ru}}$, where $n_{0\text{4-NP}}$ is the starting concentration of 4-NP substrate and n_{Ru} is the amount of Ru in the nanocatalyst (Based on the Ru content obtained from ICP-MS analysis).

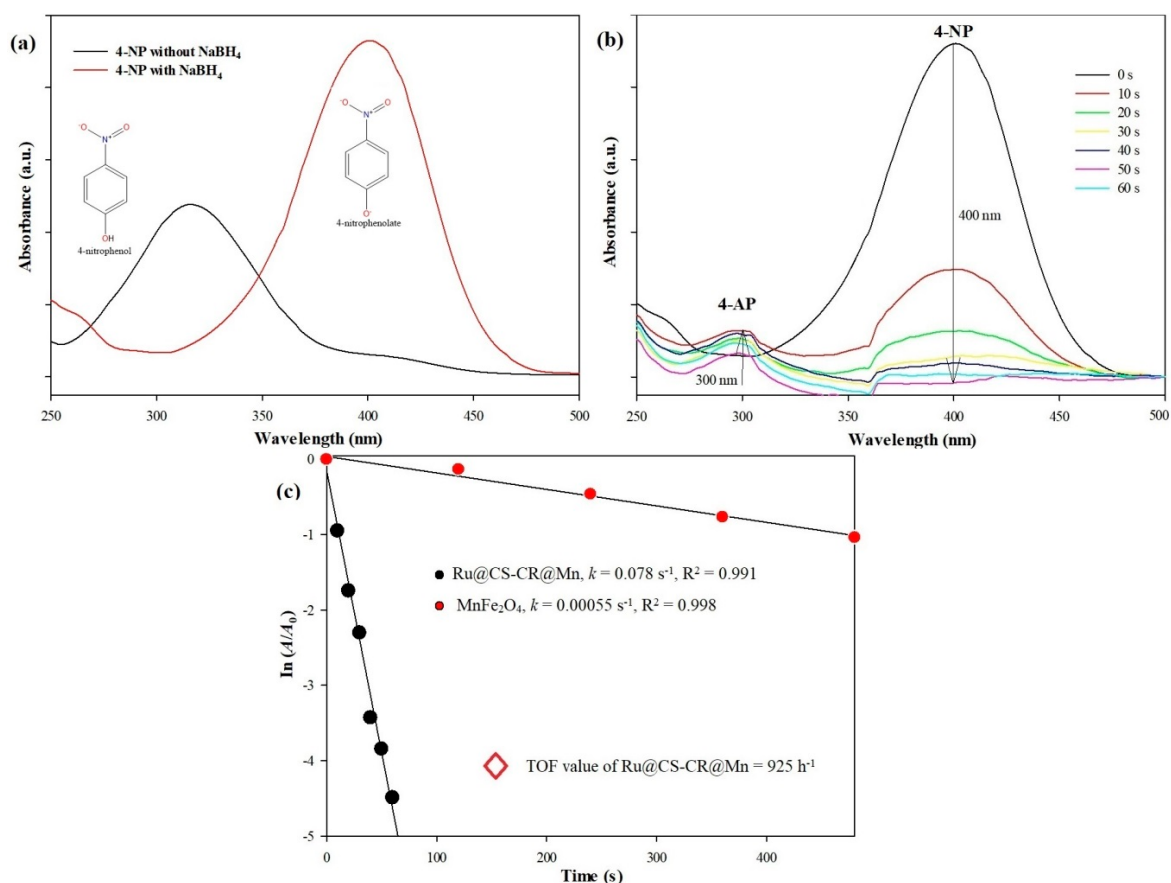


Figure 5. (a) UV-Vis spectra of the 4-NP with and without the presence of NaBH₄, (b) UV-Vis spectra of the 4-NP reduction catalyzed by the 1.0 mg of Ru@CS-CR@Mn catalyst and (c) plot of $\ln(A/A_0)$ against the completion time (t) for the reduction of 4-NP.

The 4-NP reduction reaction progress was monitored by UV-Vis spectroscopy. As can see in Figure 5a, the strong absorption peak at 400 nm is belonged to 4-nitrophenolate ion, which formed after addition of NaBH_4 into the 4-NP solution. In the absence of Ru@CS-CR@Mn catalysts, the peak at 400 nm remains unchanged for over two hours (not show). The intensity of absorption peak at 400 nm was progressively decreased upon increase of the reaction time. Meanwhile, a small new peak was gradually increased in intensity at 300 nm, which indicated the 4-NP was reduced to 4-AP [39]. Furthermore, the 4-NP reduction reaction progress can be monitored visually based on the color changes from yellowish solution (4-NP) to colorless solution (4-AP).

In Figure 5b, the 4-NP reduction reaction took approximately 60 s to complete after addition of 1.0 mg of Ru@CS-CR@Mn catalyst with a rate of constant of 0.078 s^{-1} . The kinetic profile of Ru@CS-CR@Mn -catalyzed 4-NP reduction confirmed the reduction showed a good linear relationship with the first-order kinetics as mention previously (Figure 5c). In a control experiment, MnFe_2O_4 exhibited very low catalytic activity ($k = 0.00055 \text{ s}^{-1}$) toward 4-NP reduction [31]. The control experiment in the absence of catalyst has been carried out and the results showed that the intensity of 4-NP absorption remains unchanged (data not shown). These findings indicated that the 4-NP reduction reaction is strongly depended on the active metal used.

Besides, the TOF value is one of the parameter used for comparing the catalyst performance [40]. The TOF value of the Ru@CS-CR@Mn catalyst in the 4-NP reduction was 925 h^{-1} . The TOF values of the Ru@CS-CR@Mn catalyst and other noble catalysts are listed in Table 2. The result shows that the TOF value of Ru@CS-CR@Mn catalyst is superior to some other noble catalyst (Pd, Ag, Au) in 4-NP reduction reaction except for Ru colloidal solutions that reported previously [15,41–46]. Thus, these data proved that Ru@CS-CR@Mn has superior catalytic activity in a reduction reaction of 4-NP.

Table 2. Data for the 4-NP reduction by different noble catalyst in presence of NaBH_4 .

Catalyst	Metal Loading	Completion Time (s)	Rate Constant (s^{-1})	TOF (h^{-1})	Reference
Ru colloidal solution	-	840	16.8	4800	[15]
Pd/PdO	9.5 wt. %	240	0.01	750	[41]
Pd- CeO_2	2.15 wt. %	120	-	335	[42]
Pd NP/CNT-220	1.69 wt. %	300	0.01	18	[43]
Ag@micelle-2	5.0 mg mL^{-1}	80	0.02	48.7	[44]
Ag-OMS-C	3.86 wt. %	150	0.03	91.2	[45]
AuNPs-SPEG	-	-	0.035	1.14	[46]
Ru@CS-CR@Mn	0.46 wt. %	60	0.078	925	This work

The reusability performance of Ru@CS-CR@Mn catalyst for the 4-NP reduction under the same conditions was evaluated. The results revealed that Ru@CS-CR@Mn catalyst could be reused for 10 cycles with almost 100% 4-NP conversion (Figure 6). The reaction rate for the reduction reactions gradually decreased whereas the completion time was slightly increased. This may probably occur due to the catalyst loss or aggregation of the catalysts during the reusability test [33]. Nevertheless, the results confirmed the Ru@CS-CR@Mn catalyst possesses robust stability not less than 10 consecutive cycles in the 4-NP reduction process.

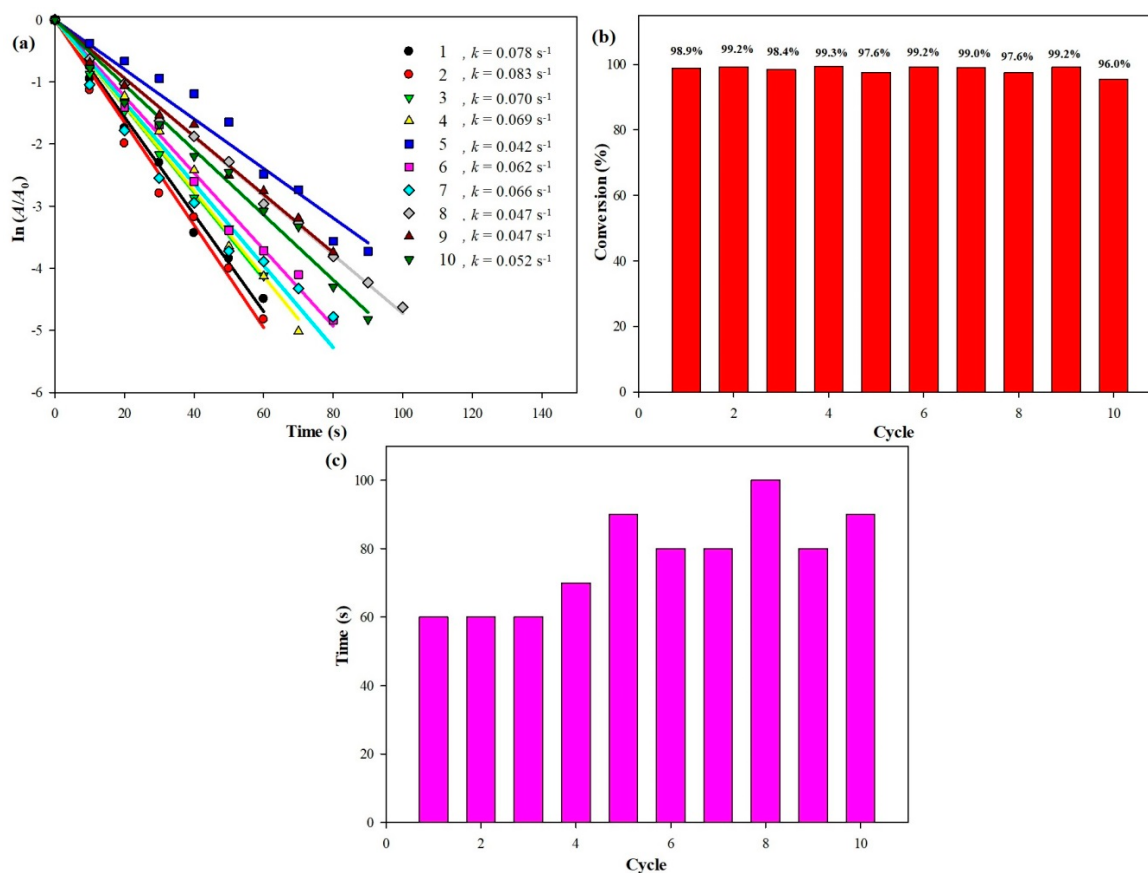


Figure 6. Reusability of Ru@CS-CR@Mn catalyst for 10 consecutive cycles: (a) rate constant, (b) 4-NP conversion and (c) completion time.

After the reusability test, the used Ru@CS-CR@Mn nanocatalyst was denoted as Ru@CS-CR@Mn_4NP and was characterized by XRD analysis. The XRD diffractogram of Ru@CS-CR@Mn_4NP did not show obvious changes compared with the fresh Ru@CS-CR@Mn catalyst, which indicated the high stability performance of the catalyst during the reusability test (Figure 7).

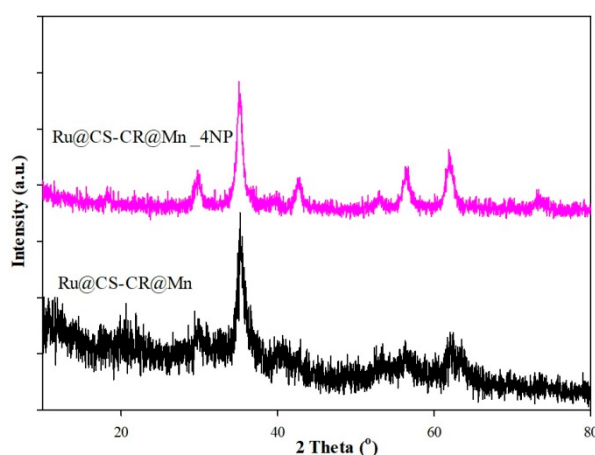


Figure 7. XRD patterns of Ru@CS-CR@Mn and Ru@CS-CR@Mn_4NP catalyst.

3. Materials and Methods

3.1. Materials

k-carrageenan was commercially obtained from Takara Corporation Sdn. Bhd. (Sabah, Malaysia). Chitosan, CS (medium molecular weight, 75–85% deacetylated), manganese(II) chloride tetrahydrate (98%), ruthenium(III) chloride hydrate (ReagentPlus), isopropanolamine (93%), 4-nitrophenol, 4-NP (+99.5%), sodium borohydride (98%), were obtained from Sigma Aldrich. Iron(III) chloride hexahydrate (for analysis) and HCl (37%, analytical grade) were purchased from Merck (Darmstadt, Germany). Acetone (analytical grade) was obtained from Fisher Chemical (Loughborough, UK). Deionized water was used throughout the experiments. All reagents were of analytical reagent grade and used without further purification.

3.2. Preparation of MnFe_2O_4 Nanoparticles

MnFe_2O_4 magnetic nanoparticles were prepared by the coprecipitation method that developed by Pereira et al [30]. Generally, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (10 mmol) were mixed with 5 ml of HCl (0.1 M, 1:4 v/v), and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (20 mmol) were dissolved in 40 ml of water. Both solutions were heated to 50 °C and then quickly added into 200 ml of MIPA (3.0 M) solution. The reaction mixture was then heated to 100 °C and continued stirring for 2 h. The freshly as-prepared MnFe_2O_4 nanoparticles, denoted as Mn, were isolated by external magnet and dried under vacuum at room temperature overnight.

3.3. Preparation of Ru@CS-CR@Mn Catalyst

The Ru@CS-CR@Mn was synthesized according to a modification of a method described by Grenha et al. and Calvo et al. by ionic complexation of chitosan-carrageenan (CS-CR) materials [32,47]. The CS-CR matrix was formed by an electrostatic interaction of CS with CR, in which the amino groups ($-\text{NH}_3^+$) of CS will interact with the sulfate groups ($-\text{OSO}_3^-$) of CR (Scheme 1). Generally, RuCl_3 (20 mg) was added in acetic acid solution (25 mL, 0.5%, v/v) and then the Mn (100 mg) was dispersed in the acetic acid solution by ultrasonication for 1 min. CS (5 mg/mL) was dissolved in the same acetic acid solution and kept under stirring at ambient temperature for 1 h. 10 mL of CR solution (1 mg/mL) was added dropwise into the CS solution. The formed product was collected, washed and dried under vacuum at 40 °C overnight. The product was expressed as Ru(III)@CS-CR@Mn . Afterward, the Ru(III)@CS-CR@Mn was dispersed in a fresh NaBH_4 solution (0.1 M, 10 mL) under continuous stirring for 3 h at room temperature (28 ± 2 °C). The material was separated, washed and dried under vacuum for overnight. The final reduced catalyst was represented as Ru@CS-CR@Mn and subjected to further analysis.

3.4. Characterization

The X-ray power diffraction patterns were examined with a Bruker D8-Advanced diffractometer in the range of $2\theta = 10^\circ$ to 80° . Inductively coupled plasma mass spectrometry (ICP-MS) was examined by using a Perkin Elmer ELAN 9000 ICP mass spectrometer. Fourier transform infrared spectra were collected with Agilent Technologies Cary 630 FTIR spectrometer in the range of $650\text{--}4000\text{ cm}^{-1}$. High-resolution transmission electron microscopy (HRTEM) images were obtained from FEI TECNAI G2 F20 X-Twin High-resolution transmission electron microscope at 200 kV. Field emission scanning electron microscopy (FESEM) was performed with a Merlin Compact Zeiss scanning electron microscope and VSM analysis was examined with LakeShore 7404 series vibration sample magnetometer. UV-Vis spectra were collected with a Shimadzu UV-2450 UV-Vis spectrophotometer.

3.5. Reduction of 4-NP to 4-AP

Catalytic activity of Ru@CS-CR@Mn was examined in the reduction of 4-nitrophenol (4-NP) in the presence of NaBH_4 (reducing agent) at ambient temperature. Briefly, 5.67 mg of NaBH_4 (0.15 mmol)

was added to 3 mL of 0.05 mM 4-NP solution, resulting in a yellow-green solution of 4-nitrophenolate. Then, 1.0 mg of Ru@CS-CR@Mn was then added to the solution and the conversion of 4-NP to 4-AP was started immediately. The reduction of 4-NP was monitored by UV-Vis spectrometer.

4. Conclusions

In summary, we have successfully developed a simple and efficient procedure for the synthesis of the hybrid magnetic catalyst (Ru@CS-CR@Mn) using Ru supported on ionically cross-linked CS-CR and MnFe₂O₄ nanoparticles, which displayed superior catalytic activities toward 4-NP reduction. The reduction of 4-NP only took 60 s to achieve a ~100% conversion with the TOF value of 925 h⁻¹. Furthermore, Ru@CS-CR@Mn exhibited superparamagnetic properties that allow the catalyst easy separated from the reaction medium. The Ru@CS-CR@Mn catalyst demonstrated a very consistent catalytic performance in the 4-NP reduction and was capable for at least 10 cycles, probably because of the highly active of Ru metal in the catalyst. Hence, the newly-prepared catalyst is a very efficient and stable catalyst, and thereby shows potential it could be extended for other catalytic applications.

Author Contributions: Conceptualization and methodology, K.H.L., A.F.P.; validation and formal analysis, K.H.L., A.F.P., and T.K.L.; Writing process, K.H.L. and T.K.L.; resources, T.K.L., K.S.L., C.F., and R.M.Y.; supervision, T.K.L., M.A.Y., C.F., and R.M.Y.; funding acquisition, T.K.L., M.A.Y. and R.M.Y. All authors discussed the results and commented on the manuscript.

Funding: This research was funded by Research University Grant (GUP-2016-063), Modal Insan UKM (MI-2018-002) and research grant (ST-2018-005) from Universiti Kebangsaan Malaysia.

Acknowledgments: The authors wish to thanks the supporting staffs of School of Chemical Sciences & Food Technology (PPSKTM), Fuell cell Institute (FCI) and Centre of Research and Innovation Management (CRIM) UKM for the instruments facilities.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Gazi, S.; Ananthakrishnan, R. Metal-free-photocatalytic reduction of 4-nitrophenol by resin-supported dye under the visible irradiation. *Appl. Catal. B* **2011**, *105*, 317–325. [\[CrossRef\]](#)
2. Le, X.D.; Dong, Z.P.; Liu, Y.S.; Jin, Z.C.; Huy, T.D.; Le, M.D.; Ma, J.T. Palladium nanoparticles immobilized on core-shell magnetic fibers as a highly efficient and recyclable heterogeneous catalyst for the reduction of 4-nitrophenol and Suzuki coupling reactions. *J. Mater. Chem. A* **2014**, *2*, 19696–19706. [\[CrossRef\]](#)
3. Ivancëv-Tumbas, I.; Hobby, R.; Küchle, B.; Panglisch, S.; Gimbel, R. p-Nitrophenol removal by combination of powdered activated carbon adsorption and ultrafiltration-comparison of different operational modes. *Water Res.* **2008**, *42*, 4117–4124. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Osin, O.A.; Yu, T.; Cai, X.; Jiang, Y.; Peng, G.; Cheng, X.; Li, R.; Qin, Y.; Lin, S. Photocatalytic degradation of 4-nitrophenol by C, N-TiO₂: Degradation efficiency vs. embryonic toxicity of the resulting compounds. *Front. Chem.* **2018**, *6*, 192. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Zhang, B.; Li, F.; Wu, T.; Sun, D.; Li, Y. Adsorption of p-nitrophenol from aqueous solutions using nanographite oxide. *Colloids Surf. A* **2015**, *464*, 78–88. [\[CrossRef\]](#)
6. Zhang, W.C.; Sun, Y.; Zhang, L. *In situ* synthesis of monodisperse silver nanoparticles on sulfhydryl-functionalized poly(glycidyl methacrylate) microspheres for catalytic reduction of 4-nitrophenol. *Ind. Eng. Chem. Res.* **2015**, *54*, 6480–6488. [\[CrossRef\]](#)
7. Gopalakrishnan, R.; Loganathan, B.; Dinesh, S.; Raghu, K. Strategic green synthesis, characterization and catalytic application to 4-nitrophenol reduction of palladium nanoparticles. *J. Clust. Sci.* **2017**, *28*, 2123–2131. [\[CrossRef\]](#)
8. Tan, W.L.; Abu Bakar, N.H.H.; Abu Bakar, M. Catalytic reduction of p-nitrophenol using chitosan stabilized copper nanoparticles. *Catal. Lett.* **2015**, *145*, 1626–1633. [\[CrossRef\]](#)
9. Kumar, M.; Deka, S. Multiply twinned AgNi alloy nanoparticles as highly active catalyst for multiple reduction and degradation reactions. *ACS Appl. Mater. Interfaces* **2014**, *6*, 16071–16081. [\[CrossRef\]](#) [\[PubMed\]](#)
10. Aditya, T.; Pal, A.; Pal, T. Nitroarene reduction: A trusted model reaction to test nanoparticle catalysts. *Chem. Comm.* **2015**, *51*, 9410–9431. [\[CrossRef\]](#) [\[PubMed\]](#)

11. Chairam, S.; Konkamdee, W.; Parakhun, R. Starch-supported gold nanoparticles and their use in 4-nitrophenol reduction. *J. Saudi Chem. Soc.* **2017**, *21*, 656–663. [[CrossRef](#)]
12. Wang, Y.; Li, Q.; Zhang, P.; O'Connor, D.; Varma, R.S.; Yu, M.; Hou, D. One-pot green synthesis of bimetallic hollow palladium-platinum nanotubes for enhanced catalytic reduction of p-nitrophenol. *J. Colloid Interface Sci.* **2019**, *539*, 161–167. [[CrossRef](#)] [[PubMed](#)]
13. Yin, H.; Kuwahara, Y.; Mori, K.; Che, M.; Yamashita, H. Plasmonic Ru/hydrogen molybdenum bronzes with tunable oxygen vacancies for light-driven reduction of p-nitrophenol. *J. Mater. Chem. A* **2019**, *7*, 3783–3789. [[CrossRef](#)]
14. Wang, X.; Tan, F.; Wang, W.; Qiao, X.; Qiu, X.; Chen, J. Anchoring of silver nanoparticles on graphitic carbon nitride sheets for the synergistic catalytic reduction of 4-nitrophenol. *Chemosphere* **2017**, *172*, 147–154. [[CrossRef](#)] [[PubMed](#)]
15. Anantharaj, S.; Jayachandran, M.; Kundu, S. Unprotected and interconnected Ru⁰ nano-chain networks: Advantages of unprotected surfaces in catalysis and electrocatalysis. *Chem. Sci.* **2016**, *7*, 3188–3205. [[CrossRef](#)]
16. Wang, C.; Ciganda, R.; Salmon, L.; Gregurec, D.; Irigoyen, J.; Moya, S.; Ruiz, J.; Astruc, D. Highly efficient transition metal nanoparticle catalysts in aqueous solutions. *Angew. Chem. Int. Ed.* **2016**, *55*, 3091–3095. [[CrossRef](#)] [[PubMed](#)]
17. Seth, J.; Dubey, P.; Chaudhari, V.R.; Prasad, B.L.V. Preparation of metal oxide supported catalysts and their utilization for understanding the effect of a support on the catalytic activity. *New J. Chem.* **2018**, *42*, 402–410. [[CrossRef](#)]
18. Kumar, P.V.; Namasivayam, D.; Lin, K.C.; Liu, S.B. Highly stable ruthenium nanoparticles on 3D mesoporous carbon: An excellent opportunity for the reduction reactions†. *J. Mater. Chem. A* **2015**, *3*, 23448–23457. [[CrossRef](#)]
19. Kashani, S.H.; Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Baltork, I.M. Ruthenium nanoparticles immobilized on nano-silica functionalized with thiol-based dendrimer: A nanocomposite material for oxidation of alcohols and epoxidation of alkenes. *Catal. Lett.* **2018**, *148*, 1110–1123. [[CrossRef](#)]
20. Zheng, K.; Shen, C.; Qiao, J.; Tong, J.; Jin, J.; Zhang, P. Novel magnetically-recyclable, nitrogen-doped Fe₃O₄@Pd NPs for Suzuki–Miyaura coupling and their application in the synthesis of crizotinib. *Catalysts* **2018**, *8*, 443. [[CrossRef](#)]
21. Subha, V.; Divya, K.; Gayathri, S. Applications of iron oxide nano composite in waste water treatment–dye decolourisation and anti-microbial activity. *MOJ Drug Des. Develop. Ther.* **2018**, *2*, 178–184. [[CrossRef](#)]
22. Ji, S.; Miao, C.; Liu, H.; Feng, L.; Yang, X.; Guo, H. A hydrothermal synthesis of Fe₃O₄@C hybrid nanoparticle and magnetic adsorptive performance to remove heavy metal ions in aqueous solution. *Nanoscale Res. Lett.* **2018**, *13*, 178–188. [[CrossRef](#)]
23. Jia, L.; Zhang, W.; Xu, J.; Cao, J.; Xu, Z.; Wang, Y. Facile fabrication of highly active magnetic aminoclay supported palladium nanoparticles for the room temperature catalytic reduction of nitrophenol and nitroanilines. *Nanomaterials* **2018**, *8*, 409. [[CrossRef](#)]
24. Hazarika, M.; Chinnamuthu, P.; Borah, J.P. MWCNT decorated MnFe₂O₄ nanoparticles as an efficient photo-catalyst for phenol degradation. *J. Mater. Sci. Mater. Electron.* **2018**, *29*, 12231–12240. [[CrossRef](#)]
25. Lu, A.H.; Salabas, E.L.; Schüth, F. Magnetic nanoparticles: Synthesis, protection, functionalization, and application. *Angew. Chem. Int. Ed.* **2007**, *46*, 1222–1244. [[CrossRef](#)]
26. Abdollahia, M.; Zeinalia, S.; Nasirimoghaddama, S.; Sabbaghi, S. Effective removal of As(III) from drinking water samples by chitosan-coated magnetic nanoparticles. *Desalination Water Treat.* **2015**, *56*, 2092–2104. [[CrossRef](#)]
27. Guibal, E. Heterogeneous catalysis on chitosan-based materials: A review. *Prog. Polym. Sci.* **2005**, *30*, 71–109. [[CrossRef](#)]
28. Cho, D.W.; Jeon, B.H.; Chon, C.M.; Schwartz, F.W.; Jeong, Y.J.; Song, H.C. Magnetic chitosan composite for adsorption of cationic and anionic dyes in aqueous solution. *J. Ind. Eng. Chem.* **2015**, *28*, 60–66. [[CrossRef](#)]
29. Elsupikhe, R.F.; Shameli, K.; Ahmad, M.B.; Ibrahim, N.A.; Zainudin, N. Green sonochemical synthesis of silver nanoparticles at varying concentrations of κ-carrageenan. *Nanoscale Res. Lett.* **2015**, *10*, 302–310. [[CrossRef](#)] [[PubMed](#)]

30. Pereira, C.; Pereira, A.M.; Fernandes, C.; Rocha, M.; Mendes, R.; Fernández-García, M.P.; Guedes, A.; Tavares, P.B.; Grenèche, J.M.; Araújo, J.P.; et al. Superparamagnetic MFe_2O_4 ($M = Fe, Co, Mn$) nanoparticles: Tuning the particle size and magnetic properties through a novel one-step coprecipitation route. *Chem. Mater.* **2012**, *24*, 1496–1504. [\[CrossRef\]](#)
31. Liew, K.H.; Rocha, M.; Pereira, C.; Pires, A.L.; Pereira, A.M.; Yarmo, M.A.; Juan, J.C.; Yusop, R.M.; Peixoto, A.F.; Freire, C. Highly active ruthenium supported on magnetically recyclable chitosan-based nanocatalyst for nitroarenes reduction. *ChemCatChem* **2017**, *9*, 3930–3941. [\[CrossRef\]](#)
32. Grenha, A.; Gomes, M.E.; Rodrigues, M.; Santo, V.E.; Mano, J.F.; Neves, N.M.; Reis, R.L. Development of new chitosan/carrageenan nanoparticles for drug delivery applications. *J. Biomed. Mater. Res. A* **2010**, *92*, 1265–1272. [\[CrossRef\]](#)
33. Li, C.; Hein, S.; Wang, K. Chitosan-carrageenan polyelectrolyte complex for the 512 delivery of protein drugs. *Biomaterials* **2013**. [\[CrossRef\]](#)
34. Janik, L.J.J.; Skjemstad, O.; Shepherd, K.D.; Spouncer, L.R. The prediction of soil carbon fractions using mid-infrared-partial least square analysis. *Aust. J. Soil. Res.* **2007**, *45*, 73–81. [\[CrossRef\]](#)
35. Baig, R.B.N.; Nadagouda, M.N.; Varma, R.S. Ruthenium on chitosan: A recyclable heterogeneous catalyst for aqueous hydration of nitriles to amides. *Green Chem.* **2014**, *16*, 2122–2127. [\[CrossRef\]](#)
36. Díaz-Hernández, A.; Gracida, J.; García-Almendárez, B.E.; Regalado, C.; Núñez, R.; Amaro-Reyes, A. Characterization of magnetic nanoparticles coated with chitosan: A potential approach for enzyme immobilization. *J. Nanomater.* **2018**. [\[CrossRef\]](#)
37. Rafique, M.Y.; Pan, L.Q.; Javed, Q.U.A.; Iqbal, M.Z.; Qiu, H.M.; Farooq, M.H.; Guo, Z.G.; Tanveer, M. Growth of monodisperse nanospheres of $MnFe_2O_4$ with enhanced magnetic and optical properties. *Chin. Phys. B* **2013**, *22*, 107101. [\[CrossRef\]](#)
38. Rocha, M.; Fernandes, C.; Pereira, C.; Rebelo, S.L.H.; Pereira, M.F.R.; Freire, C. Gold-supported magnetically recyclable nanocatalysts: A sustainable solution for the reduction of 4-nitrophenol in water. *RSC Adv.* **2015**, *5*, 5131–5141. [\[CrossRef\]](#)
39. Tang, S.C.; Vongehr, S.; Meng, X.K. Controllable incorporation of Ag and Ag–Au nanoparticles in carbon spheres for tunable optical and catalytic properties. *J. Mater. Chem.* **2010**, *20*, 5436–5445. [\[CrossRef\]](#)
40. Wang, C.; Yang, F.; Yang, W.; Ren, L.; Zhang, Y.; Jia, X.; Zhang, L.; Li, Y. PdO nanoparticles enhancing the catalytic activity of Pd/carbon nanotubes for 4-nitrophenol reduction. *RSC Adv.* **2015**, *5*, 27526–27532. [\[CrossRef\]](#)
41. Du, C.; Guo, Y.; Guo, Y.; Gong, X.; Lu, G. Polymer-templated synthesis of hollow Pd– CeO_2 nanocomposite spheres and their catalytic activity and thermal stability. *J. Mater. Chem. A* **2015**, *3*, 23230–23239. [\[CrossRef\]](#)
42. Saha, S.; Pal, A.; Kundu, S.; Basu, S.; Pal, T. Photochemical green synthesis of calcium-alginate-stabilized Ag and Au nanoparticles and their catalytic application to 4-nitrophenol reduction. *Langmuir* **2010**, *26*, 2885–2893. [\[CrossRef\]](#)
43. Gu, X.; Qi, W.; Xu, X.; Sun, Z.; Zhang, L.; Liu, W.; Pan, X.; Su, D. Covalently functionalized carbon nanotube supported Pd nanoparticles for catalytic reduction of 4-nitrophenol. *Nanoscale* **2014**, *6*, 6609–6616. [\[CrossRef\]](#)
44. Geng, Q.; Du, J. Reduction of 4-nitrophenol catalyzed by silver nanoparticles supported on polymer micelles and vesicles. *RSC Adv.* **2014**, *4*, 16425–16428. [\[CrossRef\]](#)
45. Fan, H.T.; Liu, X.G.; Xing, X.J.; Li, B.; Wang, K.; Chen, S.T.; Wu, Z.; Qiu, D.F. Ordered mesoporous silica cubic decorated with silver nanoparticles: A highly active and recyclable heterogeneous catalyst for the reduction of 4-nitrophenol. *Dalton Trans.* **2019**, *48*, 2692–2700. [\[CrossRef\]](#)
46. Ansar, S.M.; Kitchens, C.L. The Impact of Gold Nanoparticle Stabilizing Ligand on Colloidal Catalytic Reduction of 4-Nitrophenol. *ACS Catal.* **2016**, *6*, 5553–5560. [\[CrossRef\]](#)
47. Calvo, P.; Remunan-Lopez, C.; Vila-Jato, J.L.; Alonso, M.J. Novel hydrophilic chitosan-polyethylene oxide nanoparticles as protein carriers. *J. Appl. Polym. Sci.* **1997**, *63*, 125–132. [\[CrossRef\]](#)

