**ABSTRACT:** The preparation of reusable and eco-friendly materials from renewable biomass resources such as cellulose is an inevitable choice for sustainable development. In this work, cellulose was dissolved in 7 wt % NaOH/12 wt % urea aqueous solution at −12 °C with rapid stirring. Cellulose microspheres (Cels) were fabricated by a sol–gel transition method. Subsequently, novel magnetic Ag–Fe₃O₄ nanoparticles (NPs) supported on cellulose microspheres were successfully constructed by an *in situ* one-pot synthesis. The magnetic cellulose microspheres (MCels) displayed a spherical shape with mesoporous structure and had a narrow particle size distribution (10–20 μm). Many nanopores with a pore diameter of 5–40 nm were observed in MCels. The Ag–Fe₃O₄ NPs were immobilized by anchoring with the hydroxyl groups on the surface of Cels. MCels were applied as a microreactor to evaluate their catalytic activities. 4-Nitrophenol (4-NP) could be reduced to 4-aminophenol (4-AP) in 5 min, catalyzed by MCels. Moreover, the magnetic microspheres exhibited a small hysteresis loop and low coercivity. Thus, MCels could be quickly gathered in water under a magnetic field in 10 s, as well as almost 9 cycle times, maintaining relatively high catalytic activity. In this work, cellulose matrix as the catalyst support could be biodegraded completely in the environment. It provided a green process for the utilization of biomass in nanocatalytic applications.

**INTRODUCTION**

With an excessive consumption of nondegradable synthetic polymers, the ecological environment has suffered from irreparable damage and the concepts of sustainable and green development have caught public attention, especially in catalysis.¹,² Since they achieve perfect dispersion instead of aggregation, supported nanometallic catalysts with high specific surface areas (SSAs) have been employed to dramatically enhance the catalytic efficiency.³,⁴ To achieve this, porous matrices with large surface areas as well as mechanical and chemical stability are regarded as ideal candidates for the immobilization of metal catalyst NPs, such as metal oxides, metal–organic frameworks (MOFs), porous silica, and carbon-based materials (carbon nanofibers, carbon nanotubes, activated carbon, graphene oxide).⁵–¹¹ However, the high input cost, the complex preparation process, and non-degradability largely limit the extensive application of these porous materials.¹²,¹³ Considering the environmental deterioration and economic pressures, it remains a challenge to search for sustainable, biodegradable, and easily available materials to fabricate nanosized catalysts through simple and green methods.¹⁰

In recent years, biomass is attracting intensive interest as support for nanocatalysts based on their porous structure and plentiful active sites to immobilize the metal nanoparticles (NPs).⁷,¹⁴–¹⁶ Especially, cellulose as the most abundant biomass has been vigorously studied for the stabilization of metal catalyst NPs.¹⁷–²¹ For instance, Li et al. synthesized polydopamine-functionalized porous cellulose acetate microspheres with Ag–Fe₃O₄ nanoparticles supported on them.¹⁷ A cellulose-based nanocatalyst with bimetallic Fe–Cu NPs immobilized on microporous cellulose was used for quick reduction of diverse nitroarenes to amines with NaBH₄ in water within 5–14 min to afford excellent yields of products.¹² Moreover, cellulose can be directly converted into various materials through the green NaOH/urea aqueous system.¹³–²¹ Thus, we attempted to fabricate an easily recyclable cellulose-based catalyst by means of an NaOH/urea aqueous system.

Based on the above issues, a recyclable cellulose microsphere was fabricated from NaOH/urea–cellulose solution via a low-cost and energy-efficient method, namely sol–gel transition (SGT). Ag–Fe₃O₄ NPs were immobilized onto cellulose microspheres by an *in situ* redox reaction to generate a magnetic nanocatalyst. The hydrogenation of 4-NP was employed to investigate the catalytic activity and recycling...
performance of Ag–Fe₃O₄@Cels. It was not difficult to speculate that the regenerated cellulose microspheres with large specific surface areas, strong polarity, porosity, and abundant hydroxyl groups would be suitable for immobilizing and constructing functional nanocomposites for catalysis. The exploitation of cellulose from a renewable and natural biomass resource directly to fabricate novel and porous microspheres through environmentally friendly processes would be significant for green chemistry and sustainable strategies.

**RESULTS AND DISCUSSION**

A mechanism was proposed to present the probable formation process of MCels as given in Scheme 1. Large amounts of −OH groups were observed on the surface and in the pores of cellulose spheres. Fe²⁺ could be easily captured by −OH groups through strong chelation onto the surface. Following the addition of NaOH, Fe²⁺ was quickly transformed into Fe(OH)₂ particles fastened to the surface or the pores of Cels. Along with the addition of the final solution containing Ag⁺, Ag₂O was formed in the alkaline solution. Subsequently, the Ag and Fe₃O₄ nanoparticles were generated via the in situ redox reaction between Fe(OH)₂ and Ag₂O. Thus, the Ag–Fe₃O₄@Cels, namely MCels, were fabricated by the following reactions:

\[
\text{Fe}^+ + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 \tag{1}
\]
\[
2\text{Ag}^+ + 2\text{OH}^- \rightarrow \text{Ag}_2\text{O} + \text{H}_2\text{O} \tag{2}
\]
\[
2\text{Ag}_2\text{O} + 6\text{Fe(OH)}_2 \rightarrow 2\text{Fe}_3\text{O}_4 + 4\text{Ag} + 6\text{H}_2\text{O} \tag{3}
\]

The FTIR results (Figure S1) showed that the intensity of the OH band was less evident for MCels than for Cels. It was because the oxygen-containing functional groups in Cels (C−OH) were active in immobilizing the Ag–Fe₃O₄ NPs by electrostatic action, which was quite important for the uniform dispersion of Ag–Fe₃O₄ NPs. Cels exhibited a regular spherical structure with a mean diameter of 12.6 ± 8.6 μm, exhibiting good dispersity (Figure 1a,b). After the construction of MCels, as shown in Figure 1d, a layer of nontransparent substance accumulated around and on the surface of Cels. Unlike Cels, the surface of the MCels was quite rough due to the impregnation of Ag and Fe₃O₄ NPs on the surface. Figure 2d shows the relatively uniform distribution of Ag and Fe₃O₄ NPs on the surface of Cels, which was identified by XRD. The formation of Ag and Fe₃O₄ NPs contributed to the immobilization of Fe²⁺ and Ag⁺ in the pores or channels of surface. The partially enlarged image of Cels in Figure 2b suggested that there were lots of pores on the surface. The SEM image of MCels in Figure 2c showed a spherical morphology without any obvious change compared with Cels. Unlike Cels, the surface of the MCels was quite rough due to the impregnation of Ag and Fe₃O₄ NPs on the surface. Figure 2d shows the relatively uniform distribution of Ag and Fe₃O₄ NPs on the surface of Cels, which was identified by XRD. The formation of Ag and Fe₃O₄ NPs contributed to the immobilization of Fe²⁺ and Ag⁺ in the pores or channels of...
Cels through the chelation with hydroxyl groups of cellulose molecules and the in situ redox reaction between Fe(OH)$_2$ and Ag$_2$O.

The porous structure of Cels and MCels has been proved by the results of SEM. N$_2$ adsorption/desorption was employed to further investigate the pore surface area and pore size of Cels and MCels. The N$_2$ adsorption/desorption isotherms and BJH pore-size distribution of Cels, MCels-15, MCels-30, MCels-45, and MCels-60 are presented in Figure 3. The results shown in Figure 3a revealed the existence of an H3 hysteresis loop since the adsorption curve was parallel to the relative pressure for the most part, and the surface areas of Cels, MCels-15, MCels-30, MCels-45, and MCels-60 were 198.2, 112.8, 102.3, 93.6, and 86.2 m$^2$·g$^{-1}$, respectively. The results shown in Figure 3b indicated the presence of an obvious hierarchical porous architecture both in Cels and in MCels with the pore size ranging from 5 to 40 nm, suggesting that MCels retained the nanosized pores after the deposition of Ag and Fe$_3$O$_4$ NPs. The reduced surface area and the peak intensity in the pore-size distribution of MCels compared with the raw Cels were attributed to the occupation of the pores on the cellulose microsphere matrix by Ag and Fe$_3$O$_4$ nanospecies during the immobilization process. It could also be confirmed by the high-resolution SEM images (Figure 2d).

TEM characterization was performed to characterize the morphologies of the Ag and Fe$_3$O$_4$ nanospecies on the surface of cellulose microspheres. Figure 4 displays the TEM images for MCels-15 (a), MCels-30 (b), MCels-45 (c), and MCels-60 (d). The particle size distribution of Ag–Fe$_3$O$_4$ NPs in MCels-15 (e), MCels-30 (f), MCels-45 (g), and MCels-60 (h). HRTEM image with lattice fringe marks (i) and the EDS spectrum (j) of MCels-30.

![Figure 3. N$_2$ adsorption/desorption isotherms (a) and BJH pore-size distribution (b) of Cels, MCels-15, MCels-30, MCels-45, and MCels-60.](image)

![Figure 4. TEM images of MCels-15 (a), MCels-30 (b), MCels-45 (c), and MCels-60 (d). The particle size distribution of Ag–Fe$_3$O$_4$ NPs in MCels-15 (e), MCels-30 (f), MCels-45 (g), and MCels-60 (h). HRTEM image with lattice fringe marks (i) and the EDS spectrum (j) of MCels-30.](image)
specific crystal lattices for Ag and Fe3O4 nanoparticles were recorded by a high-resolution TEM (HRTEM), as shown in Figure 4i,j. The lattice spacings of 0.236 and 0.253 nm belonged to the (111) lattice plane of Ag and the (311) lattice plane of Fe3O4, respectively.26 The corresponding energy-dispersive spectrum (EDS) result also confirmed the presence of Ag and Fe elements.

The valence state and chemical environment of the main elements on the surface of MCels were determined by XPS. In the results of the fully scanned spectra from 100 to 800 eV shown in Figure 5a, C, O, Ag, and Fe were detected in MCels, while only C and O were found in raw cellulose spheres. Figure 5b shows the Ag 3d spectra at 374.13 and 368.13 eV, which are assigned to Ag 3d3/2 and Ag 3d5/2 peaks, respectively.27 The two peaks were consistent with the reported characteristic Ag0 peaks, indicating the existence of Ag. As shown in Figure 5c, the two peaks at 724.13 and 710.83 eV correspond to the binding energies of Fe 2p1/2 and Fe 2p3/2, respectively, suggesting the production of Fe2O3. It is worth noting that the binding energies of Fe were lower than the reported typical data of Fe2O3 at 725.0 and 711.5 eV.28 Interestingly, the binding energies of C 1s (284.68 eV) and O 1s (530.03 eV) in MCels displayed a positive shift to higher regions compared with Cels (286.63 and 532.98 eV), as presented in Figure 5d,e. This may be due to the electron transfer from C and O to Fe, leading to a decrease in the binding energy of Fe, but an increase in those of C and O. The results regarding the change in binding energies of C, O, and Fe proved that Fe2+ was anchored with C−OH in cellulose spheres, resulting in the successful immobilization of Ag and Fe3O4 nanoparticles. Figure 5d displays the high-resolution deconvolution of C 1s peaks of Cels and MCels. Cels have three peaks at 287.88, 286.63, and 284.78 eV corresponding to C3 (O−C=O and/or C=O), C2 (C−O), and C1 (C=C or C−H).29 The three peaks in the C 1s spectra of MCels remarkably shifted to a lower binding energy resulting from the stabilization of Fe3+ on C−OH in cellulose spheres. An obvious difference in the O 1s spectra was also detected between Cels and MCels due to the immobilization of Fe3+ by the −OH group on the surface of cellulose and the formation of Fe−O or Fe=O. These results indicated the successful immobilization of Fe3O4 and Ag NPs on the surface of Cels.

The recycling performance was decided by the magnetic properties of MCels, which were evaluated by VSM. The curves shown in Figure 6a for the four types of MCels indicated that the magnetization of MCels was remarkably increased with the increase in the loading amounts of Ag and Fe3O4 nanoparticles. In spite of the low intensity of magnetization of all samples, they presented a very small magnetic hysteresis loop and weak coercive force, demonstrating...
ing superparamagnetism. The values of saturation magnetization for MCels-15, MCels-30, MCels-45, and MCels-60 achieved from the hysteresis loops were 23.63, 36.30, 43.09, and 45.08 emu·g⁻¹, respectively, as determined by the amounts of Fe₃O₄. To directly observe the magnetic properties and recycling performance of MCels, a magnet was employed to collect and recycle the magnetic spheres dispersed in water (Figure 6b), by placing it beside the bottle, as shown in Figure 6c. The MCels could be rapidly gathered by an external magnetic field in about 10 s, accounting for the excellent magnetic responsiveness of MCels. Apart from recycling, the reuse of MCels could also be realized through a magnet, thus proving it to be a sustainable material.

Ag NPs supported on porous materials usually act as effective catalysts in many reactions. Here, the reduction reaction of 4-NP to 4-AP with excessive NaBH₄ was chosen as the model reaction to estimate the catalytic activity of MCels. Generally, the maximum absorption wavelength of 4-NP is observed at 317 nm in the UV–vis spectrum, while this value for a mixed solution of 4-NP and NaBH₄ moved to a longer wavelength of 400 nm. As presented in Figure 7a, when the as-prepared MCels-45 (50 mg·L⁻¹) was added into the mixed solution of 4-NP and NaBH₄, the absorption intensity of 4-NP sharply declined within 1 min and a new absorption peak was observed at 303 nm, attributed to the generation of 4-AP. After 5 min, no obvious absorption peak was observed at 400 nm related to 4-NP, indicating that the reaction was almost complete. The reaction time was significantly shorter than that of the Ag nanocatalyst stabilized on another matrix because most Ag nanoparticles were generated on the surface of Cels, reducing the diffusion time with the reaction solution. Comparison of the reaction conversion between different catalysts was done using the ratio C/C₀, which was calculated by the ratio of the absorbance intensity (A/A₀) of 4-NP. C represents the residual concentration of 4-NP after a certain time, and C₀ represents the initial concentration of 4-NP. For the sake of comparison and analysis, a control experiment was applied in which raw Cels with no Ag and Fe₃O₄ nanoparticles acted as the catalyst. The curves in Figure 7b demonstrated a slower decrease for MCels-15 and MCels-30, while a rapid decrease for MCels-45 and MCels-60 in the reaction conversion. This result indicates that the concentration of Ag in the Ag–Fe₃O₄ NPs immobilized on the surface of Cels (see Figure S3) plays an important role in the catalytic efficiency. The reusability and cycle times of MCels were significant for their application. Figure 7c shows the reaction conversion of 4-NP by MCels-30 for different cycle times. The conversion of 4-NP increased when increasing the reaction time in every recycle, while the catalytic activity of MCels decreased after several cycles. When reused three times, C/C₀ increased only by 0.10, indicating that the MCels showed no obvious loss of catalytic activity with the stable immobilization of Ag and Fe₃O₄ nanospecies and the perfect recycling property. After recycling 9 times, the MCels maintained relatively high catalytic activity. Besides, MCels showed good thermostability because there was no decomposition of MCels below 200 °C.

### CONCLUSIONS

Recyclable and magnetic cellulose microspheres have been successfully fabricated via the sol–gel method. Uniform Ag and Fe₃O₄ nanospecies with mean diameters of 40–50 nm were immobilized in the pores and on the surface of cellulose spheres through in situ synthesis. The hydroxyl groups distributed on the surface or in the pores of cellulose spheres acted as binding sites to capture Ag and Fe₃O₄ nanospecies. Magnetic cellulose spheres were confirmed to be excellent catalysts for the conversion of 4-NP to 4-AP, as well as showing good cyclic and reusable performance. The successful fabrication and application of recyclable and biodegradable cellulose spheres immobilizing Ag nanoparticles provided a significant research approach for the design of supported metal catalysts immobilized on porous biomass materials in a green and sustainable way.

### EXPERIMENTAL SECTION

**Materials.** Raw cellulose (cotton linter pulp, DP = 500) was obtained from Hubei Chemical Fiber Co. Ltd. China. Silver nitrate, sodium hydrate, and urea and other chemicals used in this work were purchased from Sinopharm Chemical Reagent Co. Ltd, China, and were of analytical reagent grade. All of the chemicals and reagents were used directly without further treatment.

**Preparation of the Cellulose Microspheres.** The regenerated cellulose microspheres were prepared by the sol–gel method in accordance with the literature. Typically, 4 g of raw cellulose was immediately and completely immersed in the precooled (~12 °C) 100 mL solvent containing 7% NaOH/12% urea/81% H₂O (by weight) under vigorous stirring for 5 min to obtain a transparent cellulose solution. Then, the cellulose solution was centrifuged at 7000 rpm for 15 min at 4 °C to degas and remove the insoluble impurities. 1.5 mL epichlorohydrin (ECH) was dropped into the as-degassed cellulose solution with stirring at 800 rpm for 2 h at ~10 °C to obtain a pre-cross-linked cellulose solution. A well-mixed suspension containing 300 g of isooctane and 60 g of Span 80 was dispersed in a reactor. The achieved suspension was stirred at 800 rpm for 30 min at 0 °C. Subsequently, 60 g of the pre-cross-linked cellulose solution was dropped into the suspension at 0 °C. After stirring for 30 min, the ice bath was removed.
removed and the suspension was stirred for another 3 h at room temperature to form regenerated cellulose microspheres. After removing the upper oil phase, almost 60 mL of regenerated cellulose microspheres in the substratum was fabricated and coded as Cels. The prepared cellulose microspheres were washed with ethyl alcohol and then with water three times to remove the residual isooctane, Span 80, NaOH, and urea. Finally, the as-prepared microspheres were freeze-dried and stored for further use.

**Fabrication of the Magnetic Ag–Fe3O4@Cels.** The fabrication of Ag and Fe3O4 NPs in the Ag–Fe3O4@Cels was based on the in situ redox reaction between Ag2O and Fe(OH)3 with coprecipitation according to the methods in the literature. A certain amount of FeCl2·4H2O dissolved in water. Then, the cellulose microspheres were immersed in the resultant aqueous solution. The suspension was stirred for 1 h under a nitrogen atmosphere at room temperature. Subsequently, the suspension was heated to 90 °C and the desired amount of 1 M NaOH aqueous solution was added rapidly. Finally, the mixture was stirred in air at 90 °C for 2 min after dropping into a given mass of 10 mM AgNO3 aqueous solution. The generated magnetic Ag–Fe3O4@Cels were named MCels. The MCels were coded as MCels-15, MCels-30, MCels-45, and MCels-60, according to the different amounts of FeCl2·4H2O at 15, 30, 45, and 60 mmol, corresponding to the dosages of 1 M NaOH and 0.0424 g·mL−1 AgNO3 being 5/2.5, 10/5, 15/7.5, and 20/10 mL, respectively. The MCels were washed with deionized water until attaining neutrality and were freeze-dried before use.

**Characterization.** The optical photomicrographs of cellulose microspheres were recorded on a laser scanning confocal microscope (FV120, OLYMPUS, Japan) with the samples dispersed in water. Fourier transform infrared (FTIR) spectra of cellulose microspheres were obtained using a Nicolet FTIR spectrometer (Nicolet NEXUS 670) with a wavelength range of 4000–400 cm−1. The KBr-disk method was applied for the preparation of the tested samples. Wide-angle X-ray diffraction (XRD) measurements were carried out on a WAXD diffractometer (Empyrean, PANalytical, the Netherlands) with Cu Kα radiation (λ = 0.15405 nm) at 40 kV and 30 mA. The samples were scanned in the region of 2θ = 5–80° at a rate of 2° min−1. Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) of Cels and MCels were recorded on a Pyris TGA linked to a Pyris diamond TA Lab System (PerkinElmer Co.) at a heating rate of 10 °C·min−1 from 30 to 700 °C under an air atmosphere. X-ray photoelectron spectra (XPS) were measured with a Thermo K-Alpha+ X-ray photoelectron spectrometer with Al Kα radiation as the radiation source at 15 kV and 10 mA. The surface microscopy of microspheres was achieved on an FESEM (FEI Quanta 650) with an accelerating voltage of 20 kV. The freeze-dried Cels and MCels were sputtered with gold before characterization. The high-resolution transmission electron microscopy (HRTEM) images were obtained by a Tecnai G2 F20 S-TWIN (FEI) microscope at 200 kV. The particle size of nanoparticls in the TEM image was counted by the Nano Measurer software. The energy-dispersive spectrum (EDS) was achieved by scanning from B5 to U92 with a resolution of 130 eV. The samples for HRTEM were ultrasonically dispersed in absolute ethyl alcohol for 20 min before being dropped on the copper net and sputtered with carbon for the test. The definite particle size and size distribution of the microspheres were recorded on an MS 3000 laser particle size analyzer (Malvern, U.K.) with about 0.1 g of microspheres dispersed in 500 mL water. Nitrogen physisorption properties at 77 K were measured using Micromeritics ASAP 2020 (USA). Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) analyses were done using software. Before the characterization, the microspheres were dried at 150 °C for 6 h in a vacuum to remove the water absorbed by the microspheres. BET analysis was performed for relative vapor pressures of 0.05–0.3. The BJH analysis was performed from the desorption branch of the isotherms. The magnetic properties of MCels were analyzed with a vibrating sample magnetometer (VSM, PPMS-9, Quantum Design) at 25 °C, and the hysteresis loop was measured in a magnetic field from −1 to +1 T. The catalytic activity of MCels was measured using UV–vis absorption spectra (UV-6, Shanghai Meipuda Instrument Co., Ltd., Shanghai, China).

**Catalytic Activity Evaluation.** The reduction of 4-NP at 25 °C was selected as a model reaction to evaluate the catalytic activity of MCels. Specifically, the aqueous dispersion of MCels (1.5 mL, 50 mg·L−1) was mixed with fresh NaBH4 aqueous solution (0.75 mL, 0.4 M). Subsequently, 4-NP aqueous solution (0.75 mL, 4 × 10−4 M) was added into the above mixture. The performance of the catalytic reaction was observed at certain time intervals. The control experiments were studied in identical conditions except that MCels were replaced with Cels. To investigate the recycling of the Mcel catalysts, a strong magnet was used to separate the catalysts from the reaction system. The recycled MCels were washed three times with ethanol and dried at room temperature for the next catalytic run.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00437.

**FTIR spectrum of Cels; XRD spectra of Cels and MCels-30; TGA (a) and DTG (b) curves of Cels, MCels-15, MCels-30, MCels-45, and MCels-60 (PDF)**

### AUTHOR INFORMATION

**Corresponding Authors**

Jie Cai – Key Laboratory for Deep Processing of Major Grain and Oil, College of Food Science and Engineering, Wuhan Polytechnic University, Wuhan 430023, China; Email: caijievip@hotmail.com

Ang Lu – College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China; orcid.org/0000-0001-6457-8264; Email: anglu@whu.edu.cn

Ying Pei – School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China; orcid.org/0000-0001-9631-3738; Email: peiying@zzu.edu.cn

**Authors**

Guozhen Wang – Key Laboratory for Deep Processing of Major Grain and Oil, College of Food Science and Engineering, Wuhan Polytechnic University, Wuhan 430023, China; orcid.org/0000-0002-2479-084X

Fei Li – Key Laboratory for Deep Processing of Major Grain and Oil, College of Food Science and Engineering, Wuhan Polytechnic University, Wuhan 430023, China
Lan Li — Key Laboratory for Deep Processing of Major Grain and Oil, College of Food Science and Engineering, Wuhan Polytechnic University, Wuhan 430202, China

Jiayu Zhao — Key Laboratory for Deep Processing of Major Grain and Oil, College of Food Science and Engineering, Wuhan Polytechnic University, Wuhan 430202, China

Xinxuan Ruan — Key Laboratory for Deep Processing of Major Grain and Oil, College of Food Science and Engineering, Wuhan Polytechnic University, Wuhan 430202, China

Wenping Ding — Key Laboratory for Deep Processing of Major Grain and Oil, College of Food Science and Engineering, Wuhan Polytechnic University, Wuhan 430202, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c00437

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work was supported by the Natural Science Foundation of Hubei Province of China (2019CBF333), the Open Foundation of Key Laboratory for Deep Processing of Major Grain and Oil (Wuhan Polytechnic University), the Ministry of Education (2018JBYGDKFB05 and 2018JBYQDGFKA01), the Young Elite Scientists Sponsorship Program by CAST (2018QNRC001), and the Chutian Scholar Program of Hubei Provincial Government, China.

REFERENCES

(1) Chen, L. H.; Zhu, J. Y.; Baez, C.; Kitin, P.; Elder, T. Highly thermal-stable and functional cellulose nanocrystals and nanofibrils produced using fully recyclable organic acids. Green Chem. 2016, 18, 3835–3843.

(2) Voitko, K. V. Asymmetric catalysis under 1D/2D nanostructured carbon materials. J. Nanosci. Nanotechnol. 2019, 19, 5074–5088.

(3) Chughtai, A. H.; Ahmad, N.; Younus, H. A.; Laypakov, A.; Verpoort, F. Metal-organic frameworks: versatile heterogeneous catalysts for efficient catalytic organic transformations. Chem. Soc. Rev. 2015, 44, 6804–6849.

(4) Chen, S. J.; Fu, H. B.; Zhang, L.; Wan, Y. Nanospherical mesoporous carbon-supported gold as an efficient heterogeneous catalyst in the elimination of mass transport limitations. Appl. Catal., B 2019, 248, 22–30.

(5) Cyganowski, P.; Lesniewicz, A.; Dzmitrowicz, A.; Wolska, J.; Pohl, P.; Jermakowicz-Bartkowiak, D. Molecular reactors for synthesis of polymeric nanocomposites with noble metal nanoparticles for catalytic decomposition of 4-nitrophenol. J. Colloid Interface Sci. 2019, 541, 226–233.

(6) Pei, X. L.; Deng, Y.; Duan, B.; Chan, T. S.; Lee, J. F.; Lei, A. W.; Zhang, L. N. Ultra-small Pd clusters supported by chitin nanowires as highly efficient catalysts. Nano Res. 2018, 11, 3145–3153.

(7) Baran, N. Y.; Baran, T.; Mentes, A. Production of novel palladium nanocatalyst stabilized with sustainable chitosan/cellulose composite and its catalytic performance in Suzuki-Miyaura coupling reactions. Carbohydr. Polym. 2018, 181, 596–604.

(8) Wang, S. G.; Zhang, Z. H.; Liu, B.; Li, J. L. Silica coated magnetic FeO nanoparticles supported phosphotungstic acid: a novel environmentally friendly catalyst for the synthesis of ethoxymethylfurural from H-ethoxymethylfurural and fructose. Catal. Sci. Technol. 2013, 3, 2104–2112.

(9) Das, R.; Sypa, V. S.; Paumo, H. K.; Bhattachar, M.; Maharaj, V.; Maiti, A. Silver decorated magnetic nanocomposite (FeO@PPy-MAA/Ag) as highly active catalyst towards reduction of 4-nitrophenol and toxic organic dyes. Appl. Catal., B 2019, 244, 546–558.

(10) Hodnik, N.; Baldizzone, C.; Polymeros, G.; Geiger, S.; Grote, J. P.; Cherevko, S.; Mingers, A.; Zerahdjian, A.; Mayrhofer, K. J. Platinum recycling going green via induced surface potential alteration enabling fast and efficient dissolution. Nat. Commun. 2016, 7, No. 13164.

(11) Liu, Y.; Wang, X. P.; Chen, C.; Li, L.; Yu, H. L.; Wu, Q.; Xie, C. X.; Yu, S. T.; Liu, S. W. Hydrogenation of Rosin to hydrogenated rosin by Ru/FeO@C Magnetic Catalyst. Catal. Lett. 2018, 148, 3147–3157.

(12) Duan, B.; Huang, Y.; Lu, A.; Zhang, L. N. Recent advances in chitin-based materials constructed via physical methods. Prog. Polym. Sci. 2018, 82, 1–33.

(13) Cai, J.; Zhou, R.; Li, T. T.; He, J. R.; Wang, G. Z.; Wang, H. B.; Xiong, H. G. Bamboo cellulose-derived cellulose acetate for electropinning nanofibers: synthesis, characterization and kinetics. Cellulose 2018, 25, 391–398.

(14) Wang, G.; Chen, Y.; Xu, G.; Pei, Y. Effective removing of methylene blue from aqueous solution by tannins immobilized on cellulose microfibers. Int. J. Biol. Macromol. 2019, 129, 198–206.

(15) Abdulwahab, M. I.; Khamkewat, A.; Jongsomjit, B.; Phisalaphong, M. Bacterial Cellulose Supported Alumina Catalyst for Ethanol Dehydration. Catal. Lett. 2017, 144, 2462–2472.

(16) Rodrigues, D. M.; Hunter, L. G.; Bernard, F. L.; Rojas, M. F.; Dalla Vecchia, F.; Einloft, S. Harnessing CO2 into Carbanones Using Heterogeneous Waste Derivative Cellulose-Based Polymeric liquids as Catalysts. Catal. Lett. 2019, 149, 733–743.

(17) Peng, S.; Gao, F.; Zeng, D.; Peng, C.; Chen, Y. M.; Li, M. Synthesis of Ag-FeO nanoparticle supported on polydopamine-functionalized porous cellulose acetate microspheres: catalytic and antibacterial applications. Cellulose 2018, 25, 4771–4782.

(18) Guo, L.; Duan, B.; Zhang, L. N. Construction of controllable size silver nanoparticles immobilized on nanofibers of chitin microspheres via green pathway. Nano Res. 2016, 9, 2149–2161.

(19) Maleki, A.; Movahed, H.; Ravaghi, P. Magnetic cellulose/Ag as a novel eco-friendly nanobiocomposite to catalyze synthesis of chromene-linked nicotinonitriles. Carbohydr. Polym. 2017, 156, 259–267.

(20) Shojaei, S.; Ghasemi, Z.; Shahrisa, A. Cu(I)@Fe3O4 nanoparticles supported on imidazolium-based ionic liquid-grafted cellulose: Green and efficient nanocatalyst for multicomponent synthesis of N-sulfonylamidines and N-sulfonylacrylamidines. Appl. Organomet. Chem. 2017, 31, No. e3788.

(21) Pei, Y. L.; Zhao, J. X.; Shi, R. N.; Wang, X. H.; Li, Z.; Ren, J. Hierarchical Porous Carbon-Supported Copper Nanoparticles as an Efficient Catalyst for the Dimethyl Carbonate Synthesis. Catal. Lett. 2019, 149, 3184–3193.

(22) Karami, S.; Zeynizadeh, B.; Shokri, Z. Cellulose supported bimetallic Fe-Cu nanoparticles: a magnetically recoverable nano-catalyst for quick reduction of nitroarones to amines in water. Cellulose 2018, 25, 3295–3305.

(23) Cai, J.; Liu, Y. T.; Zhang, L. N. Dilute solution properties of cellulose in LiOH/urea aqueous system. J. Polym. Sci., Part B: Polym. Phys. 2006, 44, 3093–3101.

(24) Wang, G. Z.; Meng, Y.; Zhou, J. P.; Zhang, L. N. Selective hydrothermal degradation of cellulose to formic acid in alkaline solutions. Cellulose 2018, 25, 5659–5668.

(25) Luo, X. G.; Liu, S. L.; Zhou, J. P.; Zhang, L. N. In situ synthesis of FeO/cellulose microspheres with magnetic-induced protein delivery. J. Mater. Chem. 2009, 19, 3538–3545.

(26) Lu, W. S.; Shen, Y. H.; Xie, A. J.; Zhang, W. Q. Green synthesis and characterization of superparamagnetic FeO nanoparticles. J. Magn. Magn. Mater. 2010, 322, 1828–1833.

(27) Subash, B.; Krishnakumar, B.; Swaminathan, M.; Shanthy, M. Highly efficient, solar active, and reusable photocatalyst: Zr-loaded Ag-ZnO for reactive red 120 dye degradation with synergistic effect and dye-sensitized mechanism. Langmuir 2013, 29, 939–949.

(28) Cheng, F. Y.; Su, C. H.; Yang, Y. S.; Yeh, C. S.; Tsai, C. Y.; Wu, C. L.; Wu, M. T.; Shieh, D. B. Characterization of aqueous dispersions of FeO nanoparticles and their biomedical applications. Biomaterials 2005, 26, 729–738.
(29) Österberg, M.; Peresin, M. S.; Johansson, L. S.; Tammelin, T. Clean and reactive nanostructured cellulose surface. *Cellulose* 2013, 20, 983−990.

(30) Xu, D. F.; Chen, C. J.; Xie, J.; Zhang, B.; Miao, L.; Cai, J.; Huang, Y. H.; Zhang, L. N. A hierarchical N/S-codoped carbon anode fabricated facilely from cellulose/polyaniline microspheres for high-performance sodium-ion batteries. *Adv. Energy Mater.* 2016, 6, No. 1501929.

(31) Xu, D. F.; Xiao, X.; Cai, J.; Zhou, J.; Zhang, L. N. Highly rate and cycling stable electrode materials constructed from polyaniline/cellulose nanoporous microspheres. *J. Mater. Chem. A* 2015, 3, 16424−16429.