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Electrospun Cellulose Nanofiber Composites in Catalysis: A Review

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Abstract: Although there are many methods of fabricating nanofibers, electrospinning has become a very widespread method for the achieving nanofibers in low cost and simple manner. Nanofiber and its composites are found to be the efficient in many research fields such as filters, medicine, sensors, energy and so on. Due to high specific surface area to volume ratio, nanofibers show high activity in catalysis. The advantages are mainly due to the diameter–length proportion. So far, there are various electrospun nanofibers and composites are utilized. Carbon fiber, cellulose nanofiber, polyurethane based nanofibers are used either as spun or in the form of composites. Among them, cellulose and carbon nanofibers are investigated widely due to its chemical stability in organic solvents. In this review article, we mainly focus on the preparation, characterization and catalytic organic reactions of electrospun nanofiber (composites) derived from regenerated cellulose nanofiber.

Keywords: nanofibers; electrospinning; catalysis; organic reactions; cellulose; composite

1. Introduction

Electrostatic fiber fabrication, also known as “electrospinning”, has emerged as the most preferred choice for producing continuous fibers with diameters below 1 µm.[1-3] Both synthetic, natural polymers and co-polymers are successfully electrospun. Natural polymers such as collagen, cellulose, silk fibroin, keratin, gelatin and polysaccharides (chitosan, alginate) are used to prepare the corresponding electrospun nanofibers by electrospinning.[4-9] Similarly, a large number of biocompatible and biodegradable synthetic polymers, such as polycaprolactone (PCL), poly(lactic acid) (PLA), polypropylene (PP), polyvinylpyrrolidone (PVP), polystyrene (PS), polyvinyl alcohol (PAN), polyvinylidene fluoride (PVDF), Polyurethane (PU), polyvinyl alcohol (PVA), and poly(lactic-co-glycolic acid) (PLGA), have been directly electrospun into nanofibers.[10-13] The electrospun nanofibers and their composites are used in various application such as catalysis, energy, biomedical, sensors, filters and so on. In fact, the structure of nanofibers is highly unique, and they possess very high specific surface area.[14-21]

Fig. 1 shows the schematic diagram of a conventional electrospinning setup. A typical electrospinning setup is mainly composed of a high-voltage power supply, a needle spinneret, and a grounded conductive collector. Electrospinning process is based on the uniaxial stretching or elongation of a viscoelastic jet derived from a polymer solution. The electrospinning process mainly involves strong electrostatic force as the driving force for initiating the electrospinning process.[22-25]

During the electrospinning process, when high voltage is supplied, the polymer solution droplet at the needle tip deforms into a cone shape (generally called a Taylor cone) under the electrostatic forces.[26] The electrostatic repulsion counteracts the surface tension, while the coulomb forces are exerted by the external electric field.[27] The electrified jet will experience stretching and thrashing process to be deposited on the counter-electrode in formation of continuous and uniform nanofibres. Herein we have focused only electrospun cellulose nanofibers and their composites as catalysts in heterogeneous organic catalytic reactions. In fact, both the functionalized cellulose nanocomposite nanofibers are widely utilized as support materials for decoration of active catalytic species. The surface of cellulose nanofibers can be easily modified and the stability of the fiber in various organic solvents is also attractive (due to the existence of multiple hydrogen bonds). Moreover, the biocompatibility of the cellulose nanofiber is very good when compare to carbon fibers. Good spinnability of the cellulose acetate polymer makes it possible for the development of mass production, which is highly important in industrial applications.

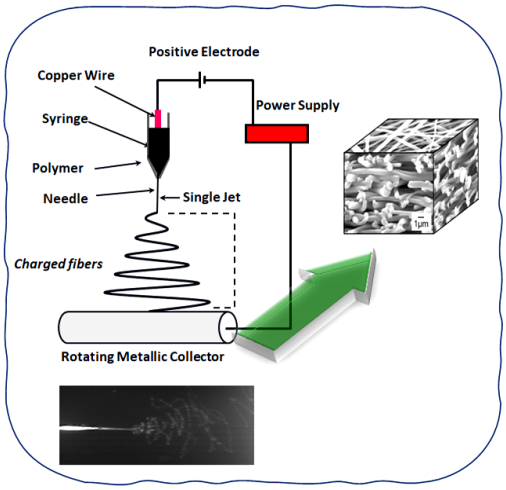


Fig. 1. Schematic diagram of a conventional electrospinning setup.

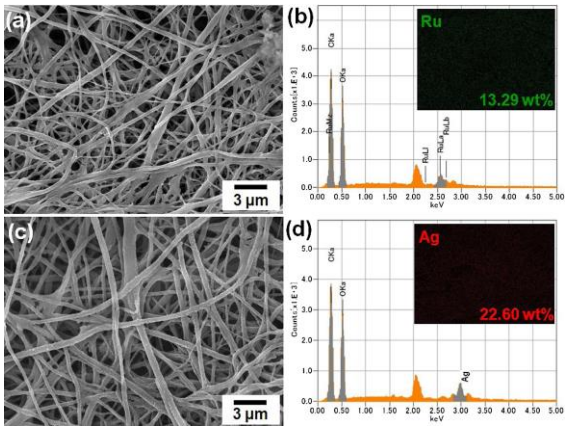


Fig. 3. SEM images of (a)RuNPs/CNFs and (c)AgNPs/CNFs. EDS spectra of (b) RuNPs/CNFs and (d) AgNPs/CNFs, and the insets show the corresponding EDS mapping of (inset in b) Ru and (inset in d) Ag.[31]

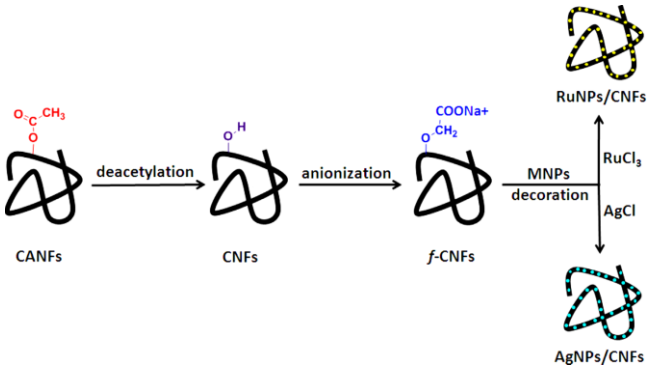
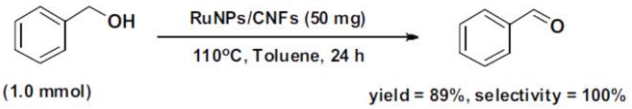


Fig. 2. Schematic illustration for the preparation of Ru-cellulose nanocomposites and Ag-cellulose nanocomposites.[31] (CANFs- cellulose acetate nanofibers, CNFs-cellulose nanofibers, f-CNFs- functionalized cellulose nanofibers, RuNPs/CNFs - Ru-cellulose nanocomposites, and AgNPs/CNFs - Ag-cellulose nanocomposite).



Scheme 1. Ru-cellulose composite-catalyzed oxidation of benzylalcohol to benzaldehyde.[31]

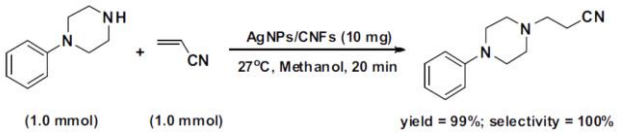
2. Oxidation of alcohols

In organic chemistry, selective oxidation of alcohols to carbonyl compounds is one of the most important reactions.[28] Traditionally, costly and highly toxic stoichiometric reagents such as iodine, manganese or chromium oxide, are used to convert the alcohols into aldehydes or ketones. The common traditional process often suffered from the use of high amount of environmentally hazardous metal. Although, there are several green oxidants are reported for the conversion of aromatic alcohols to aldehydes or ketone (TEMPO and DDQ are some of the used oxidants), transition metals based catalytic conversion of the alcohols are green, efficient, and cost-effective.[29] Different types of supports such as carbon nanoparticles, graphene oxide (GO), carbon nanotubes (CNTs), Al_2O_3, CeO_2, ZrO_2 and SiO_2 have been used for the preparation of the catalysts. Most widely used metals are Ru, Pd, Pt and Au.[30]

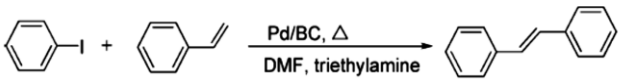
Kim and group[31-33] prepared various electrospun cellulose nanofiber composites based on transition metals such as Ru, Ag, Au, Ni and Cu. Surface modification has been carried out before decoration of metal nanoparticles. Ru nanoparticles decorated cellulose nanofiber composite was achieved by Kim and group. In order to achieve the cellulose nanofibers, cellulose acetate solution of 16-18 wt% was prepared in DMF/acetone mixture. Cellulose acetate nanofibers are obtained by spinning the CA solution under the electric field of 12 kV. The tip to collector distance was set to 15 cm, and the humidity was about 75-85%. The obtained fibers are dried and then deacetylated it in NaOH solution for 24 h at room temperature. The decoration of Ru-nanoparticles on to the cellulose nanofibers are obtained by simple $NaBH_4$ reduction of $RuCl_3$. Similarly, Ag-nanoparticles are decorated to obtain on the cellulose nanofibers to obtain the Ag-cellulose nanofiber composite. Fig. 2 shows the Schematic illustration for the preparation of Ru-cellulose nanocomposites and Ag-cellulose nanocomposites. Ref X (CANFs-cellulose acetate nanofibers, CNFs-cellulose nanofibers, f-CNFs-functionalized cellulose nanofibers).

Cellulose nanocomposites are characterized by various techniques such as FT-IR, SEM-EDS, TEM, AFM, XRD, and XPS, so on. Fig. 3 shows the SEM-EDS images of the Ru-cellulose nanofiber and Ag-cellulose nanofiber composites. The weight percentage of the Ru and Ag are found. The homogeneous dispersion of the metals is also found to be homogeneous.

The prepared Ru-cellulose nanofibers and Ag-cellulose nanofibers are used as efficient heterogenous catalyst for the organic reactions.[31] The Ru-cellulose nanofiber composite showed high conversion towards oxidation of benzyl alcohol to benzaldehyde. The reaction condition was initially optimized, and they found that the catalyst is actively working under mild reaction conditions. The Ru-cellulose catalyst (50 mg) showed better activity when the benzyl alcohol was stirred in toluene at 110°C, for 24 h under air atmosphere. It gave yield of 89% with excellent selectivity of 100%. Reusability test showed that the composite catalyst is reusable at least for four times without the activity decline. It was found that the Ru-cellulose catalyst is effective, reusable and heterogenous. Scheme 1 shows the Ru-cellulose composite-catalyzed oxidation of benzylalcohol to benzaldehyde.



Scheme 2. Ag/CNFs-catalyzed *aza*-Michael reaction of 1-phenylpiperazine with acrylonitrile.[31]



Scheme 3. Heck Reaction with Pd/BC Catalyst for up to 5 Cycles.[35]

Alike, the Ru-cellulose nanofibers, the Ag-cellulose nanofibers are tested as catalyst for the aza-Michael reaction of 1-phenylpiperazine with acrylonitrile.[31] Scheme 2. Ag/CNFs-catalyzed aza-Michael reaction of 1-phenylpiperazine with acrylonitrile. Kim et al, found that the Ag-cellulose composite catalyst showed excellent yield and selectivity in aza-Michael reaction (Scheme 2). Moreover, the catalyst exhibits excellent reusability and stability.

3. Heck Coupling Reaction

The transition-metal-catalyzed C–C cross-coupling reaction is one of the most vital syntheses of organic building blocks such as natural products, pharmaceuticals, and agricultural derivatives.[34] Due to excellent product yields with good selectivity, Pd-based catalytic Heck coupling is the most efficient and preferred over other catalytic systems.

Zhou et al.,[35] prepared Pd nanoparticles supported bacterial cellulose nanofibers by facile hydrothermal reduction. After being characterized, the Pd/BC catalyst was employed for the Heck reaction (Scheme 3). They found that the Pd/BC catalyst was a highly efficient and recyclable catalyst for standard Heck coupling reaction. The Pd/BC catalyst is recyclable with least 5 times, with the much decline in the catalytic activity.

4. Reduction of p-Nitrophenol

Nitrophenols are a common organic pollutant that occurs in industrial wastewater. They are stable in wastewater and often cause environmental pollution due to its carcinogenesis, hepatotoxicity and mutagenesis.[36] In order to avoid such an environmental issue, the conversion of nitrophenol to aminophenol from wastewater has been demonstrated. The simple and easy reduction of p-nitrophenol to p-aminophenol, is vital and the resultant aminophenol has significant use in various fine chemical industries. Till date, number of nanocomposites are reported for the reduction of p-nitrophenol to p-aminophenol.[37-39]

Kim and group prepared Au/CNF, Ni/CNF and Ag/CNF composites by using a simple wet reduction method using $NaBH_4$ as a reducing.[31-33] The obtained Au/CNF, Ni/CNF and Ag/CNF composites are characterized by means of SEM-EDS, TEM, FT-IR, XRD and XPS.[33] Significant metal-support interaction has been studied by means of XPS. They found that the Au/CNF, Ni/CNF and Ag/CNF demonstrated excellent catalytic activity towards the reduction of nitrophenols to aminophenols in water. The cellulose composites demonstrated excellent activity even with a very low amount of catalyst to achieve 100% reduction of 4- and 2-NP with a higher reaction rate (within 5 min). The calculated rate constant (k_{app}) values were determined for the cellulose nanocomposites. The catalytic performance of Au/CNF, Ni/CNF and Ag/CNF has been compared with previously reported results.

Green synthesis of nanocomposites has attracted huge consideration in recent years.[33] Bimetallic Ag–Au cellulose nanofiber composite (Ag@Au/CNCs) was prepared via a very simple green preparation method by Gopiraman et al. An aqueous leaves extract of Moringa oleifera was used to obtain the bimetallic Ag@Au/CNC nanocomposite. They found that the catalyst performs remarkably well and gave excellent k_{app} values of 15.59 and 22.83 × 10^{-3} s^{-1} for the 2- and 4-nitrophenol reduction process, respectively. In addition to that, the Ag@Au/CNC catalyst can be reused ion same reaction and also in *aza*-Michael reaction (Fig. 4).

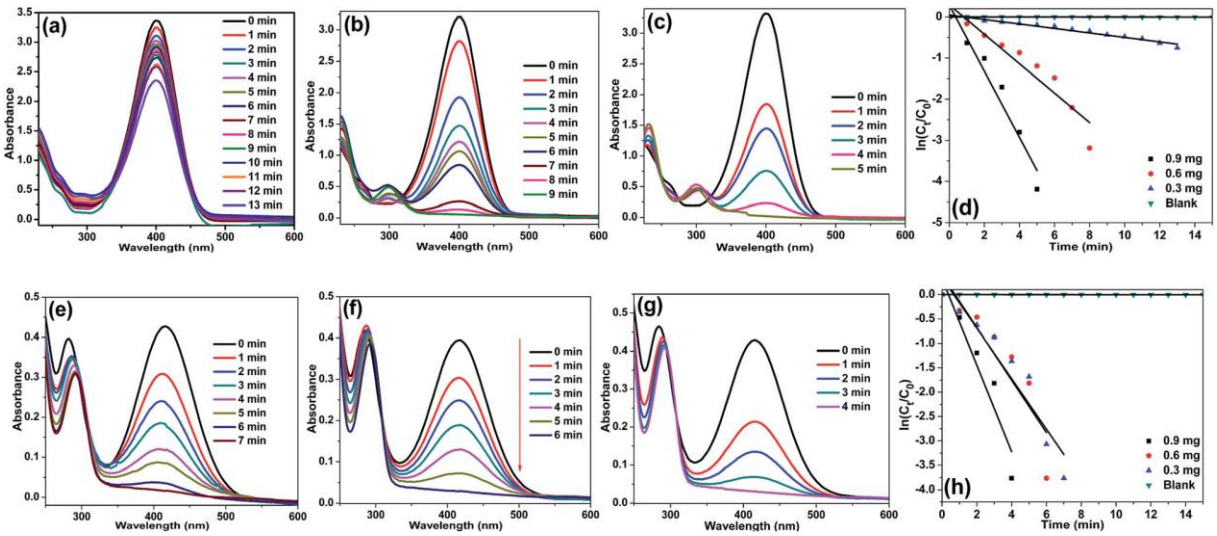
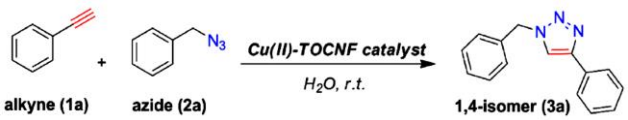


Fig. 4. UV-Vis spectra for the reduction of (a–c) 4-NP and (e–g) 2-NP in aqueous solution recorded every 1 min using different amounts of Ni/ CNF: (a, e) 0.3 mg, (b, f) 0.6 mg and (c, g) 0.9 mg, and plots of ln[Ct/C0] versus reaction time for reduction of (d) 4-NP and (h) 2-NP with $NaBH_4$ over Ni/CNFs.



Scheme 4. The [3 + 2] cycloaddition reaction of benzyl azide and phenylacetylene catalyzed by Cu(II)-TOCNF.[41]

5. [3+2] Cycloaddition Reaction

Click chemistry is one of the modern ligation approaches adopted for the synthesis of molecules with pharmacological scope in good to excellent yields, regio- and stereoselective manners under very mild conditions. It is a sustainable approach.[40] The copper-catalyzed [3 + 2] cycloaddition reaction of azide and alkynes (CuAAC) is the most well-known and representative click chemistry reaction that affords the biologically active five-membered heterocyclic scaffold, 1,2,3-triazoles. Ablouh et al., prepared Cu(II)-TOCNF catalyst for [3 + 2] cycloaddition reaction of benzyl azide and phenylacetylene (Scheme 4). They found that nanofiber Cu-composite is highly efficient and reusable.[41]

6. Conclusions

In conclusion, recent developments of cellulose nanofibers supported active metal nanoparticle catalysts are reviewed. Various preparation and characterization techniques are discussed. Cellulose nanocomposites and their catalytic activity in various organic reactions such as oxidation, reduction and coupling reactions are well documented.

Conflicts of Interest

The authors declare no conflict of interest.

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