Cellulose Nanocrystal–ZnO Nanohybrids for Controlling Photocatalytic Activity and UV Protection in Cosmetic Formulation

Fatima Awan,† Muhammad Shahidul Islam,† Yeyu Ma,† Cindy Yang,† Zengqian Shi,† Richard M. Berry,‡ and Kam C. Tam*†‡

†Department of Chemical Engineering, Waterloo Institute for Nanotechnology, University of Waterloo, 200 University Avenue West, Waterloo, Ontario N2L 3G1, Canada
‡CelluForce Inc., 625, Président-Kennedy Avenue, Montreal, Quebec H3A 1K2, Canada

ABSTRACT: A high-performance semiconductor zinc oxide (ZnO) on melamine formaldehyde-coated cellulose nanocrystals (MFCNCs) was synthesized and evaluated for its application in smart cosmetics. These ZnO@MFCNC hybrid nanostructures were evaluated for their in vitro sun protection factor performance and photocatalytic activity under simulated UV and solar radiation. The photodegradation kinetics of a model pigment (methylene blue) was fitted to the Langmuir–Hinshelwood model. A 4-fold increase in the photocatalytic activity of ZnO@MFCNCs was observed when compared to pure ZnO. This is associated with (i) increased specific surface area provided by the MFCNC template, (ii) confined surface energy and controlled growth of ZnO nanoparticles, and (iii) entrapment of photoinduced charge carriers in the pores of the core–shell MFCNC rod, followed by fast promotion of interfacial e-charge transfer to the surface of the catalyst. The present study demonstrates how an increase in photocatalytic activity can be engineered without the introduction of structural defects or band gap tailoring of the semiconductor. The aqueous-based ZnO@MFCNC hybrid system displayed attractive UV-absorption and photocatalytic characteristics, offering the conversion of this renewable and sustainable technology into intelligent cosmetic formulations.

INTRODUCTION

Recent advances in the epitaxy of semiconductor materials have made it possible to fabricate metal oxide structures, where the confined electrons (e−) and holes (h+) could potentially be used to fine-tune the redox functionalities.1,2 For solid-state systems, ZnO semiconductors with a wide band gap energy of 3.37 eV and with inherent UV-absorbing characteristics are promising materials because of their high quantum efficiency. They have found applications in optical devices, sensors, transparent electrodes, solar cells, photocatalysis, antibacterial activity, and cosmetics.3–5 For these principal applications, the structural defects, morphology, size, surface area, and crystallinity are prime factors that determine the efficacy of the metal oxide. Research on these systems has focused on strategies to enhance the properties mainly through the introduction of oxygen vacancies, structural defects on the surface of the crystal, and widening the band gap of the metal oxide to limit the fast recombination of photogenerated charge carriers.4 Doping with a variety of materials including both metal ions6–8 and metal oxides9–11 has shown that the band gap can be tailored and the range is promising for functional optoelectronic devices. However, in applications that require formulation in solution, the use of colloidal ZnO nanocrystals has encountered various challenges because of their tendency to aggregate through Ostwald ripening associated with their high surface energy.3 As a result, these nanoparticles (NPs) are unstable during storage and their surface reactivity is reduced, which hinders their application in waste water treatment, photocatalysis, personal care, and biological systems. The possibility of using hybrid nanocomposites to fabricate functional systems in a simple aqueous solution process could overcome this issue and allow broader engineering application. One such hybrid that has the flexibility to meet these demands is a cellulose-based nanorod derived from wood pulp known as cellulose nanocrystal (CNC). The biocompatible 150 × 5 nm dimensional crystalline domains, extracted from wood fiber, are excellent substrates for the growth of semiconductor ZnO NPs. Large scale production of CNCs has been demonstrated by CelluForce Inc. in Montreal, Canada. The naturally uniform nanocrystal offers high specific surface area, long term stability in water, consistent dimensions, and high mechanical strength.12 A comparison on the preparation methods, size, morphology, and application of reported CNC–ZnO nanocomposites is summarized in Table 1.
Table 1. Summary of Preparation Methods and Application of CNC–ZnO Nanohybrids

| CNC source                  | preparation method      | morphology                  | size    | application                        | refs |
|-----------------------------|-------------------------|----------------------------|---------|------------------------------------|------|
| commercial viscose acetal   | precipitation           | flower-like nanorod clusters | 2.56 μm | antibacterial & photocatalytic     | 13   |
| acetal fibers               |                         |                            |         |                                    |      |
| microcrystalline cellulose  | precipitation           | sphere-like structure       | 143.1 nm | antibacterial & photocatalytic     | 14   |
| microcrystalline cellulose  | hydrothermal            | sheet-like converted to flower-like structure | 210 nm | antibacterial & UV-shielding       | 15   |
| oil palm empty fruit bunches| in situ solution casting technique | irregular disc-like structure | 65 nm  | antibacterial & photocatalytic     | 16   |
| Whatman filter paper        | precipitation           | hexagonal wurtzite structure | 19.3 nm | antimicrobial                      | 17   |
| MF coated CNC               | nanotemplate mediated controlled chelation | leaf-like growth            | 15.1 nm | UV protection & photocatalytic     | present work |

Figure 1. (A) FTIR spectra of ZnO, ZnO@MFCNC, and MFCNC measured between 4000 and 400 cm$^{-1}$. (B) TGA measurements of ZnO, ZnO@MFCNC, and MFCNC obtained at a heating rate of 20 °C/min under air.

The present study is directed toward evaluating the combination of semiconductor ZnO with a biocompatible CNC template and the advantage it offers in controlling the size of NP for high performance smart cosmetic systems. We focus on the design and synthesis of an optimal and highly porous nanohybrid system for use as a UV filter and a photocatalytic agent for the degradation of dye pigments or organic pollutants. This nanostructure was developed using a melamine-formaldehyde (MF)-coated CNC template that provides a mesoporous and nitrogen-rich substrate for the chelated growth of ZnO NPs in aqueous solution, without the need of high temperature calcination, surfactants, or capping agents. First, the sun protection factor (SPF) of the ZnO@MFCNC was evaluated through spectrophotometric analysis, and the role of the template in controlling the size of ZnO NPs to enhance the SPF values was demonstrated. Second, the photocatalytic degradation of a model pigment (methylene blue) under UV and solar radiation was evaluated using a pseudo-first order Langmuir–Hinshelwood model and explained with the solid band theory. The ZnO@MFCNC hybrid produced a 4-fold increase in photocatalytic performance through (i) the increased surface area of the MFCNC matrix, (ii) the confined surface energy and growth of the ZnO NPs, and (iii) the fast promotion of interfacial charge transfer to the surface of the catalyst. This last effect is in part due to the mesoporous core–shell structure of the MFCNC that traps the photoinduced charge carriers and prevents $e^−/h^+$ recombination without the need for tailoring the band gap or using structural defects on the surface. A complete analysis and characterization of the system using Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), zeta potential, UV–vis spectroscopy, and transmission electron spectroscopy (TEM) measurements validated the properties and performance of the ZnO nanohybrid system.

### RESULTS AND DISCUSSION

The FTIR spectra shown in Figure 1A offer some insight into the chemical functionalities of the nanocomposite, as well as the MFCNC and pure ZnO structure. Pure ZnO is normally recognized in the infrared (IR) spectrum by the characteristic Zn–O stretching vibration between 430 and 500 cm$^{-1}$, and broad peaks in the range of 3800–3900 cm$^{-1}$ attributed to adsorbed H$_2$O molecules present on the lattice. For comparison, the IR spectrum for the MFCNC–ZnO (Figure 1A) hybrid shows a distinct absorption at 428 cm$^{-1}$ (Figure 1A, spectrum b), which confirms the presence of ZnO in the nanocomposite. Another noticeable peak at 813 cm$^{-1}$ arises from the 1,3,5-triazine ring of melamine, which confirms the presence of MFCNC in the hybrid. This FTIR spectrum was compared with that of MFCNC (Figure 1A, spectrum c), which shows the typical peaks at 814 and 1565 cm$^{-1}$ arising from the 1,3,5-triazine ring in the melamine structure, the C–H bending vibration absorption of the methylene group at 1330 cm$^{-1}$, and the characteristic bands at 1020 cm$^{-1}$ assigned to the $–$CH$_2$–O–CH$_2$ or $–$CH$_3$–OH ether linkage of the MF resin. It should be noted that the ZnO stretching vibration at 430 cm$^{-1}$ is absent from the pure MFCNC spectrum.

Further support on the mass loading of active ZnO on the surface of MFCNCs was determined from TGA. On the basis of the weight loss profiles of the three TGA curves (illustrated in Figure 1B), the residual contents of ZnO, ZnO@MFCNC, and MFCNC determined at 700 °C were 96.42, 86.73, and 9.54%, respectively. From the analysis, the content of ZnO was calculated to be 88.85%, based on eq 1.
Thermal stability of ZnO was observed in the TGA curve of pure ZnO, confirming the presence of chemical groups such as ZnOH\(^+\), ZnOH, and ZnO on the surface of ZnO NPs. The degradation beyond 350°C was mainly attributed to the size and crystal size of ZnO in the ZnO@MFCNC hybrid was estimated to be 120 nm, whereas the crystallite size of ZnO in the ZnO@MFCNC hybrid was 15.19 ± (1 nm). The estimated crystallite sizes of the two samples agree with the XRD patterns shown in Figure 2A because the larger crystal size that is linked to pure ZnO, is characterized with more pronounced sharp intensity peaks, whereas the smaller and broader peaks that are observed for the ZnO@MFCNC spectrum are linked to a smaller crystal size. Additionally, the presence of these crystal planes and intensity peaks confirmed the successful formation of ZnO NPs on the surface of MFCNCs.

The stability of the NPs was evaluated from zeta potential measurements of the ZnO@MFCNC complex and the metal oxide aqueous suspensions as a function of pH. This method is ideal for assessing the colloidal stability of the dispersion through evaluating the surface charge of the NPs. For the targeted sunscreen application, it is important to have a dispersion that is stable under acidic conditions at the natural skin surface (pH of below 5). Research studies have indicated that a pH of less than 5 is critical for maintaining the biophysical parameters and resident skin microflora on the epidermal surface. Figure 2B shows a strong pH dependency of the three systems; MFCNC, ZnO@MFCNC, and ZnO based on the electrophoretic mobility in well-dispersed Millipore water. The presence of chemical groups such as ZnOH\(^+\), ZnOH, and ZnO on the surface of ZnO NP is highly pH dependent. As such, a low positive charge of around +10 mV (between pH 3 and 5) observed for pure ZnO in acidic solution can be attributed to the partial transfer of protons (H\(^+\)) from the acidic environment, leading to an unstable Zn(OH)\(^+\)\(_n\) surface chemical composition. In comparison, it is interesting to note that the ZnO@MFCNC hybrid yielded a strong positive charge (+35 mV) in acidic conditions with pH < 4.5 because of the protonation of amine groups and a triazine ring, revealing a strong (+) charge from nitrogen (N1) on the melamine structure. With a nitrogen-rich polymer backbone covering the surface of CNC, there is a large positive charge, making the ZnO@MFCNC nanohybrid electrochemically stable in aqueous solution. Beyond the pH constant for melamine in water (5.0), the zeta potential decreased from +34.1 mV at pH 4 to +22 mV at pH 5, indicating the practical usage of the nanohybrid in the acidic condition (pH < 5).

The morphology of the hybrid system and the form of ZnO NPs were characterized using TEM. Figure 3A,B show the increase in the diameter and slight darkening of CNCs when coated with MF as observed previously. The ZnO@MFCNC hybrid exhibited a unique leaf-like growth of ZnO and MFCNCs on the CNC rods, as shown in the inset of Figure 3C. Although the size of the MFCNCs remained unchanged, the average diameter of ZnO NPs on the surface of CNCs was less than 20–25 nm. In contrast, the ZnO particles synthesized without the MFCNC template displayed micron-sized clusters of particles (>200 nm), primarily because of the high interface energy of NPs that lead to the formation of aggregates in solution.

**SPF Measurements.** The efficacy of a sunscreen was determined by a quantitative measurement of the SPF, which is a numerical-rating system that reflects the degree of protection provided by a sunscreen product. The SPF is based on the ratio of the least amount of UV energy (UVB) required to produce minimal erythema on sunscreen-protected skin over the amount of UV energy that reaches unprotected skin. The SPF is calculated using the following formula:

\[
\text{SPF} = \frac{2000}{	ext{amount of UV energy reaching unprotected skin}}
\]

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\]
of energy required to produce the same erythema on unprotected skin.\textsuperscript{29,30} The solar spectrum is composed of UVA (320−400 nm) and UVB (290−320 nm) radiation, where UVA is primarily involved in penetrating the epidermal and dermal layers of the skin that damage the keratinocytes, which is known to cause skin cancer.\textsuperscript{31,32} Although the effects of UVA sound dramatic, the risk of UVB exposure is approximately 1000× more erythemogenic compared to UVA, which can cause severe photo damage and sunburns because of the shorter UVB wavelength.\textsuperscript{29} As such, the SPF is primarily a measure of protection against UVB. Here the photoprotection of the hybrid structure and pure ZnO aqueous solutions were determined based on an in vitro spectroscopic method to calculate the SPF values using the well-developed Mansur mathematical expression (eq 3)\textsuperscript{33}

\[
\text{SPF} = \text{CF} \times \sum_{\lambda=290}^{320} \text{EE}(\lambda) \times I(\lambda) \times \text{Abs}(\lambda)
\]

where CF is the correction factor (10), EE(\lambda) is the erythemogenic effect and solar radiation intensity at wavelength I(\lambda), and Abs(\lambda) is UV spectrophotometric absorbance values at wavelength \lambda determined at every 5 nm increments. The values of EE \times I were normalized constants determined by Sayre et al., 1979\textsuperscript{34} as shown in Table 2.

Figure 4 shows the comparative SPF values of the ZnO@MFCNC nanohybrid and pure ZnO prepared from various hydroxide ratios. The results from the experimental studies demonstrated that ZnO deposited on the surface of the MFCNC substrate and the pure ZnO system displayed good SPF values of between 10 and 14 when the ratio of ([MFCNC]/[Zn\textsuperscript{2+}])/[OH\textsuperscript{−}] ranged from 1:2 to 1:10. In cases where ZnO@MFCNC displayed a better SPF value than pure ZnO, it is likely to be related to the better dispersion stability of the ZnO@MFCNC system. The role of the MFCNC matrix is obvious from these results as it (i) contributes to an increased surface area because of the sponge-like porous matrix, (ii) offers the chelation of zinc ion (Zn\textsuperscript{2+}) with enhanced affinity through the rich nitrogen groups of the MF resin,\textsuperscript{35,36} and (iii) promotes the confined growth of the metal oxide in the mesopores of the MF resin leading to a controlled NP size that offers better UV absorption compared to pure micron-size ZnO.

By systematically varying the ratio of MFCNC-Zn\textsuperscript{2+} to hydroxide, an optimal composition of [Zn\textsuperscript{2+}]/[OH\textsuperscript{−}] of 1:3 was observed. It is suggested that this optimal ratio for the measurement of SPF is directly related to the particle size and morphology, where the reduction in the particle size, from micro to nano, directly affects the SPF. From our observation, it is evident that for the hydroxide ratio of between 4 and 10, the reaction between the zinc ion and hydroxide proceeded rapidly, producing larger particles that were less stable, in contrast to the optimal ratio of 1:3. By further increasing the hydroxide ratio beyond 10, no ZnO crystal was produced, which was confirmed by the absence of the characteristic exciton energy peak of ZnO at 350 nm in the UV region, in addition to the disappearance of the cloudy aggregates.\textsuperscript{37} The result demonstrated that the alkaline ratio controlled the ZnO particle formation after the initial nucleation on the MFCNC substrate.

**UV Absorbance & Optical Properties.** The formation of the ZnO crystal on the surface of MFCNCs was validated by the presence of the characteristic UV absorption peak at 350 nm for ZnO, in addition to the peak at 209 nm because of the triazine ring of MF.\textsuperscript{38} The excited electronic states of semiconductor ZnO NPs with a direct band gap energy of 3.31 eV differ to a great degree from that of the bulk ZnO. This change causes a quantum confinement effect in ZnO NPs.\textsuperscript{39,40} The widening of

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**Table 2. Normalized EE \times I Values Corresponding to Wavelength (nm) for the Calculation of SPF\textsuperscript{34}**

| wavelength (nm) | EE \times I |
|----------------|-------------|
| 290            | 0.0150      |
| 295            | 0.0817      |
| 300            | 0.2874      |
| 305            | 0.3278      |
| 310            | 0.1864      |
| 315            | 0.0839      |
| 320            | 0.0180      |

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**Figure 3. TEM micrographs of (A) pristine CNCs; (B) MF coated CNCs; (C) leaf-like growth of ZnO NPs on the surface of MFCNCs; and (D) pure ZnO particles >100 nm.**

**Figure 4. Bar graph illustrating the comparative SPF values of aqueous ZnO@MFCNCS and pure ZnO solutions, with increasing [OH\textsuperscript{−}] ratios.**
the band gap energy corresponds to a reduction in the NP size and is evidenced by an overall blue shift in the spectrum. From the optical measurements of the ZnO@MFCNC nanohybrid structure, there was a visible blue shift detected in the wavelength from the bulk ZnO at 365 nm to the ZnO@MFCNC at 350 nm, as illustrated in the inset of Figure 5. The blue shift is a good indication of the relative reduction in the particle size compared to pure ZnO, and it confirmed the importance of a chelating template of the porous MFCNC in controlling the NP formation in aqueous solution.

Photocatalytic Evaluation under Solar Simulation and UV Radiation. The rate of degradation of methylene blue (MB), as determined by colorimetric measurements (Figure 6A,B), was used to assess the photocatalytic performance of the ZnO@MFCNC nanohybrid. A substantial enhancement over the bulk ZnO system was found with the ZnO@MFCNC system. The pseudo-first order linear kinetic rate analysis shown in Figure 6C was fitted to the Langmuir—Hinshelwood model (eq 4)

\[
-\ln \left( \frac{C_t}{C_0} \right) = kt
\]

where \( C_t \) is the concentration at irradiation time (\( t \)), \( C_0 \) is the initial concentration at irradiation time 0, and \( k \) is the first-order rate constant. Linear regressions of the data presented in Figure 6C revealed a 4-fold increase in the kinetic rate for the ZnO@MFCNC system (0.0117 min\(^{-1}\)) compared to ZnO (0.00314 min\(^{-1}\)), and an even faster rate of 0.0387 min\(^{-1}\) was observed for the study under sunlight of the CNC-supported nanohybrid. The ZnO@MFCNC system showed a complete degradation under solar stimulation after 60 min, and 96.49% degradation under artificial UV light after 200 min, as illustrated in Figure 6D, whereas bulk ZnO displayed only half the degradation (51.14%) at 200 min, with complete degradation observed after 6 h. The kinetics under sunlight for the CNC-supported hybrid system indicated that the efficiency of dye degradation is better (0.0387 min\(^{-1}\)) under sunlight in comparison to UV alone.
(0.0117 min⁻¹), as shown in Figure 6. We postulate the faster kinetics to be primarily attributed to sunlight irradiation,41,42 with both UV and visible incorporated activation of the MFCNC-supported catalyst. The faster kinetics can be defined by the UV + visible (sunlight intensity) over the 60 min interval, where first the light activates the surface of the catalyst, and progressively penetrates the porous MFCNC network and the ZnO catalyst. The results offer evidence that the hybrid system was activated by both the UV, as well as the visible region for photocatalytic degradation, making it advantageous for practical outdoor applications.

These results were primarily associated with the molecular activity at the atomic level, followed by series of photocatalytic redox reactions at the surface of the semiconductor ZnO@MFCNC. The emphasis of the optical absorption in colloidal semiconductors is interestingly dissimilar from bulk materials.11,43 The electronic conduction in a solid could be explained through the molecular orbital (MO) theory, where the MOs are treated as energy bands instead of discrete levels because of the small difference in energy.40,43 As in the case of the solid semiconductor ZnO@MFCNC, electrons occupy the energy bands according to their energy.

Upon UV excitation, the electrons in the highest occupied orbital of the valence band (VB) are promoted to the unoccupied orbital of the conduction band (CB) above it; leaving behind a hole (positive charge) in the VB.44 The space between these energy bands is the band gap which acts as a barrier to electronic mobility. The e⁻/h⁺ formation dictates photocatalysis, where e⁻/h⁺ pairs migrate to the semiconductor surface and participate in a redox reaction with the adsorbed organic compound which in this case is methylene blue.6,7,9,44 The migration rate increases when there is a widening of the band gap which occurs with a reduction in the particle size. The faster rate allows e⁻ or h⁺ to react to a greater degree with surface-adsorbed species rather than recombine; thus, improving the catalytic efficiency.29,42 Here, the role of the nanotemplate of the mesoporous MFCNC becomes important, as it confines the growth of ZnO because of the high specific surface provided by the MFCNC (212.8 m² g⁻¹), where the surface area for ZnO NPs in the wurtzite phase is approximately 29.35 m² g⁻¹.45 This phenomenon has three related consequences, namely: (1) it controls the NP growth, (2) it increases the specific surface area of the semiconductor ZnO, and (3) it effectively prevents e⁻/h⁺ recombination and increases the concentration of the photoinduced charge carriers at the surface of the catalyst, which has major implications for the photocatalytic performance of the structure. A schematic illustration of a proposed mechanism, with explanation of the redox reactions is described in Figure 7.

With UV excitation energy exceeding the band gap, electrons (e⁻) are promoted from the ground state to the CB, resulting in a vacancy (h⁺) in the VB. The e⁻/h⁺ formation dictates the photocatalytic activity of the semiconductor hybrid. The photogenerated h⁺ oxidizes the H₂O molecules adsorbed on the surface of ZnO to OH radicals. In the upper band, the excited e⁻ of CB reacts with pre-adsorbed O₂ molecules to form reactive oxygen species (ROS) (i.e. superoxide anion radical *O₂⁻).46 Given the high quantum yield of photogenerated holes, actual degradation of the dye can arise from direct transfer of photogenerated carriers or through the formation of ROS, which complete the reaction by degrading any organic pollutants in primary contact. The photocatalytic activity of ZnO in altering the optical properties of dye pigments can be utilized to design smart cosmetic products, where the tone color of the cosmetic on skin can be tuned to fade as a function of exposure to sunlight. In addition, in countries where air pollution from organic debris is a significant concern, these photocatalysts can be actively utilized as a method to degrade the contaminants, making it an important aspect of the proposed system.

Table 3 shows a comparison of the kinetics for the photocatalytic performance of other ZnO-based systems.

Table 3. Comparison of the Photocatalytic Performance of ZnO-Based Systems for the Degradation of Organic Pollutants

| ZnO based photocatalytic systems | model pollutant | rate constant (min⁻¹) UV | rate constant (min⁻¹) sunlight | ref |
|---------------------------------|----------------|-------------------------|-------------------------------|-----|
| Fe⁺ doped ZnO calcined@400 °C  | 2-CP           | not studied             | 0.0265                        | 47  |
| MnO₂O₄ doped ZnO               | 4-CP           | not studied             | 0.0133                        | 48  |
| TiO₂/ZnO chitosan complex      | MO             | not studied             | 0.0256                        | 49  |
| Au–ZnO heterostructures       | MB             | 0.021                   | 0.0350                        | 50  |
| ZnO chelated on mesoporous MFCNC matrix | MB             | 0.0117                   | 0.0387                        | present work |

reported in the literature for the degradation of organic pollutants. Our synthesized hybrid material demonstrates comparable rate constants for irradiation under UV and ameliorated values for the solar-radiated samples.

EXPERIMENTAL METHODS

Materials. CNCs with dimensions 150 nm in length and 5 nm wide were supplied by Cellulose Inc, Quebec, Canada. All of the analytical grade chemicals were purchased from Sigma-Aldrich and used as received.

Synthesis of the ZnO@MFCNC Colloidal Nanohybrid. MF-coated CNCs (MFCNCs) were prepared via the polycondensation of MF precursor on the CNC rod as described previously by Wu et al. 2016.19 The optimal hybrid ratio was obtained by dispersing 143 mg of MFCNC in 15 mL of water. After which, 165 mg of zinc acetate dihydrate was dissolved in another 15 mL of water and added dropwise to the MFCNC solution and stirred at 5 °C for 1 h, where the positive zinc ions

Figure 7. Proposed mechanism of degradation and schematic representation of semiconductor ZnO grown on the surface of MFCNCs.
were chelated by the nitrogen groups of the MFCNC rods. Then, 30 mL of 0.0225 molar NaOH was introduced dropwise to hydrolyze the Zn$^{2+}$@MFCNC solution, which was stirred at room temperature for 2 h. The samples were exposed to hydrothermal treatment at 100 °C for 1 h, and purified through dialysis. The preparation of pure ZnO followed the same procedure but without the addition of MFCNC; 165 mg of zinc acetate dihydrate (Zn$^{2+}$) was predissolved in 15 mL of water and reacted with 30 mL of 0.0225 molar NaOH at room temperature for 2 h. This was followed by hydrothermal treatment and purification. A schematic describing the synthesis procedure is illustrated in Figure 8.

**SPF Measurements.** The absorption characteristics of the sunscreen agents were determined based on spectrophotometric analysis of dilute aqueous suspensions of ZnO@MFCNC and pure ZnO based on 5% active ingredient. Samples were diluted in water at a final concentration of 2 μL/mL and analyzed by UV spectrophotometry from 290 to 800 nm at 5 nm intervals using a 1 cm quartz cell according to Mansur’s method. Water was used as a blank sample for the baseline correction. All of the tested materials were measured three times to obtain the standard error for the SPF measurements.

**Photocatalytic Evaluation.** UV: 50 mg of ZnO@MFCNC powder was mixed with 50 mL of 0.02 mg/mL methylene blue (MB) solution. The mixture was sonicated and vortexed to prepare a uniform dispersion of the hybrid powder, which was continuously stirred in the dark for 1 h to achieve an equilibrium absorption-desorption state. A Blak-Ray B-100AP-R High Intensity (100 W) 365 nm 2.5 A, 115V-60 Hz Lamp was used for UV irradiation of the samples. The solution was exposed to high-intensity UV irradiation, and 3 mL aliquots were withdrawn at 20 min intervals, diluted 10 times, and centrifuged for 10 min at 7000 rpm. The absorbance was recorded using an ultraviolet-visible (UV-vis) spectrophotometer (Cary Bio 100). TGA was performed using a TGA Q600 from TA Instruments (New Castle, Delaware). The experiments were conducted at a heating rate of 20 °C/min in the presence of air, from 25 to 800 °C. The morphology of the uranyl-stained CNCs was obtained with a JEM-2100 high resolution transmission electron microscope. MFCNC, ZnO@MFCNC, and unmodified ZnO particles were characterized using a Philips CM10 transmission electron microscope. The XRD patterns of the samples were performed with a Rigaku D/MAX-RB diffractometer using filtered Cu Kα radiation. FTIR spectra were recorded using a PerkinElmer 1720 spectrophotometer of freeze-dried samples mixed with KBr, at a resolution of 4 cm$^{-1}$, and analyzed using OPUS software. The zeta potentials of the solutions were measured as a function of pH from 3.0 to 5.0 every 0.5 units. This range was tested to check the stability of the system by measuring the surface charge of the NPs using Zetasizer Malvern Nano ZS90.

**CONCLUSIONS**

We have demonstrated that surface-modified porous CNCs in aqueous solution can be used to control the growth of semiconductor ZnO nanocrystals. We have evaluated and characterized the surface active ZnO@MFCNC nanohybrid as an ultraviolet filter and a photocatalytic agent. The material has high UV absorption with an SPF value of 14 based on 5% active ingredient. It also provides a 4-fold increase in photocatalysis under UV and solar radiation. This work shows that the introduction of structural defects and the tailoring of the band gap are not the only means to enhance the photocatalytic activity of ZnO. It shows that greater activity can be engineered through the control of the size, geometry, and orientation of the semiconductor via the use of a porous template. The nanohybrid produced has several advantages: it confines the surface energy and growth of ZnO NPs, and it promotes interfacial $e^-/h^+$ charge transfer to the surface of the catalyst through entrapment of the photoinduced charge carriers in the pores of the MFCNC rod which in turn prevents the $e^-/h^+$ recombination. In summary, by

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**Figure 8.** Schematic illustration of the synthesis of semiconductor ZnO on the surface of MF-coated CNC rods.
combining the functionality of the N-rich mesoporous MFCNC with semiconductor ZnO, we have developed a nanostructure that may find application in the design of smart cosmetic products.

**AUTHOR INFORMATION**

**Corresponding Author**
*E-mail: mktam@uwaterloo.ca*. Phone: 1-519-888-4567 ext. 38339. Fax: 1-519-888-4347 (K.C.T.).

**ORCID**
Kam C. Tam: 0000-0002-7603-5635

**Notes**
The authors declare no competing financial interest.

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