Electronic Supplementary Material (ESI) for RSC Advances

Supporting information

1.1 Preparation of CuO NPs supported on different CNs

CuO NPs supported on different CNs were prepared to demonstrate the reproducibility of the preparation of CNs. Their catalytic performance was also investigated. The CNs were obtained by hydrolyzing commercial microcrystalline cellulose (MCC), MCC derived from waste cotton fabrics and wood pulp using 63.5% sulfuric acid at 45 ^{o}C. MCC was prepared according to the work of Xiong[1] and the preparing method for CNs was based on the study of Bondeson[2]. The two kinds of MCC and wood pulp were mixed with sulfuric acid (64 wt%) and were heated with stirring at 45 ^{o}C for 130 min. Then the suspensions were repeatedly centrifuged (3 cycles, 10 min at 12,000 rpm for a cycle) and washed with deionized water. Dialysis was performed to remove residual acid in the suspension until the dialyzate maintained a constant pH. The resultant suspension was concentrated to a desired concentration and sonicated for 30 min at room temperature.

25 ml $CuSO_4$ (0.4 mM) aqueous solution was mixed with a suspension of 25 ml of CNs (0.2 wt%). The mixture was kept under magnetic stirring for a while to homogenize the suspension. A solution of $NaBH_4$ (2 ml, 14.4 mM) in deionized water was added to the resulted suspension under ambient condition. The resulted suspension was stirred for 30 min. The CNs-supported CuO NPs suspension was obtained.

1.2 The catalytic properties of CuO NPs supported on different CNs

The catalytic properties of CuO NPs supported on different CNs were evaluated by the reduction of 4-nitrophenol (NP) to 4-aminophenol (AP) with $NaBH_4$ under the same experimental condition as the submitted manuscript. Fig. S1 shows the UV-vis spectra and the conversion of 4-NP during the reactions. It can be observed from the figure that the catalysts supported on CNs derived from different natural resources have limited difference on the catalytic performance. The result indicates that the synthesis method for the CNs is reproducible.

2. The conversion of 4-NP

The conversion of 4-NP in the reaction catalyzed by unsupported CuO NPs, CNs-supported CuO NPs and CNs-supported Cu NPs is shown in Fig. S2. It is clear that the conversion of CNs-supported CuO NPs nanohybrids reached nearly 100% at 600s while that of the unsupported CuO NPs was merely 68.8%. The CNs-supported CuO NPs nanohybrids show remarkable advantage in catalytic activity over the unsupported CuO NPs. Besides, the catalytic activity of CNs-supported Cu NPs nanohybrids is slightly better.

3. Preparation of unsupported CuO NPs

The digital photographs of the initial $CuSO_4$ aqueous solution and resulted CuO NPs suspension was were shown in Fig. S3. The initial $CuSO_4$ aqueous solution was almost colorless due to the low concentration of Cu^{2+} (0.2 mM). However, with Cu^{2+} turned into CuO NPs, the resulted CuO suspension became pale blue because of the surface plasma resonance of CuO NPs.

4. XRD studies

The XRD patterns of CNs and CNs-supported CuO NPs are shown in Fig. S3. Compared with the pattern of pristine CNs, several new peaks appear in the pattern of the prepared nanohybrid. Two peaks at 35°, 38° and 52° correspond to the crystal planes (002), (111) and (020) of crystalline CuO (JCPDS 45-0397), respectively, indicating the oxidation of Cu to CuO. Besides, it should be noted that no characteristic peaks for Cu and Cu_2O are presented in the pattern. The peak around 35° is influenced by a characteristic peak of CNs centered near 35°. Because of the extremely low concentration of CuO on CNs, the characteristic peaks of CuO are faint. In both patterns, an intense peak can be observed at $2\theta=23°$, which is attributed to the (200) diffraction planes of cellulose I (Z. Cai and J. Kim, *Cellulose*, 2010, 17, 83-91.). This result indicates that the crystalline structure of CNs maintained after the deposition of CuO NPs.

5. Morphological studies of GO-supported CuO NPs and MCC

The particle size distribution of the prepared SiO_2-supported CuO NPs and Al_2O_3-supported CuO NPs was measured by Mastersizer 2000 (Malvein Instruments, Ltd, Britain) and shown in Fig.S4. The average volume diameter of the SiO_2-supported CuO NPs and Al_2O_3-supported CuO NPs is 26.2 and 69.6 μm, respectively.

Fig. S5 presents the TEM image of the GO-supported CuO NPs nanohybrids. The prepared CuO NPs, which are indicated by red arrows, are scattered on the surface of GO sheet. The image of MCC is presented in Fig. S6. It is clear that the diameter of rod-like MCC is in a range of 10-30 μm and the length is 100-300 μm. The particle size distribution is shown in the inserted image and the average volume diameter of MCC is 28.1 μm. The size of MCC is significantly larger than that of CNs.

References:

1. R. Xiong, X. Zhang, D. Tian, Z. Zhou and C. Lu, *Cellulose*, 2012, 4, 1189-1198.

2. D. Bondeson, A. Mathew and K. Oksman, *Cellulose*, 2006, 13, 171-180.

3. Z. Cai and J. Kim, *Cellulose*, 2010, 17, 83-91.