In situ synthesis of Cu nanocatalysts on ZnO whiskers embedded in a microstructured paper composite for autothermal hydrogen production†

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Cu nanoparticles (CuNPs) were successfully synthesized *in situ* on ZnO whiskers as a selective scaffold, which were supported in a microstructured paper matrix composed of inorganic fibers; as-prepared paper composites were easy to handle in practical use and demonstrated excellent catalytic performance in the methanol reforming process for effective hydrogen production.

Metal catalysts have become a major center of attraction in a wide range of industrial processes such as energy conversion, fine chemicals production and environmental clean-up. With the recent escalation of energy, environment and resource problems, there is a growing interest in the development of new catalytic materials that can promote the desired reactions more effectively and selectively.[1] For example, Cu/ZnO catalysts, which are conventionally used in the methanol reforming process to produce hydrogen for fuel cell applications, have been intensively upgraded by fine-tuning the elemental composition and nanometer-scale morphology of the catalyst surface for improving their catalytic activity.[2] Most metal catalysts are generally prepared in powdered form by the co-precipitation method.[3] Such powdered catalysts are inconvenient to handle in practical usage, and are therefore molded into pellets, spheres or rods. However, their catalytic performance is markedly decreased as compared with that of the original catalyst powder, since the accessibility of reactants to the catalytic active sites is limited to the outer surface of the molded solid catalysts.

Recent years have seen considerable progress in the research and development of metal nanoparticles for use as new catalytic materials with a large surface area-to-volume ratio.[4] In most cases, the electronic properties of these nanoparticles are significantly different from those of the corresponding bulk metals, leading to large enhancements in catalytic activity.[1,4] However, metal nanoparticles are extremely difficult to handle in their original form since they are immediately aggregated so minimizing their large surface area. Such inevitable aggregation of nanoparticles frequently yields bulk-like materials and results in a substantial reduction of catalytic activity. Thus, there is a strong requirement to find novel ways of making the best use of nanoparticles in potential applications without spoiling their excellent functionalities; an area of ongoing research is the immobilization of metal nanoparticles on easy-to-handle supports such as porous membranes and nanostructured sheets of inorganic nanobelts, by the layer-by-layer adsorption method using polyelectrolytes and by the versatile surface modifications, respectively.[5]

Structured catalysts with micrometer-scale pores are promising materials currently attracting attention due to their effective diffusion of heat and reactants especially for flow-type gas–solid reactions. Several structured supports have been developed, *e.g.* foam, string, honeycomb and porous anodic alumina;[6,7] catalyst particles are coated onto the surfaces of these supports mainly by washcoating or *via* the impregnation method. In our previous reports, Cu/ZnO catalyst powders were successfully supported on a microstructured matrix composed of ceramic fiber-networks by using a high-speed and low-cost papermaking technique.[8,9] As-prepared materials, denoted paper-structured catalysts, were applied to methanol reforming to produce hydrogen for fuel cell applications. The as-prepared paper-structured catalyst is flexible, lightweight, easy to handle, and has a high catalytic activity equivalent to that of the original catalyst powder, surpassing by far the catalytic activity of any known commercial pellet-type catalyst. Furthermore, the paper-structured catalyst remarkably suppressed undesirable carbon monoxide by-production, which is known to act as a catalytic poison for Pt anode electrocatalysts in fuel cells. Such unique features were possibly induced by the unique fiber-network microstructure (average pore size: *ca.* 20 μm and porosity: *ca.* 50%) of the paper composites, which allows the effective transfer of heat and reactants to the catalyst surfaces. Herein, we describe the direct *in situ* synthesis of catalyst nanoparticles on paper composites: Cu nanoparticles (abbreviated as CuNPs) were successfully synthesized on ZnO whiskers which were beforehand embedded in a microstructured paper composite. The CuNPs@ZnO whisker-containing paper composite had a paper-like flexibility and an excellent catalytic performance in the autothermal reforming (ATR) process of methanol (eqn (1)):[9] in the case of 80% conversion of methanol, the suppression of carbon monoxide by-production to *ca.* 14% was achieved at a lower reaction temperature of 60 K as compared with conventional Cu/ZnO powders.

$$4CH_3OH + 3H_2O + 0.5O_2 \rightarrow 11H_2 + 4CO_2; \quad \Delta_r H^\circ{}_{573} \approx 0\ \text{kJ mol}^{-1} \tag{1}$$

ZnO whiskers were suspended in an aqueous solution of $Cu(NO_3)_2$, followed by stirring for 20 min, filtration and

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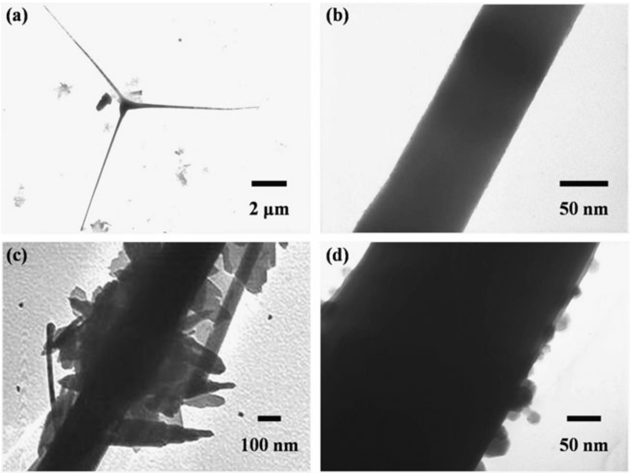

Fig. 1 TEM images of original ZnO whiskers (a, b) and ZnO whiskers treated with Cu nitrate solution; as-dried (c) and reduced (d).

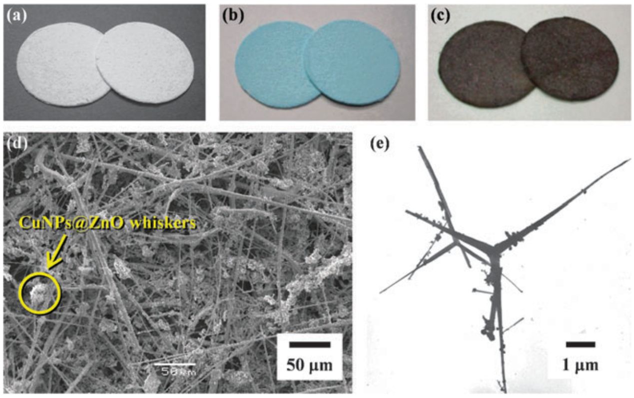

Fig. 2 Optical images of an original ZnO whisker-containing paper composite (a) and a ZnO whisker-containing paper composite treated with Cu nitrate solution; as-dried (b) and reduced (c), SEM image of a ZnO whisker-containing paper composite after CuNPs synthesis (d) and TEM image of CuNPs@ZnO whiskers (e). Fig. 2(d) shows an SEM image of the surface of the paper composite in Fig. 2(c).

sufficiently washing with deionized water. The ZnO whiskers and Cu nitrate solution immediately changed in color from white to blue and from blue to transparent, respectively (see ESI†). The obtained whiskers were first dried at 105 °C for 12 h, and then completely reduced in a hydrogen flow at 250 °C for 1.5 h to a dark red product. Fig. 1 displays the transmission electron microscopy (TEM) images of the original ZnO whiskers and ZnO whiskers treated with Cu nitrate solution. The ZnO whiskers used in this study were tetrapod-like nanofibers (Fig. 1(a) and (b)). When the ZnO whiskers were treated with Cu nitrate solution and then dried, several needle-like crystals became attached to the surface of the ZnO whiskers (Fig. 1(c)). After hydrogen reduction, nanoparticles of 20–50 nm size in diameter were formed on the ZnO whiskers (Fig. 1(d)).

The chemical states of the component elements were analyzed by X-ray photoelectron spectroscopy (XPS) (see ESI†). The ZnO whiskers treated with Cu nitrate solution after drying displayed the Cu 2p peak at *ca.* 935 eV and a satellite peak at ~945 eV, both of which correspond to the characteristic peaks of Cu^{2+} ions.[6] The N 1s peak at *ca.* 407 eV and O 1s peak around *ca.* 532 eV were assigned to NO_3^- and OH^- ions, respectively. The O 1s peak at *ca.* 530 eV was derived from the oxygen species of ZnO. After hydrogen reduction, the clear shift of the principal Cu 2p peak towards *ca.* 932 eV was observed; both the N 1s peak at *ca.* 407 eV and the O 1s peak around 532 eV disappeared completely after treatment with $Cu(NO_3)_2$, indicating that the Cu species were completely reduced from Cu^{2+} to Cu^0. X-Ray diffractometry (XRD) was conducted to analyze the crystal structure (see ESI†) of the ZnO whiskers. ZnO whiskers treated with Cu nitrate solution after drying showed the typical peaks of crystalline ZnO and two new peaks (2θ = *ca.* 13 and 26°), which are ascribed to $Cu_2(OH)_3(NO_3)$.[10] These results suggested that the Cu species in nitrate solution were adsorbed on the ZnO whiskers in the state of $Cu_2(OH)_3(NO_3)$. Furthermore, the XRD pattern of the ZnO whiskers treated with Cu nitrate solution after reduction clearly indicated the formation of Cu nanocrystals (Cu crystallite size: *ca.* 20 nm); and thus it was evidenced that the nanoparticles shown in Fig. 1(d) corresponded to CuNPs. Even after sonication at 100 W power for 10 min, nearly no CuNPs dropped out of the ZnO whiskers, suggesting that the CuNPs were strongly bonded to the surface of the ZnO whiskers. Such a phenomenon possibly relates to the ionization tendency because there was little change in color of the ZnO whiskers and nitrate solutions in the case of using aqueous solutions of $Co(NO_3)_2$ or $Ni(NO_3)_2$ (see ESI†).

In our previous reports, Cu/ZnO catalyst powders were embedded into paper-like catalyst composites comprising inorganic fibers as structural components by a papermaking technique.[8,9] In the present study, we performed the direct synthesis of CuNPs on a paper composite pre-composed of ZnO whiskers and ceramic fibers. ZnO whisker-containing paper composites were at first prepared using our established papermaking technique; then the retention of inorganic components reached to nearly 100%. Subsequently, ZnO whisker-containing paper composites were immersed in the aqueous solution of $Cu(NO_3)_2$, followed by the sequential treatments of pick-up, washing, drying and hydrogen reduction. The optical images of the original ZnO whisker-containing paper and ZnO whisker-containing paper treated with Cu nitrate solution are shown in Fig. 2(a)–(c). These paper composites are cardboard-like materials, flexible and easy to handle in practical use. Similar color changes were observed for these paper composites as were observed for ZnO whiskers (see ESI†). The XRD patterns were also identical (data not shown). Interestingly, no Cu species from the nitrate solution were adsorbed on to paper composites without ZnO whiskers; thus it was indicated that CuNPs were successfully synthesized only on the ZnO whiskers embedded within the paper-structured composite. Fig. 2(d) and (e) display scanning electron microscopic (SEM) images of the surface of the ZnO whisker-containing paper composite after synthesis of the CuNPs and the TEM image of CuNPs on ZnO whiskers (abbreviated as CuNPs@ZnO whiskers), respectively. CuNPs@ZnO whiskers were well-scattered throughout the ceramic fiber networks. The characteristic microstructure (average pore size: *ca.* 16 μm, porosity: *ca.* 50%) of the paper composite remained almost unchanged after synthesis of the CuNPs (see ESI†). Thus, the direct synthesis of CuNPs on a microstructured paper composite was successfully achieved by using pre-compounded ZnO whiskers as a selective scaffold for CuNPs. To our knowledge, this is the first report of the 'on-paper' synthesis of metal nanoparticles.

Fig. 3 demonstrates the ATR performances of Cu/ZnO powders, CuNPs@ZnO whiskers and CuNPs@ZnO whisker-containing paper composites (abbreviated as CuNPs@ZnO paper). Cu/ZnO powders were prepared by the co-precipitation method according to the previous reports.[3] In all cases, the weight ratio of Cu to ZnO (Cu : ZnO = 1.0 : 5.2), the actual amount of Cu/ZnO components (1.24 g) and the occupied volume in the reactor (8×10^3 mm^3) were perfectly adjusted to be identical. At the same reaction temperature (250 °C), CuNPs@ZnO whiskers exhibited a considerably higher methanol conversion and lower carbon monoxide concentration as compared with a conventional Cu/ZnO powder catalyst. The ZnO whiskers used in this study exhibited no catalytic activity toward the methanol reforming reaction; thus it was suggested that CuNPs prepared by our simple method have a higher catalytic activity than Cu catalysts prepared by the conventional co-precipitation method. Moreover, the CuNPs@ZnO composite paper comprising CuNPs directly synthesized on the surface of the ZnO whiskers in the paper composite displayed a higher methanol conversion and hydrogen production than CuNPs@ZnO whiskers, although the carbon monoxide concentration was almost the same. Such an interesting phenomenon was attributed to the paper-specific structural effects reported in our previous studies.[8,9] In the case of Cu/ZnO powder, it took a reaction temperature of 310 °C to accomplish the same methanol conversion (*ca.* 80%) afforded by the CuNPs@ZnO paper at a reaction temperature of 250 °C; and then the undesirable carbon monoxide concentration increased to >9000 ppm. Thus, the CuNPs@ZnO composite paper achieved an energy saving of 60 K and a suppression of carbon monoxide by-production to *ca.* 14% as compared with the conventional Cu/ZnO powders. These results suggest that the combination of CuNPs with a high catalytic activity and a paper-structured support with a fiber-network microstructure are particularly effective for the ATR reaction to produce pure hydrogen.

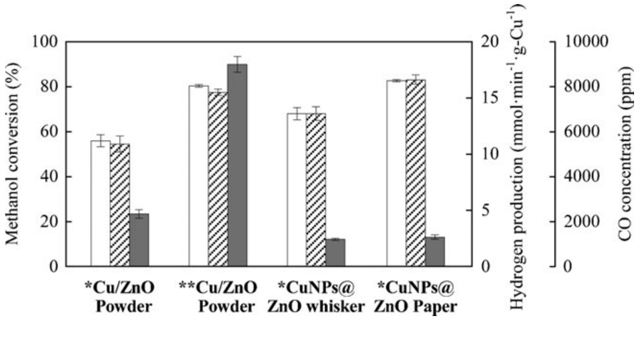

Fig. 3 ATR performances of Cu/ZnO powder, CuNPs@ZnO whiskers and CuNPs@ZnO paper; methanol conversion (open bars), hydrogen production (striped bars) and CO concentration (filled bars). Reaction temperature: 250 °C* or 310 °C**. Cu : ZnO = 1.0 : 5.2 (weight ratio). Cu content: 0.2 g/8×10^3 mm^3. Cu/ZnO powders were prepared by the co-precipitation method.

To conclude, we have demonstrated the *in situ* synthesis of CuNPs on microstructured paper composites composed of ZnO whiskers and ceramic fibers through the selective adsorption of Cu species on ZnO whiskers. The easy-to-fabricate CuNPs@ZnO paper composites showed an excellent catalytic performance in the ATR process for the production of hydrogen for fuel cell applications. This facile technique has great potential for future applications in the on-paper synthesis of other metal nanoparticles such as Ag, Pt and Au, which have a lower ionization tendency than Cu. The metal nanoparticles@ZnO paper composites with paper-like flexibility described here are designed to fit various reactor configurations, and are thus expected to be promising materials for improving the practical utility and catalytic performance of these reactor systems for a wide range of industrial chemical processes.

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