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Cu/ZnO based bulk catalysts have been commonly used to achieve for hydrogen production from methanol steam reforming under relatively low operating temperature. However, the bulk catalysts cannot be good alternative for micro reform due to mainly pressure drop in the micro channels for portable power supply. To address this issue, we developed novel thin film type Cu nanoparticle/ZnO nanowire catalysts for portable power supply and demonstrated their performance with the variation of Cu morphology according to the changes of Cu deposition and reduction time. In addition, the advanced methods to control Cu morphology were investigated as introducing the additive metals or varying process conditions of precipitation or calcination. Our results showed clearly that the morphology of Cu nanoparticle on single crystal ZnO nanowire play a great role in the methanol steam reforming processes. The morphology changes of Cu during chemical reaction were investigated systematically. Finally, we will discuss the optimal morphology of Cu nanoparticle on ZnO nanowire toward best catalytic performance.