Synthesis and Optical Properties of $M_xZn_{1-x}O$ Nanosponge (M = Mn, Fe, Co, Ni)

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ZnO doping with transition metal impurities has been widely investigated for extending the photo responses into the visible spectral range, thereby making them suitable candidates for photochemical conversion of solar energy into electrical or chemical potential. For Co^{2+} doped ZnO, the photochemistry was reported to proceed via excitation of a sub-bandgap absorption feature attributed by low-energy Co^{2+} d-d excitation which doped ZnO (Co^{2+}:ZnO). Therefore, utilizing mix-metal oxide materials, the optic and other chemical or physical properties, such as photoconversion efficiency and photoabsorption of solar-energy could be controllable by adjusting precursor and decomposition temperature.

Prior to this study, we reported a new coordination polymer $Zn(tda)H_2O$ that exhibits interesting thermodecomposition behavior to form porous ZnO nanocomposites with high defect concentration and strong green emission light. Further studies on the replacement of metal site to other transition metals (Mn, Fe, Co and Ni) have resulted in a series of M:ZnO nanocomposites. In this report, we report the synthesis and optic property studies of M:ZnO.

The synthesis of $M_xZn_{1-x}(tda)H_2O$ were carried out under hydrothermal conditions (180 ^oC, 1 day) using metal powder Zn, Mn Fe, Co, Ni, thiodiacetate, and deionized water. Needle shape crystals of $M_xZn_{1-x}(tda)H_2O$ were obtain with yield close to 90 % (according Zn). Porous product of metal doped $M_xZn_{1-x}O$ were obtained by placing crystalline samples of $M_xZn_{1-x}(tda)H_2O$ in a furnace, follow by heating at 550 ^oC (or temperature between 300 and 550 ^oC) for 24hr then cooled down to room temperature naturally.

Powder X-ray diffraction pattern of all metal-doped ZnO exhibits wurtzite-type structure and no diffraction peaks due to impurity phases. According to Scherrer equation, the average particle sizes of these oxide products are close to 30 nm, which confirms the presence of nanocrystalline M:ZnO. The SEM images of M:ZnO($Co_{0.05}Zn_{0.95}O$) show foam-like structure and the powder samples of Co/Zn, Ni/Zn, Fe/Zn and Mn/Zn products exhibit pink, light green, light yellow and white colors, respectively (**Figure 1.**).

XANES spectra show Co K edges with different doping concentration of Co^{2+} in $M_xZn_{1-x}O$(NSRRC BL17C). Comparing with Co_3O_4 and CoO(cubic phase) standard material, the Co K edge absorptions of $Co_{0.05}Zn_{0.95}O$ and $Co_{0.1}Zn_{0.9}O$ indicated that Co^{2+} ions in these materials were located in tetrahedral coordination environment. As Co^{2+} doping concentration exceed 15%, the absorption energy shifted to higher energy due to the formation of octahedrally coordinated Co^{2+} ions (**Figure 2.**).

In summary, we develop a new method to prepared tunable dopant concentration of M:ZnO (M=Mn, Fe, Co and Ni) nanocomposites by thermodecomposing the solid precursor $M_xZn_{1-x}(tda)H_2O$. The sharp pre-edge absorption curves for x = 0.05, 0.1 indicate tetrahedral environment of Co^{2+} ion.The M;ZnO exhibit strong absorption in 600-700nm. ZnO with M^{2+} doping also shows enhancement in photocurrent in near-UV region and the onset of the ZnO absorption band edge is shifted to lower energies.

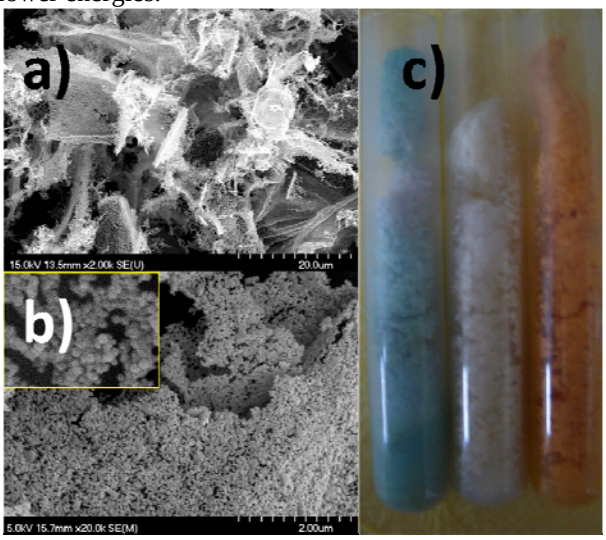

Figure 1. a) and b) are SEM images of $Co_{0.05}Zn_{0.95}O$ from thermo-decomposing process at 550°C. Inset image in b) shows the fine structure of a single layer. c) The photograph of $Co_xZn_{1-x}O$(green), ZnO(white), and $Fe_xZn_{1-x}O$(orange) that show colorful and homogeneous products with interesting expansion phenomenon.

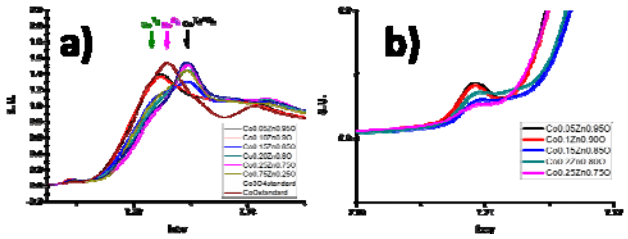

Figure 2. a) XANES spectra of Co K edge with different doping concentration of Co^{2+} in $M_xZn_{1-x}O$. b) The pre-edge absorption of Co K edge with different doping concentration of Co^{2+} in $M_xZn_{1-x}O$.The sharp pre-edge absorption curves for x = 0.05, 0.1 indicate tetrahedral environment of Co^{2+} ion.