ZnO-incorporated mesostructured silica nanoparticles (MSN) catalysts (ZM) were prepared by the introduction of Zn ions into the framework of MSN via a simple electrochemical system in the presence of various concentrations of NH4OH aqueous solution. The physicochemical properties of the catalysts were studied by XRD, 29Si MAS NMR, nitrogen adsorption-desorption, FE-SEM, TEM, FTIR, and photoluminescence spectroscopy. Characterization results demonstrated that the alkaline aqueous electrolyte simply generated abundant silanol groups on the surface of the catalysts as a consequence of desilication to form the hierarchical-like structure of the MSN. Subsequent restructuring of the silica network by the creation of oxygen vacancies and formation of Si-O-Zn during the electrolysis, as well as formation of new Si-O-Si bonds during calcination seemed to be the main factors that enhanced the catalytic performance of photodecolorization of methyl orange. A ZM prepared in the presence of 1.0 M NH4OH (ZM-1.0) was determined to be the most effective catalyst. The catalyst displays a higher first-order kinetics rate of 3.87 × 10^-1 h^-1 than unsupported ZnO (1.13 × 10^-1 h^-1) that prepared under the same conditions in the absence of MSN. The experiment on effect of scavengers showed that hydroxyl radicals generated from the three main sources: reduced O2 at the conduction band, decomposed water at the valence band and irradiated H2O2 in the solution, are key factors that influenced the reaction. It is also noted that the recycled ZM-1.0 catalyst maintained its activity up to five runs without serious catalyst deactivation.