

Hydrothermal Synthesis of New Silver-Vanadate Hybrid Solids And Their Optical and Photocatalytic Properties

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Three new silver-vanadate hybrids, $[\text{Ag}(\text{bpy})]_4\text{V}_4\text{O}_{12}\cdot 2\text{H}_2\text{O}$ (**I**), $[\text{Ag}(\text{dpa})]_4\text{V}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$ (**II**) and $\text{Ag}_4(\text{pzc})_2\text{V}_2\text{O}_6$ (**III**) (bpy = 4,4'-bipyridyl, dpa = 1,2-bis(4-pyridyl)-ethane, pzc = pyrazine-2-carboxylic acid), were synthesized by hydrothermal methods and characterized using single crystal X-ray diffraction (**I**, $P2_1/c$, $Z = 4$, $a = 11.375(2) \text{ \AA}$, $b = 14.281(4) \text{ \AA}$, $c = 13.597(3) \text{ \AA}$, $\beta = 91.462(1)^\circ$; **II**, $P2_1/c$, $Z = 8$, $a = 13.5748(3) \text{ \AA}$, $b = 15.3372(4) \text{ \AA}$, $c = 14.1854(3) \text{ \AA}$, $\beta = 114.141(1)^\circ$; **III**, $P-1$, $Z = 2$, $a = 3.570(1) \text{ \AA}$, $b = 11.837(4) \text{ \AA}$, $c = 19.283(5) \text{ \AA}$, $\alpha = 89.98(1)^\circ$, $\beta = 87.62^\circ$, $\gamma = 86.24^\circ$), thermogravimetric analysis (TGA), and UV-Vis diffuse reflectance. The structures of **I** and **II** are constructed from neutral bimetallic-oxide $\{\text{Ag}_4\text{V}_4\text{O}_{12}\}_n$ cluster layers that are pillared by organic ligands (bpy for **I**, dpa for **II**) to the Ag sites in each layer, while the structure of **III** is comprised of a $\{\text{Ag}_2(\text{pzc})\}_n^{n+}$ 3D network with $\{\text{VO}_3\}_n^{n-}$ infinite ladder chains in the channels. These hybrids are stable in air, but decompose upon heating with the removal of the organic ligands at temperature $>180^\circ\text{C}$ for **I**, $>120^\circ\text{C}$ for **II** and $>300^\circ\text{C}$ for **III**. UV-Vis diffuse reflectance measurements show optical band gaps of 2.77 eV for **I**, 2.95 eV for **II**, and 2.45 eV for **III**. Their photocatalytic activities have been evaluated for the decomposition of methylene blue (MB) under both UV light ($\lambda < 400 \text{ nm}$) and visible light ($\lambda > 400 \text{ nm}$). **III** shows high rates for the decomposition of MB under both UV and visible-light irradiation. **I** and **II** are only active for the decomposition of MB under UV light. The effect of the three different ligands on their atomic and electronic structures and photocatalytic activities are analyzed and discussed.

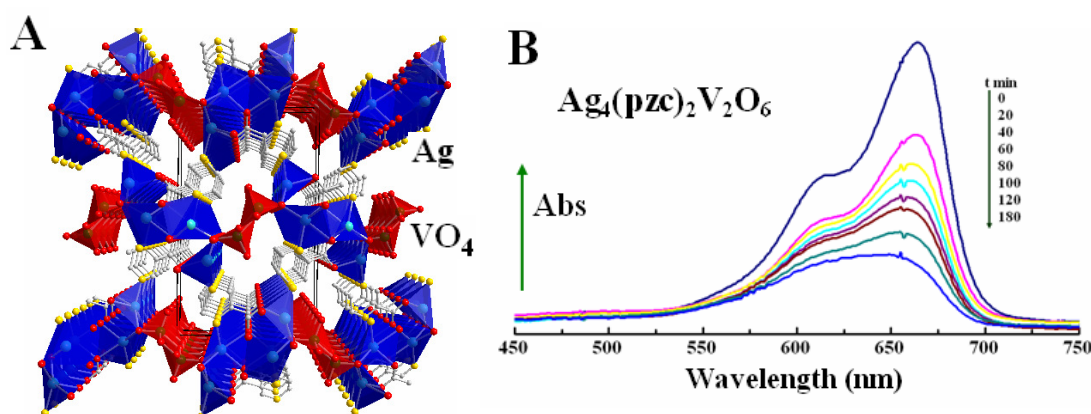


Figure. (A) $\sim[100]$ polyhedra view of the $\text{Ag}_4(\text{pzc})_2\text{V}_2\text{O}_6$ structures with the unit cell outlined. (B) Absorption spectra of a solution of MB (6.0 mg/L, 50mL) in the presence of $\sim 150\text{mg}$ of sample **III** suspension under visible light irradiation.