Electronic Supplementary Information

Novel high-efficiency visible-light response $Ag_4(GeO_4)$ photocatalyst

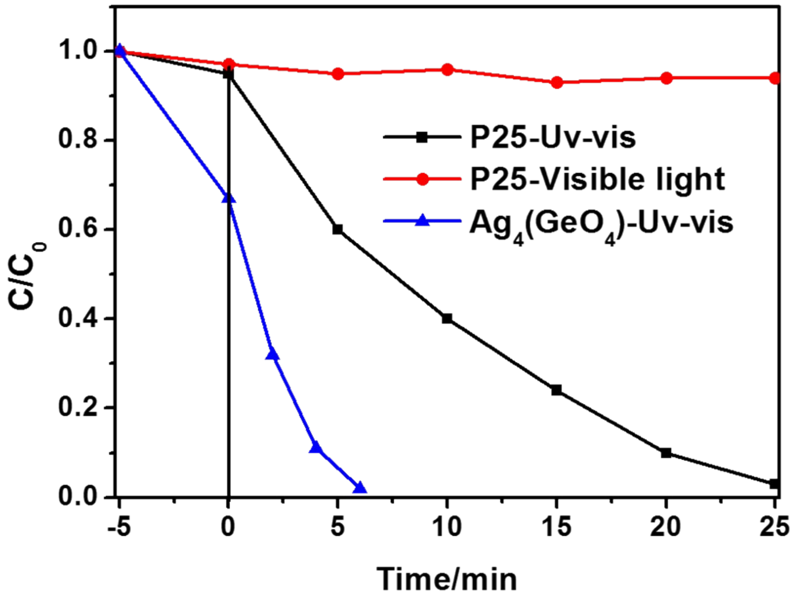

Fig.S1 Photodegradation of MB solution under visible or UV-Vis light irradiation with commercial P25 and $Ag_4(GeO_4)$

	$Ag_4(GeO_4)$	Ag_2O	C_3N_4
k	0.125	0.043	0.021
k_{BET}	0.00665	0.00796	0.0015

Table1. Degradation constants of the samples before (k) and after (k_{BET}) being normalized with surface areas.

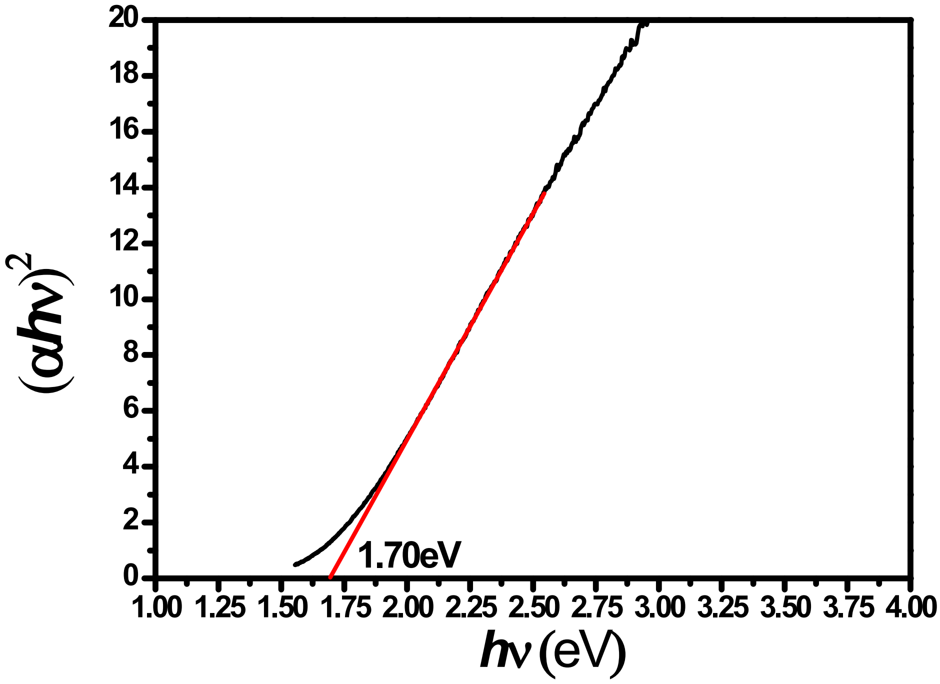

Fig.S2 $(ah\nu)^2$ versus $(h\nu)$ plot of the $Ag_4(GeO_4)$ sample.

Calculations of the VB and CB edges of $Ag_4(GeO_4)$

For a semiconductor, the absorbance near the absorption edge is described by the

formula: $\alpha h\nu = A(h\nu - Eg)n/2$, where α is the absorption coefficient, $h\nu$ is the photon energy, A is a constant and Eg is the band gap. For $Ag_4(GeO_4)$, n = 4 for indirect transition, the result is shown in Fig.S2.

The VB edge of a semiconductor at the point of zero charge (E_{VB}^{0}) is empirically expressed as[1-3],

$$E_{VB}^{0} = \chi_{comp} - 2.30RT(pH_{zpc} - pH)/F - E^e - \frac{1}{2}E_g \qquad (1)$$

In this formular R is the gas contant, T is temperature, and F is Faraday constant. Eg is the band gap of the semiconductor, and E^e the energy of the free electrons on the hydrogen scale (i. e., E^e =4.5 eV).Under the reasonable assumption that the solution's pH value at the zero point of charge, pH_{ZPC}, is very close to the solution's pH value, pH, we obtain

$$E_{VB}^{0} \approx E_{VB} \approx \chi_{comp} - E^e - \frac{1}{2}E_g \qquad (2)$$

χ_{comp} is the electronegativity of a compound which is given by the geometric mean of the electronegativity of the constituent atoms, which expressed as the mean geometric of absolute electronegativity of all the constituent atoms, E_e means the free electrons energy contrasting to the hydrogen scale (4.5 eV vs NHE), E_g is the semiconductor band gap energy. that is [4],

$$\chi_{comp} = \sqrt[N]{\chi_1^r \chi_2^s \cdots \chi_3^p \chi_4^q}, \quad (3)$$

where χ and N are the electro negativity of the constituent atom, the number of the species, and the total number of atoms in the compound, respectively . The superscripts r, s, p, ... , q refer to the numbers of the atoms 1, 2, ... , n-1 and n, respectively in the molecule, respectively, so that r + s +······+ p + q = N. From its UV/Vis diffuse reflectance spectrum, the band gap of $Ag_9(SiO_4)_2NO_3$ is estimated to be 1.70 eV. The values of O, Ge and Ag are 7.54, 4.78, 4.44 respectively [5].

Thus, from Eq. 2, the VB edge of $Ag_4(GeO_4)$ is estimated to be 2.01 eV with respect to the normal hydrogen electode (NHE) Consequently, on the basis of its band gap (1.70 eV), the VB edge of $Ag_4(GeO_4)$ is determined to be 0.31 eV with respect to the NHE.

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[2]M. A. Butler, D. S. Ginley, J. Electrochem. Soc. 1978, 125, 228-232.

[3]Y. Xu, M. Schoonen, Am. Mineral, 2000, 85, 543-556.

[4]R. T. Sanderson, Chemical Periodicity, Reinhold, New York 1960.

[5]D. Yu, Z.-D. Chen, F. Wang, S.-Z. Li, Acta Phys. Chim. Sin. 2001, 17, 15-22.

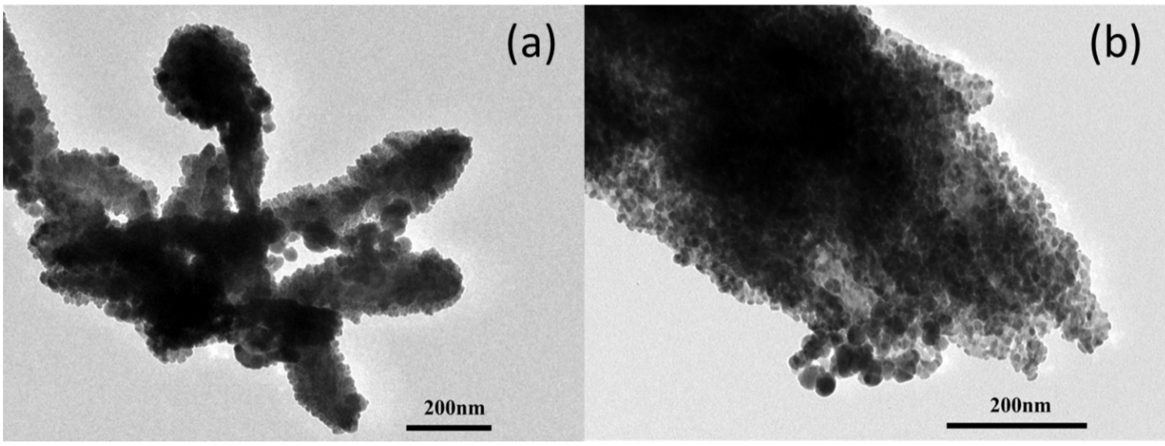

Fig.S3 TEM images of the $Ag_4(GeO_4)$ sample.

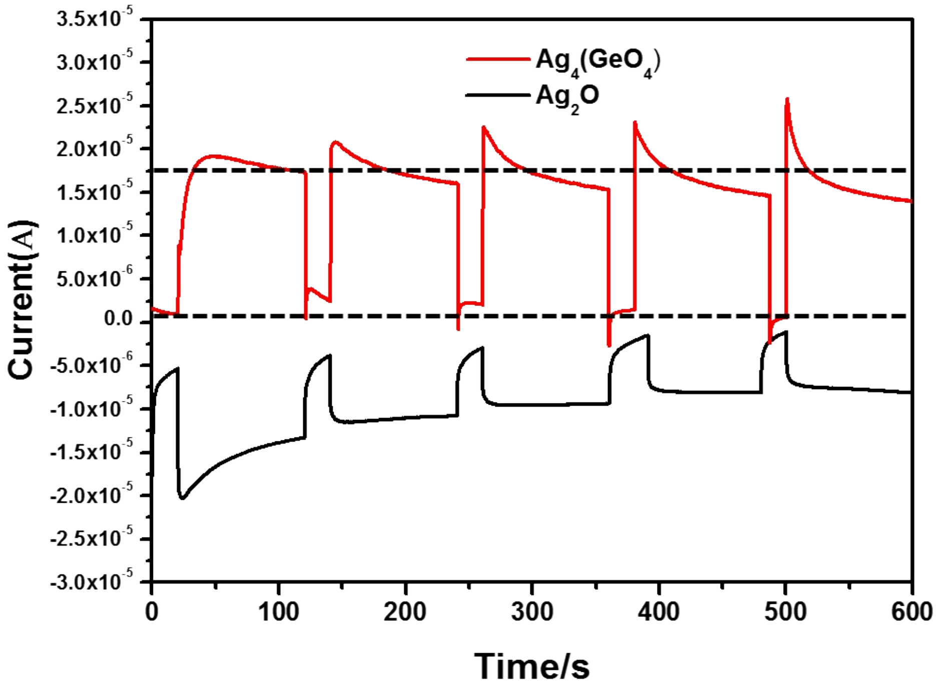

Fig.S4 Photocurrents of the $Ag_4(GeO_4)$ and Ag_2Osample.