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三元杂化 TiO_2-SiO_2-POMs 催化剂的合成及其在可见光降解罗丹明 B 中的应用

王晓夏[1]　徐华龙[1,*]　沈　伟[1]　RUHLMANN Laurent[2]　秦　枫[1]
SORGUES Sébastien[3]　COLBEAU-JUSTIN Christophe[3]

([1] 复旦大学化学系, 上海市分子催化与功能材料重点实验室, 复旦大学先进材料实验室, 上海 200433; [2]Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, Institut de Chimie, UMR au CNRS n° 7177, Université de Strasbourg, France; [3]Laboratoire de Chimie Physique, UMR au CNRS n° 8000, Université Paris-Sud 11, Orsay, France)

Synthesis of Ternary Hybrid TiO_2-SiO_2-POMCatalysts and Its Application in Degrading Rhodamine B under Visible Light Illumination

WANG Xiao-Xia[1]　XU Hua-Long[1,*]　SHEN Wei[1]　RUHLMANN Laurent[2]
QIN Feng[1]　SORGUES Sébastien[3]　COLBEAU-JUSTIN Christophe[3]

([1]*Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Laboratory of Advanced Materials, Fudan University, Shanghai 200433, P. R. China*; [2]*Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, Institut de Chimie, UMR au CNRS n° 7177, Université de Strasbourg, France*; [3]*Laboratoire de Chimie Physique, UMR au CNRS n° 8000, Université Paris-Sud 11, Orsay, France*)

∗Corresponding author. Email: shuhl@fudan.edu.cn; Tel: +86-21-65642401.

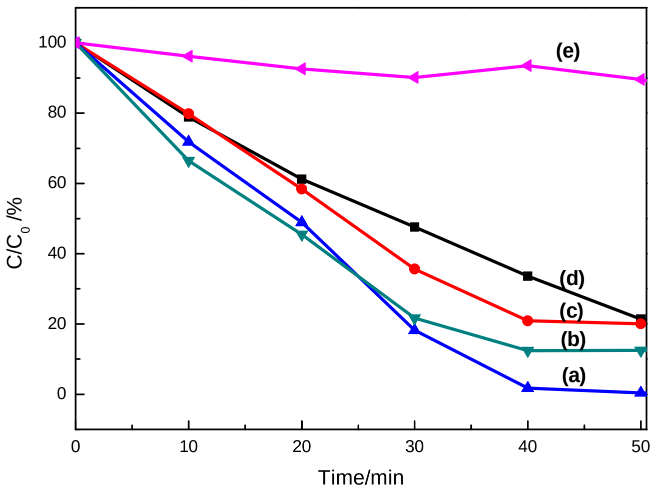


Fig.S1 Photodegradation of Rhodamine B by different POMs impregnated on P25 (3 mg in total amount, 3 mL 0.1 mmol·L^{-1} Rhodamine B, bubbled in air, using a 385 nm wavelength cut-off filter)

(a) P25-$SiW_{12}O_{40}^{4-}$; (b) P25-$[Mn_2(H_2O)_2Fe_2(P_2W_{15}O_{56})_2]^{14-}$; (c) P25-$PW_{12}O_{40}^{3-}$; (d) P25; (e) no catalyst

The hybrids (a), (b) and (c) were synthesized by impregnation method.[1] $SiW_{12}O_{40}^{4-}$ was selected as the main POMs applied in the following experiments, due to its high conversion ability. $FeW_{11}O_{39}^{9-}$ mentioned by Li *et al.*[17] was not considered here because $SiW_{12}O_{40}^{4-}$ is more stable than $FeW_{11}O_{39}^{9-}$ where in low pH demetallation could occur.

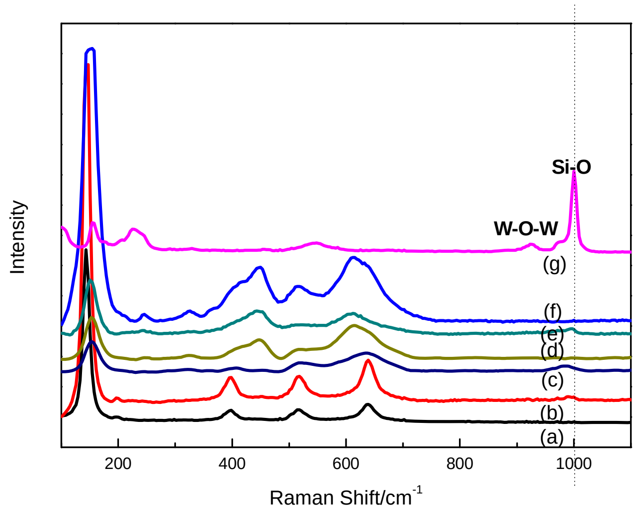


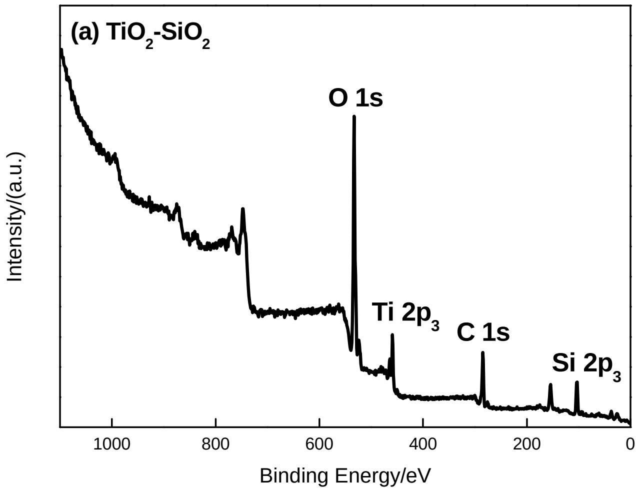
Fig.S2 Raman scattering spectra of the catalysts

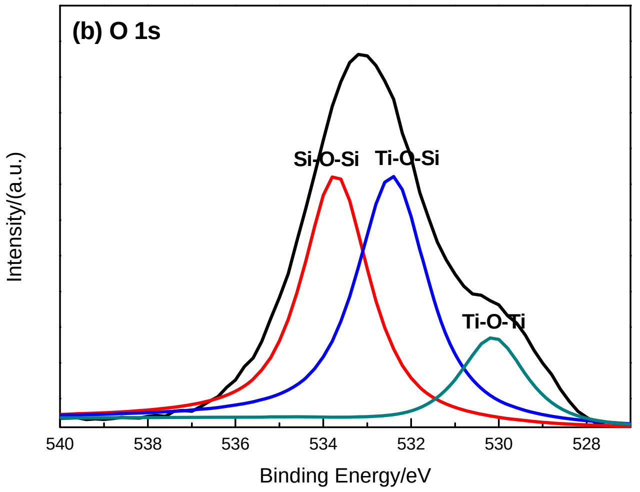
(a) P25; (b) P25-$SiW_{12}O_{40}^{4-}$; (c) TiO_2-SiO_2-$SiW_{12}O_{40}^{4-}$; (d) TiO_2-SiO_2; (e) TiO_2-$SiW_{12}O_{40}^{4-}$; (f) TiO_2; (g) $SiW_{12}O_{40}^{4-}$

Raman spectra are as Fig. S2 shows. The peaks relating SiW_{12} are assigned as follows: 999.9 cm $^{-1}$ (strong) is the symmetric Si-O bond of stretching vibrations of SiO_4 sites, and 929.7 cm $^{-1}$ (weak) is the W-O-W bond of stretching vibrations.

In the plots, P25-$SiW_{12}O_{40}^{4-}$ shows very tiny peaks of $SiW_{12}O_{40}^{4-}$ but still has a small peak, while sol-gel TiO_2-$SiW_{12}O_{40}^{4-}$ shows a broadened peak approximately at 996.7 cm $^{-1}$, weakening the sharp peak of Si-O and blurring the peak of W-O-W. This change indicates some new structure has formed when $SiW_{12}O_{40}^{4-}$ contacts the surface of TiO_2.

The symmetric Si-O bond in the spectrum of TiO_2-SiO_2-$SiW_{12}O_{40}^{4-}$, which peaks at 885.1 cm $^{-1}$, has drifted to smaller Raman shift. The vibration of Si-O in $SiW_{12}O_{40}^{4-}$ is weakened and broadened. Whereby, Si-O has altered further with the input of SiO_2, indicating that a new structure is certainly formed when SiO_2 contacts the surface of TiO_2.


(a) TiO$_2$-SiO$_2$
O 1s
Ti 2p$_3$
C 1s
Si 2p$_3$
Intensity/(a.u.)
1000
800
600
400
200
0
Binding Energy/eV


(b) O 1s
Si-O-Si
Ti-O-Si
Ti-O-Ti
Intensity/(a.u.)
540
538
536
534
532
530
528
Binding Energy/eV

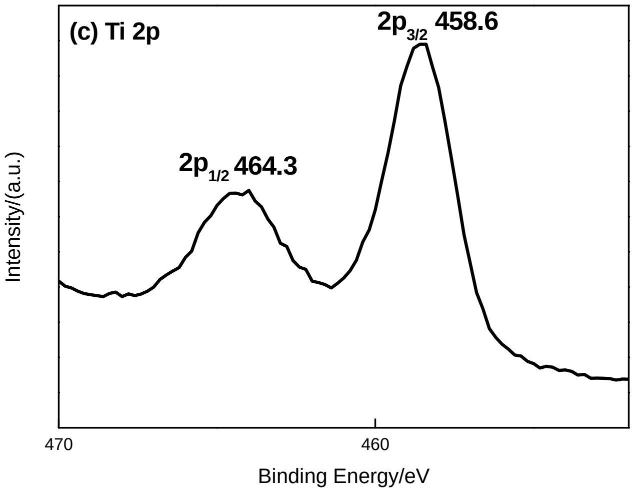

(c) Ti 2p
2p$_{3/2}$ 458.6
2p$_{1/2}$ 464.3
Intensity/(a.u.)
470
460
Binding Energy/eV

Fig.S3 XPS patterns of TiO_2-SiO_2 (Full Spectra is (a)), including the bonding circumstances of O 1s (b) and Ti 2p (c)

Stable Ti-O-Si bond in TiO_2-SiO_2 is formed during the calcination. The three peaks are: Si-O-Si, 533.7 eV; Ti-O-Si, 532.4 eV; Ti-O-Ti, 530.1 eV respectively (Fig. S3 (b)). They are credible since they are very similar to those in the results of Zhang *et al.*[20], as they showed as: Si-O-Si, 533 eV; Ti-O-Si, 532.2 eV; Ti-O-Ti, 529.7 eV. Silicon substitutes for some of the lattice titanium atoms and form a Ti–O–Si structure. XPS signals of Ti 2*p* were observed at binding energies at around 458.5 eV (Ti $2p_{3/2}$) and 464.3 eV (Ti $2p_{1/2}$), as shown in Fig. S3 (c). The Ti 2*p* peaks were in good agreement with pure TiO_2. Ti 2*p* peaks were in good agreement with pure TiO_2. This also indicates that the titanium atom is bond with oxygen but not silicon.

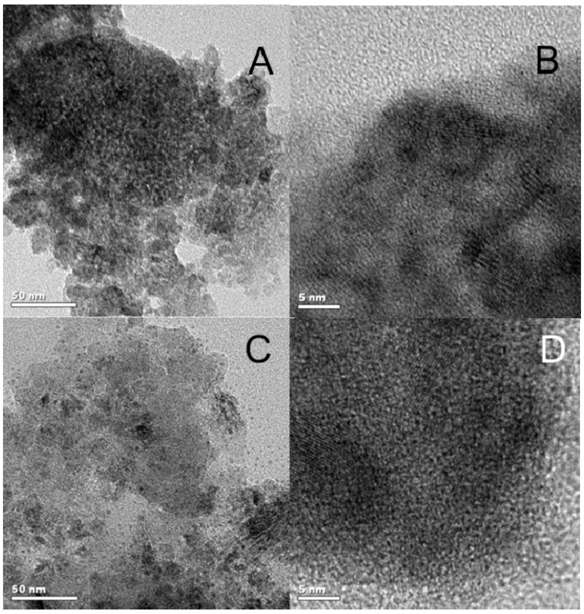


Fig.S4 TEM photos of TiO_2-$SiW_{12}O_{40}^{4-}$ (A, B) and TiO_2-SiO_2-$SiW_{12}O_{40}^{4-}$ (C, D)

TiO_2 agglomerates as dark particles indicated in A, B. The introduction of SiO_2 improves the dispersion of TiO_2, which is clearly exibited in C, D. This phenomenon keeps in accordance with increasing surface area in Table 1. In C and D, the light background consists of SiO_2 particles, on which darker clusters are TiO_2 particles.

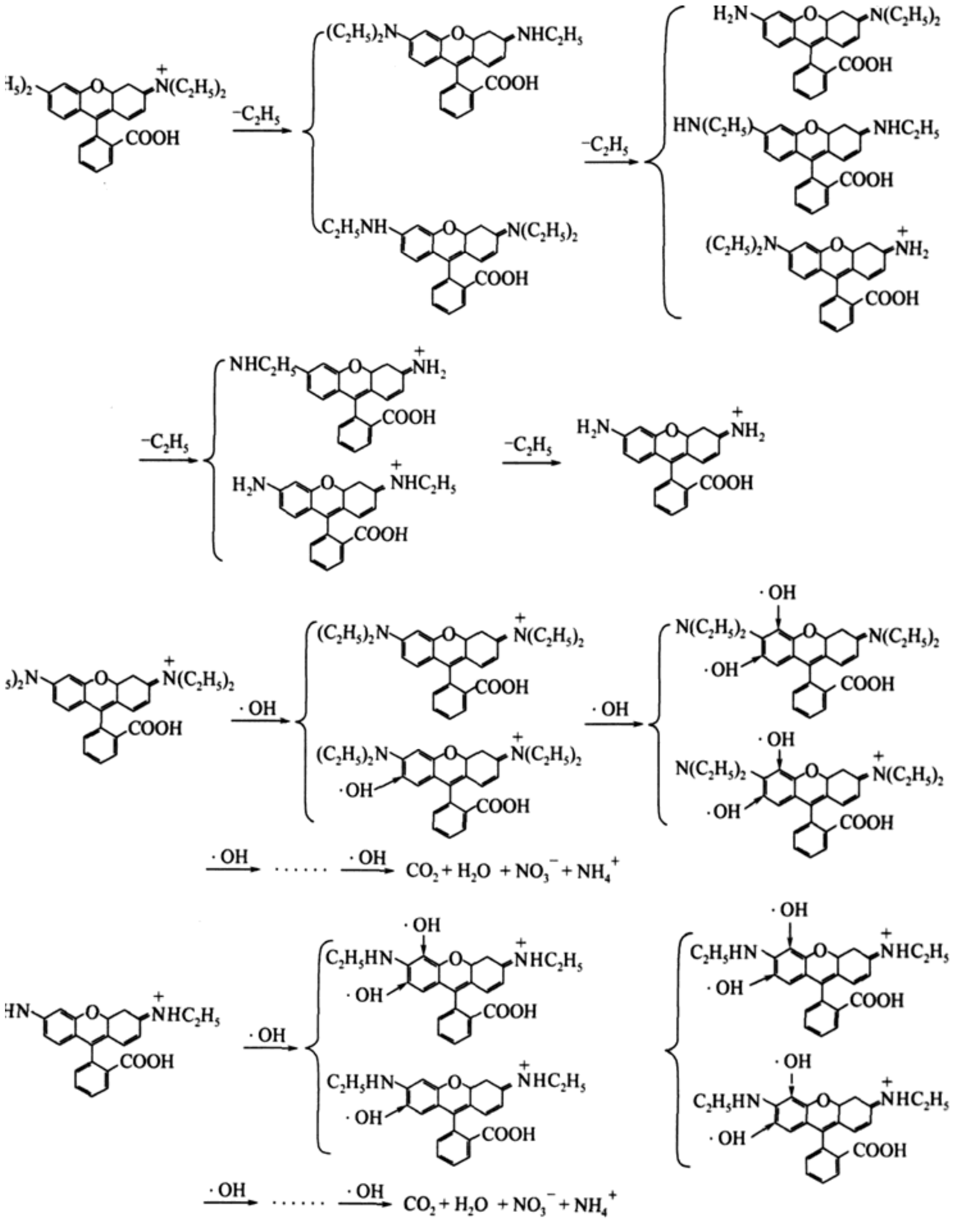


Fig.S5 Schematic diagram of the photodegradation reaction of RhB, including (a) the de-ethylation process and (b) the break and oxidation of benzene ring. The reaction can be continued as (c) the furthered hydroxylation and oxidization of RhB missing a unit of ethyl group.

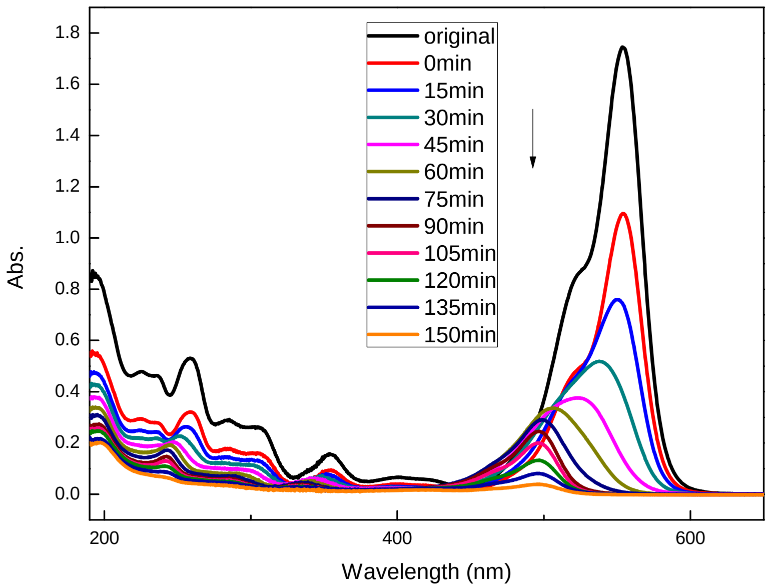


Fig.S6 UV-Vis absorption spectra of RhB catalyzed by TiO_2-SiO_2-$SiW_{12}O_{40}^{4-}$

References

(1) Tachikawa, T.; Tojo, S.; Fujitsuka, M.; Majima, T. *Chem. Eur. J.* **2006,** *12*, 3124.