Electronic Supplementary Information

A novel self-assembling nanoparticle of Ag/Bi with high reactive efficiency

Jianyu Gong,[a] Chung-Seop Lee,[a] Yoon-Young Chang[b] and Yoon-Seok Chang [a] *

[a] *School of Environmental Science and Engineering,*

Pohang University of Science and Technology (POSTECH),

Pohang, 790-784, Republic of Korea

[b] *Department of Environmental Engineering,*

Kwangwoon University, Seoul, 139-701, Republic of Korea

*Corresponding author contact information:

Email : yschang@postech.ac.kr, Phone: +82-54-279-2281, Fax: +82-54-279-8299

Reagents

Bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$, >99%), silver nitrate ($AgNO_3$, >99%), sodium borohydride ($NaBH_4$, >98%), ferrous sulfate ($FeSO_4 \cdot 7H_2O$, >99%), palladium acetate ($Pd(C_2H_3O_2)_2$, >47.4%) acetone (>99%), coumarin (>98%), isopropanol (>99%), 1,4-benzoquinone (>98%), trifluoroacetic acid (>99%), 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, >97%) and phenol (>98%) were supplied by Sigma-Aldrich.

Preparation of Ag/Bi

In a typical synthesis, 0.3 g of $Bi(NO_3)_3 \cdot 5H_2O$ and 0.15 g of $AgNO_3$ were mixed with 100 mL of water. Then, 10 mL of $NaBH_4$ (0.16 g / 10mL) was then added dropwise into the mixture. The mixture was maintained under a nitrogen atmosphere, and finally dried at 40 °C under vacuum for 12 h.

Preparation of nZVI and Pd/nZVI

To produce the modified nZVI, 2 g of $FeSO_4 \cdot 7H_2O$ was mixed with 200 mL of water. Then, 10 mL of $NaBH_4$ (0.16 g/L) was then added dropwise into the mixture. The mixture was maintained under a nitrogen atmosphere, and finally dried at 60 °C under vacuum for 12 h. To synthesize Pd/nZVI, the process is similar with the method mentioned above in the presence of 5 mL acetone solution with palladium acetate (0.1 mM).

Cost-effectiveness of Ag/Bi

In this study, the reactions (1) and (2) were proposed for the processes to synthesize Ag/Bi and nZVI, respectively, as shown below:

$Bi(NO_3)_3 \cdot 5H_2O + AgNO_3 + 4NaBH_4 + 7H_2O \rightarrow Ag/Bi\downarrow + 14H_2\uparrow + 4B(OH)_3 + 4NaNO_3$ (1)

$FeSO_4 \cdot 7H_2O + 2NaBH_4 \rightarrow Fe\downarrow + 7H_2\uparrow + 2B(OH)_3 + Na_2SO_4 + H_2O$ (2)

From the calculations based on those equations and the prices from Sigma Aldrich, to obtain 1 g of Ag/Bi with the ratio of 0.5:1, we need 0.73 g of $Bi(NO_3)_3 \cdot 5H_2O$, 0.36 g of $AgNO_3$ and

0.42 g of $NaBH_4$, suggesting the total cost is \$ 2.2/g. On the other hand, to get the same amount of nZVI (1g), we need 4.96 g of $FeSO_4·7H_2O$ and 1.35 g of $NaBH_4$, suggesting the total cost is \$ 4.6/g. The quotation is listed below:

Table S1 The quotation of compounds from Sigma

Chemical	Sigma's price (\$)
$Bi(NO_3)_3·5H_2O$	220.2 / 500g
$AgNO_3$	146.1 / 500g
$FeSO_4·7H_2O$	73.72 / 250g
$NaBH_4$	253.2 / 100g

Obviously, it looks to us that Ag/Bi might be cheaper than nZVI with much higher reactivity.

Characterizations

A JEOL JSM-7401FSEM with an energy dispersive (EDX) X-ray system and an HRTEM (JEOL JEM-2200FS) equipped with an electron energy loss spectrometer were employed to characterize the morphology of the nanoparticles. Phase detection and analysis were accomplished using an XRD (2θ ranged from 10° to 90°) at 40 kV and 40 mA (MAC Science Co., Japan) using Cu $K\alpha$ radiation (k = 0.154 nm). The XRD results were analyzed by High-score software. The XPS analysis was conducted on a VG ESCALAB 220iXL. BET surface area and pore size distribution were measured by N_2 adsorption and desorption using an ASAP 2010 system at 77 K. The fluorescence spectra were recorded on an RF-5301 PC fluorometer (SHIMADZU, Japan). Size distribution of particles was measured by an ELSZ-1000 particle size analyzer. Electron spin resonance (ESR) signals of DMPO-•OH were detected using a Bruker A200 Spectrometer.

Reactive activity test

The reactive activity of the prepared samples was evaluated by measuring the degradation of phenol. Those batch experiments have been conducted in a 100 mL vial sealed with cap. 50 mg (1 g/L) catalyst was added into 50 mL aqueous solution of phenol (50 mg/L).The reactions were sampling after desired time. The quenching experiments using different radical scavengers were conducted similar with the above degradations in the presence of scavengers. Each of degradation was repeated three times and calculated the mean value as the result with error bars.

The phenol concentration was determined via HPLC on an Agilent 1100 chromatograph (Agilent, USA) equipped with an Amethyst C18 column (250 mm× 4.6 mm) and a UV detector. The mobile phase used was a mixture of methanol and water (60:40, v/v) at a flow rate of 1 mL min^{-1}. The UV detector was operated at 270 nm.

Hydroxyl radical (•OH) formation was monitored using coumarin (0.1 mM) as the fluorescence probe. The umbelliferone concentration was recorded in terms of fluorescent spectra at an absorption range of 380 nm to 600 nm using an excitation wavelength of 350 nm.

Hydroxyl radical (•OH) formation was further detected by electron spin resonance (ESR). A popular spin trap, DMPO, was selected to trap •OH. The setting was as follows: microwave power of 20 mW; microwave frequency at 9.86 GHz; modulation frequency of 100 kHz; and modulation amplitude of 1 G.

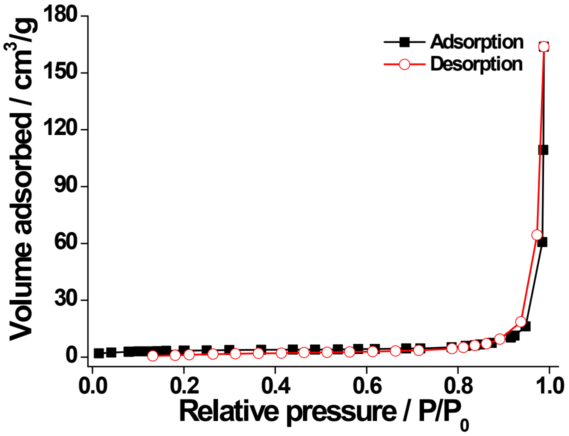


Fig. S1 Nitrogen adsorption-desorption isotherms of Ag/Bi.

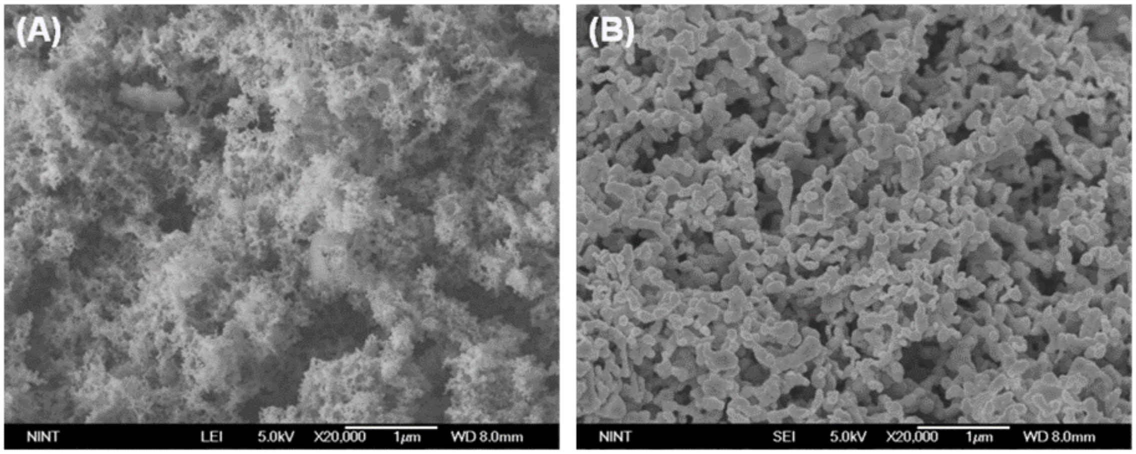


Fig. S2 SEM images of (A) Bi and (B) Ag

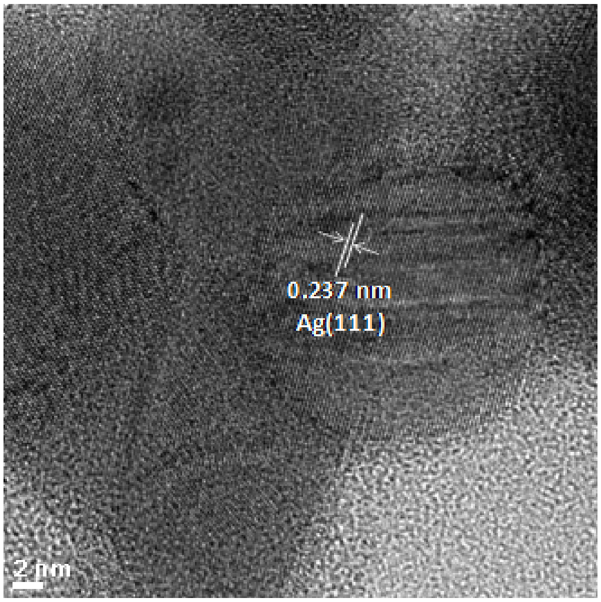


Fig. S3 TEM image of Ag/Bi particles

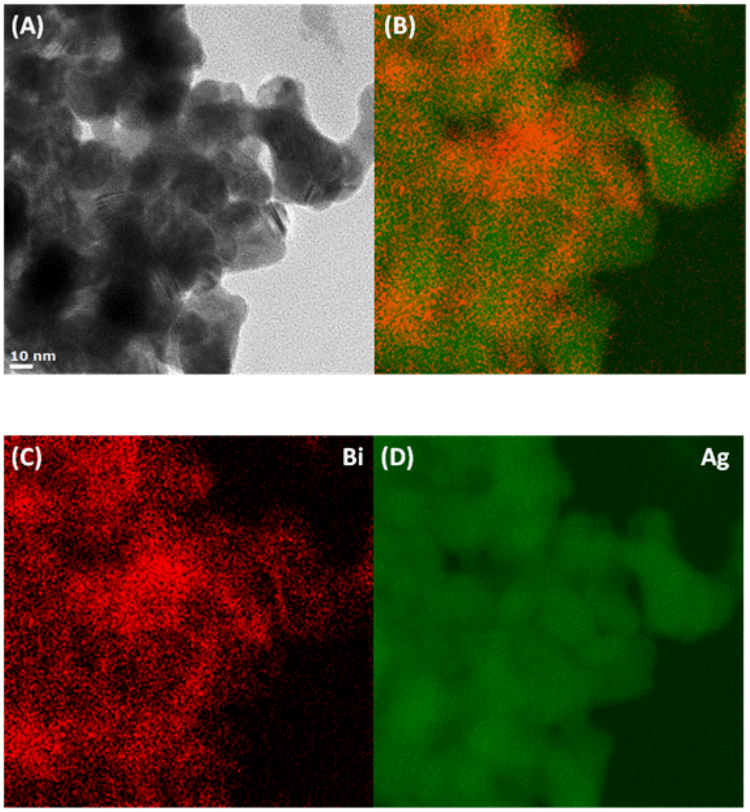


Fig. S4 (A) TEM image of Ag/Bi. (B) EELS map of overlay of Ag/Bi, and the element of (C) Bi and (D) Ag.

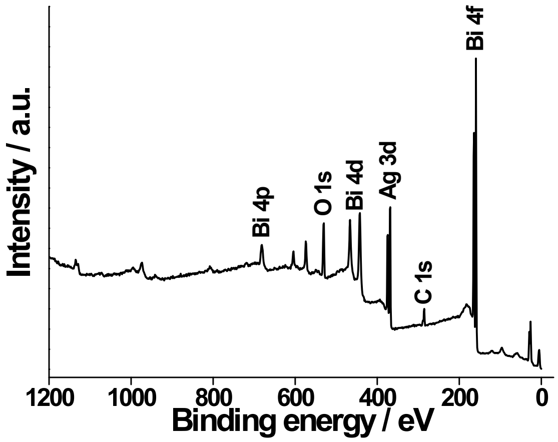


Fig. S5 XPS global spectra of Ag/Bi

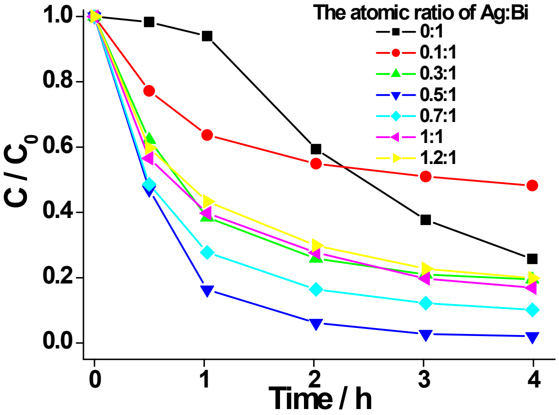


Fig. S6 Comparison of degradation of phenol by Ag/Bi as-prepared with different ratio of Ag to Bi.

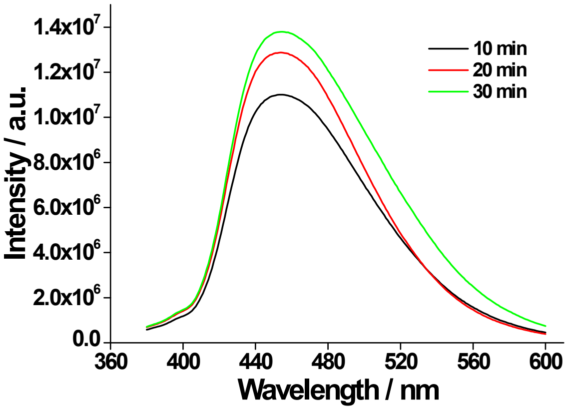
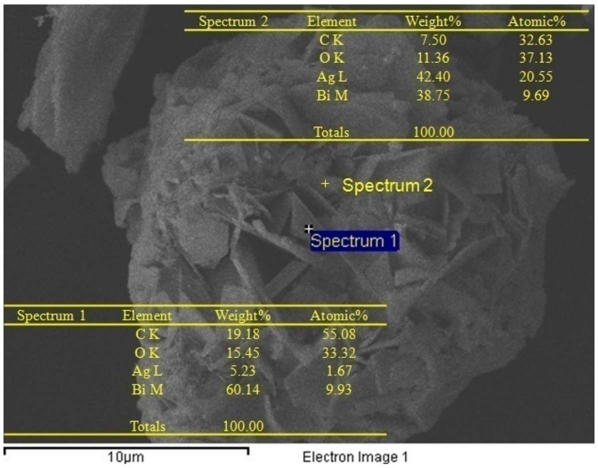


Fig. S7 Fluorescence spectra of umbelliferone in 0.1 mM coumarin solution in the presence of nZVI.



Spectrum 2	Element	Weight%	Atomic%
	C K	7.50	32.63
	O K	11.36	37.13
	Ag L	42.40	20.55
	Bi M	38.75	9.69
	Totals	100.00	

Spectrum 1	Element	Weight%	Atomic%
	C K	19.18	55.08
	O K	15.45	33.32
	Ag L	5.23	1.67
	Bi M	60.14	9.93
	Totals	100.00	

Fig. S8 SEM image of Ag/Bi after the degradation of phenol with EDX analysis. The inset tables of bottom and above are corresponding to spectrum 1 and 2, respectively.