Supporting Information

ZnO-Bi2O3/Graphitic Carbon Nitride Photocatalytic System with H2O2-Assisted Enhanced Degradation of Indigo Carmine under Visible Light

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**Synthesis**

200 mL of Melamine solution at various levels of molarity (*x* = 0, 1, 2, and 4) was heated to 75 ± 5 °C until melamine was dissolved completely. Then, the mixture of Zn(NO3)2. 6H2O and Bi(NO3)3. 5H2O with molar ratio of 3:1 in 100 mL of nitric acid solution (5%) and an alkaline solution of 1M NaOH were added to melamine solution at a flow rate of 2 mL⋅min-1 using syringe pump. The pH of the mixture was maintained at 10 during the synthesis. The mixture was fixed at 75 ± 5 °C for 24 h. After that the prepared materials were centrifuged, washed, and dried at 70 °C for 10 h, followed by heating at 520 °C for 3 h to get the mixed-metal oxides (ZnO-Bi2O3) and mixed-metal oxides-graphiticcarbon nitride (ZnO-Bi2O3-*x*C3N4). The as-prepared materials were labeled as ZnO-Bi2O3-*x*C3N4 (*x* = 0, 1, 2, and 4) and are hereafter referred to as ZnO-Bi2O3, ZnO-Bi2O3-*1*C3N4, ZnO-Bi2O3-*2*C3N4, and ZnO-Bi2O3-3C3N4.

**Characterizations of the prepared materials**

XRD patterns of powder samples were obtained using a Rigaku Ultima IV X-ray diffractometer (Japan). The XRD patterns of C3N4, ZnO-Bi2O3, and ZnO-Bi2O3-*x*C3N4 are shown in Figure S1(A). As seen in the XRD pattern of ZnO-Bi2O3, there are several strong peaks at 2*θ* = 28.0, 31.8, 32.8, 46.3, 47.0, 54.4, 55.8, and 58.0 corresponding to tetragonal zinc bismuth oxide (JCPDS No. 043-0449) and peaks at 2*θ* = 31.5, 34.4, 36.1, 57.0, and 63.0 corresponding to pristine hexagonal zinc oxide (JCPDS No. 079-0207). Most of the diffraction peaks are sharp and symmetrical, indicating good crystallinity. Pristine C3N4 typically presents main diffraction peaks around 27.3° (JCPDS No. 87-1526). The diffraction patterns of the ZnO-Bi2O3-*x*C3N4 samples were characterized by a new peak at 24.7°in comparison with pristine ZnO-Bi2O3. In addition, the ZnO-Bi2O3-*x*C3N4 patterns showed a sharp and strong peak at 27.7°. There are slight shift of the diffraction peak in comparison with the peak at 28° of ZnO-Bi2O3 and 27.3° of C3N4 to indicate hybridization between C3N4 and ZnO-Bi2O3.

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| **(D)**  **(C)**  **(A)**  **(B)** |
| **Figure S1:** (A) XRD patterns; (B) FT-IR spectra, (C) UV-Vis absorption spectra, and (D) Tauc plot with a) C3N4; b) ZnO-Bi2O3 ; and c–e) ZnO-Bi2O3-*x*C3N4 (*x* = 1, 2, and 3). |

The FT-IR spectra of the C3N4, ZnO-Bi2O3, and ZnO-Bi2O3-*x*C3N4 samples are displayed in Figure S1(B). The broad bands around 3200 cm-1 are assigned O-H stretching vibration of adsorbed water [3]. The absorption band at 510-520 cm-1 in ZnO-Bi2O3 and ZnO-Bi2O3-*x*C3N4 spectra verified the existence of Zn-O bond. The bands at 1250-1650 cm-1, 800 cm-1, and 3200 cm-1 in FT-IR spectrum of C3N4 shows the typical stretching mode of C-N heterocycles, the breathing mode of the tri-s-triazine ring, and the stretching vibration mode of Na-H, respectively [4 -6].

The UV-Vis diffuse reflectance spectrum (DRS) was recorded on a Jasco V670 UV-Vis spectrophotometer (Japan) with an integrating sphere attachment. The UV-Vis absorption edges of the as-prepared samples are shown in Figure S1(C). The absorption edges of ZnO-Bi2O3-*x*C3N4 are blue-shifted in comparison with those of pristine C3N4 and pristine ZnO-Bi2O3. The moving absorption edges of the ZnO-Bi2O3-*x*C3N4 samples compared to those of pristine C3N4 and ZnO-Bi2O3 are attributed to the strong interaction between C3N4 and ZnO-Bi2O3 in the resulting ZnO-Bi2O3-*x*C3N4 photocatalysts. The band gap energy (E*­*g) of the as-prepared materials was estimated using the Kubelka-Munk function and the results are shown in Figure S1(D). The band gap energy of the pristine ZnO-Bi2O3 appeared at 2.95 eV and 2.20 eV, indicating beside mixed metal oxides ZnO-Bi2O3 phase, a single ZnO impurity phase has appeared. For pristine C3N4, the band gap energy appeared at 2.67 eV. In case of ZnO-Bi2O3-*x*C3N4 catalysts, the band gap energy appeared at 2.60 and ~3.05 eV. These band gap values further suggest the visible light-responsive properties of the ZnO-Bi2O3-*x*C3N4 catalysts and their promising ability as photocatalysts under visible light irradiation.

For observing morphology of the samples, SEM images were recorded using a Tescan MIRA-3 LM scanning electron microscope (U.S.) with an accelerating voltage of 20 kV. Figure S2 shows SEM image of C3N4, ZnO-Bi2O3, and ZnO-Bi2O3-*x*C3N4. The C3N4 sample consisted of layers, as shown in Figure S2(A). The as-prepared ZnO-Bi2O3 sample (Figure S2(B)) exhibited morphological abnormalities with stacked particles by the collapse of the layered structure. The individual plates of ZnO-Bi2O3 are flat and the edges of the plates appear in the form of round shapes. An interesting observation was made in case of ZnO-Bi2O3-*x*C3N4 samples, which tend to grow flower/rod-like shapes (Figure S2(C)-(E)).

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| **(B)**  **(C)**  **(E)**  **(A)**  **(D)** |
| **Figure S2**: SEM images of as-prepared materials A) C3N4; B) ZnO-Bi2O3 ; and C–E) ZnO-Bi2O3-*x*C3N4 (*x* = 1, 2, and 3). |

The specific surface area (BET surface area) was measured with an Autosorb-1 (Quantachrome, USA) apparatus. Multi-point BET plot of catalysts are shown in Figure S3.

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| **(A)** | **(B)** |
| **Figure S3**: BET curves of the sample (A) ZnO-Bi2O3 and (B) ZnO-Bi2O3-*2*C3N4. | |

***References***

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