Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

In situ synthesis of metal (Bi^0)-semiconductor [BiOX (X = Cl, Br, and I)] nanocomposites as a highly effective catalyst for the reduction of 4-nitrophenol to 4-aminophenol

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2.2.2 Synthesis of metallic Bi^0 particles

We have synthesized metallic bismuth particles in aqueous medium. Initially, we combined 2 grams of bismuth nitrate with 80 ml of distilled water and 3 ml-5 ml of nitric acid in a sealed glass reactor. We then agitated the mixture until the solution became clear. Additionally, a new solution of $NaBH_4$ was created in a beaker by dissolving 700 mg of $NaBH_4$ in 10 ml of distilled water[43]. Further, this solution was injected slowly using a syringe into the sealed reactor while it was being stirred and ensured that the reactor already contained a transparent solution of bismuth nitrate. A dark black precipitate was generated upon the addition of $NaBH_4$ solution. Following the creation of the black precipitate, stirring was halted, and the remaining water was promptly eliminated from the reactor. The precipitate was collected by rinsing it with isopropanol two to three times and dried at a temperature of 60 °C in an oven for a duration of four hours. The obtained dry black powder was ground for further analysis.

Samples	Crystallite size (nm)
BOC	17 ± 4
BOB	16 ± 4
BOI	15 ± 4

Table S1: Crystallite size of BOC, BOB, and BOI with respect to (001) planes.

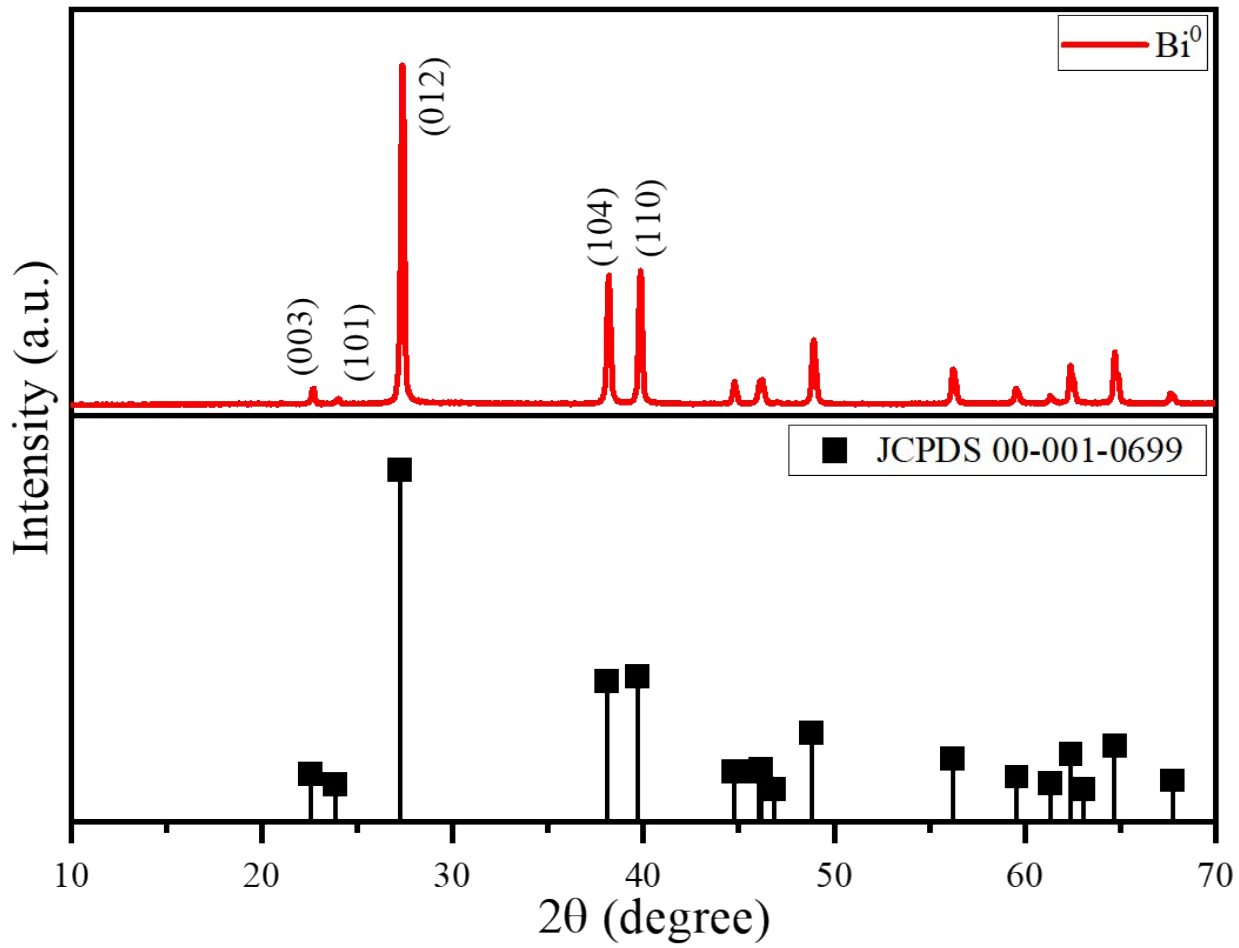


Figure S1: XRD spectrum of individually synthesized Bi^0.

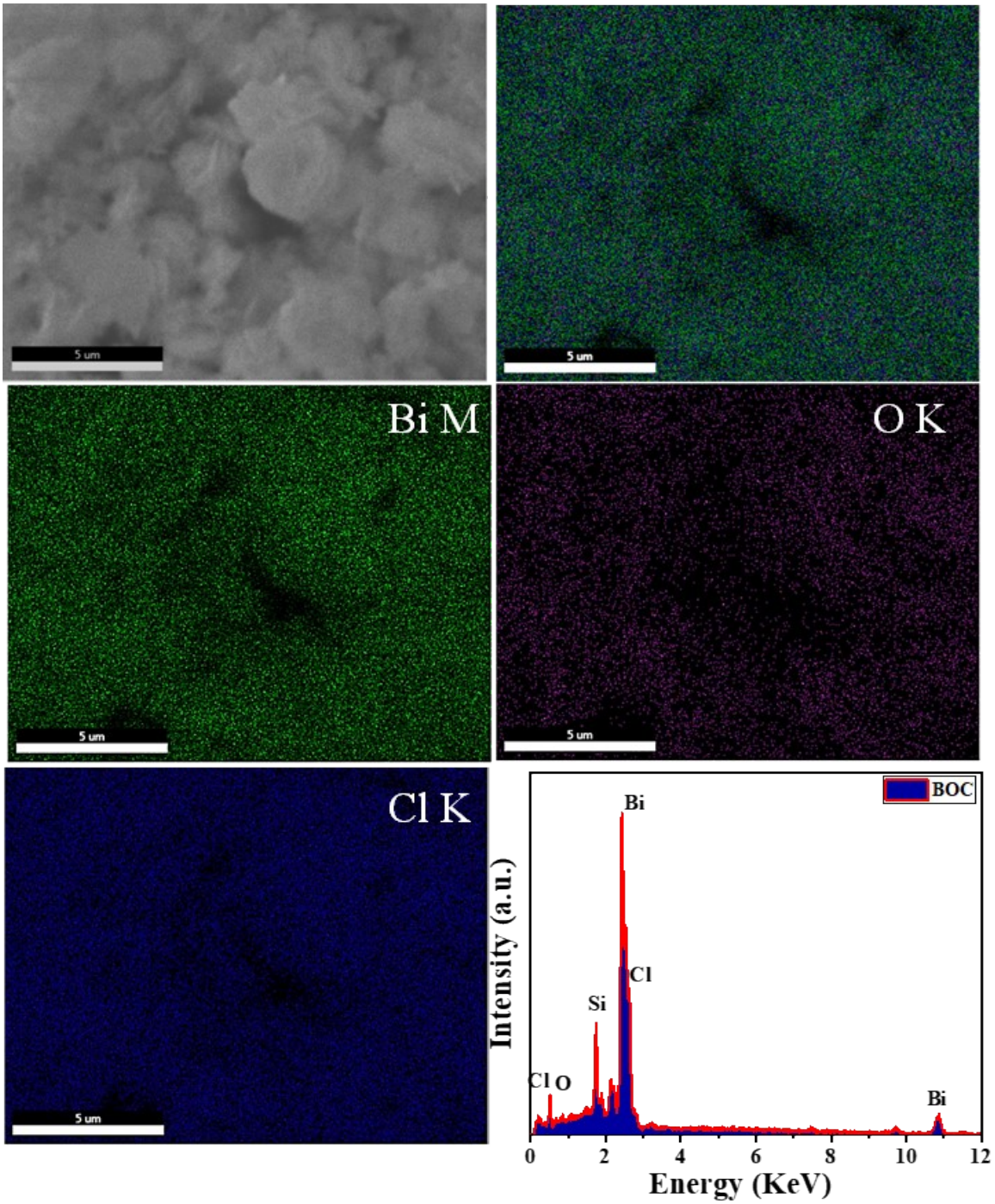

5 um
5 um
Bi M
5 um
O K
5 um
Cl K
5 um
BOC
Bi
Cl
Si
Cl O
Bi
Intensity (a.u.)
0
2
4
6
8
10
12
Energy (KeV)

Figure S2: Elemental mapping and EDAX spectrum of BOC sample.

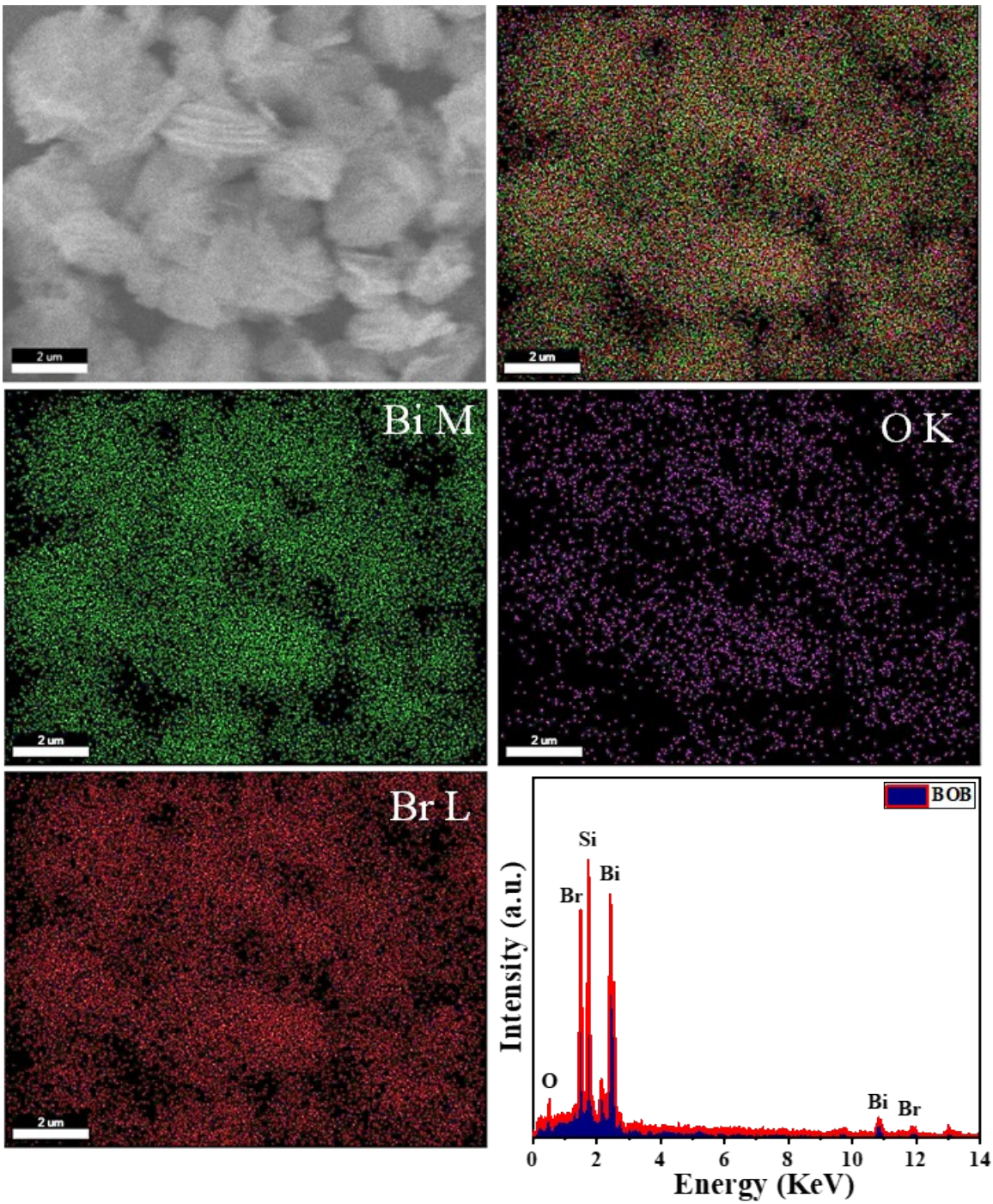


Figure S3: Elemental mapping and EDAX spectrum of BOB sample

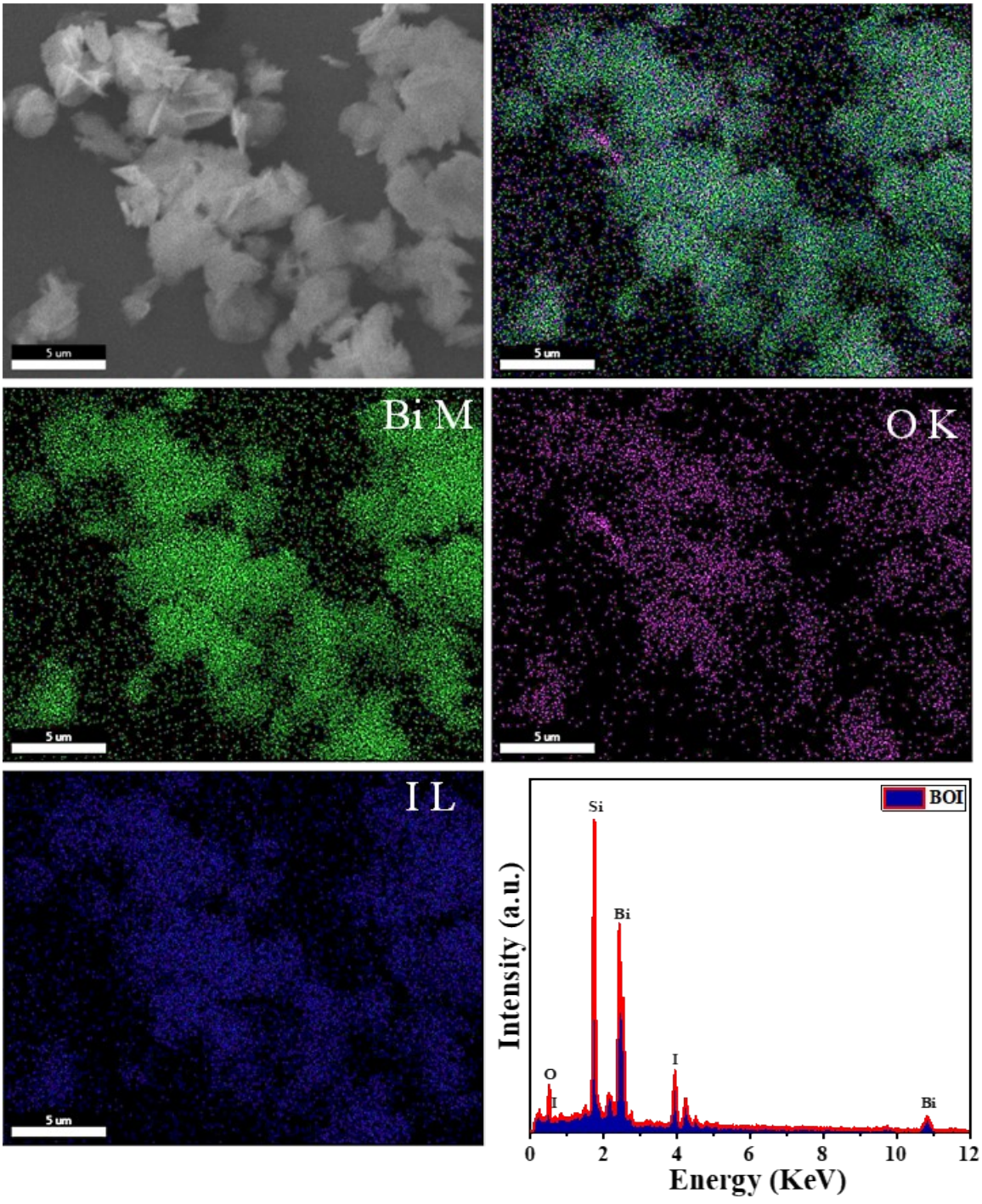
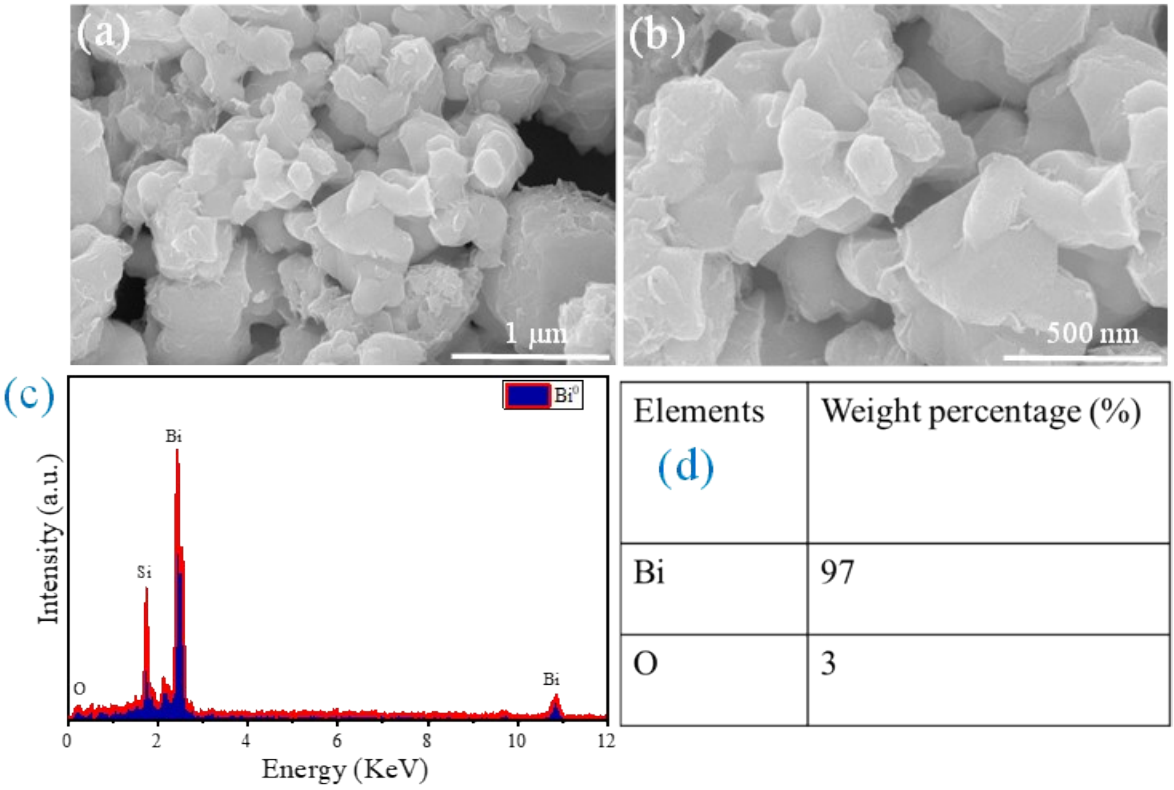


Figure S4: Elemental mapping and EDAX spectrum of BOI sample.



(d)

Elements	Weight percentage (%)
Bi	97
O	3

Figure S5: (a), (b) morphology of Bi^0 at 1µm and 500 nm scale, (c) EDAX spectrum of Bi^0, and (d) weight percentage of Bi^0.

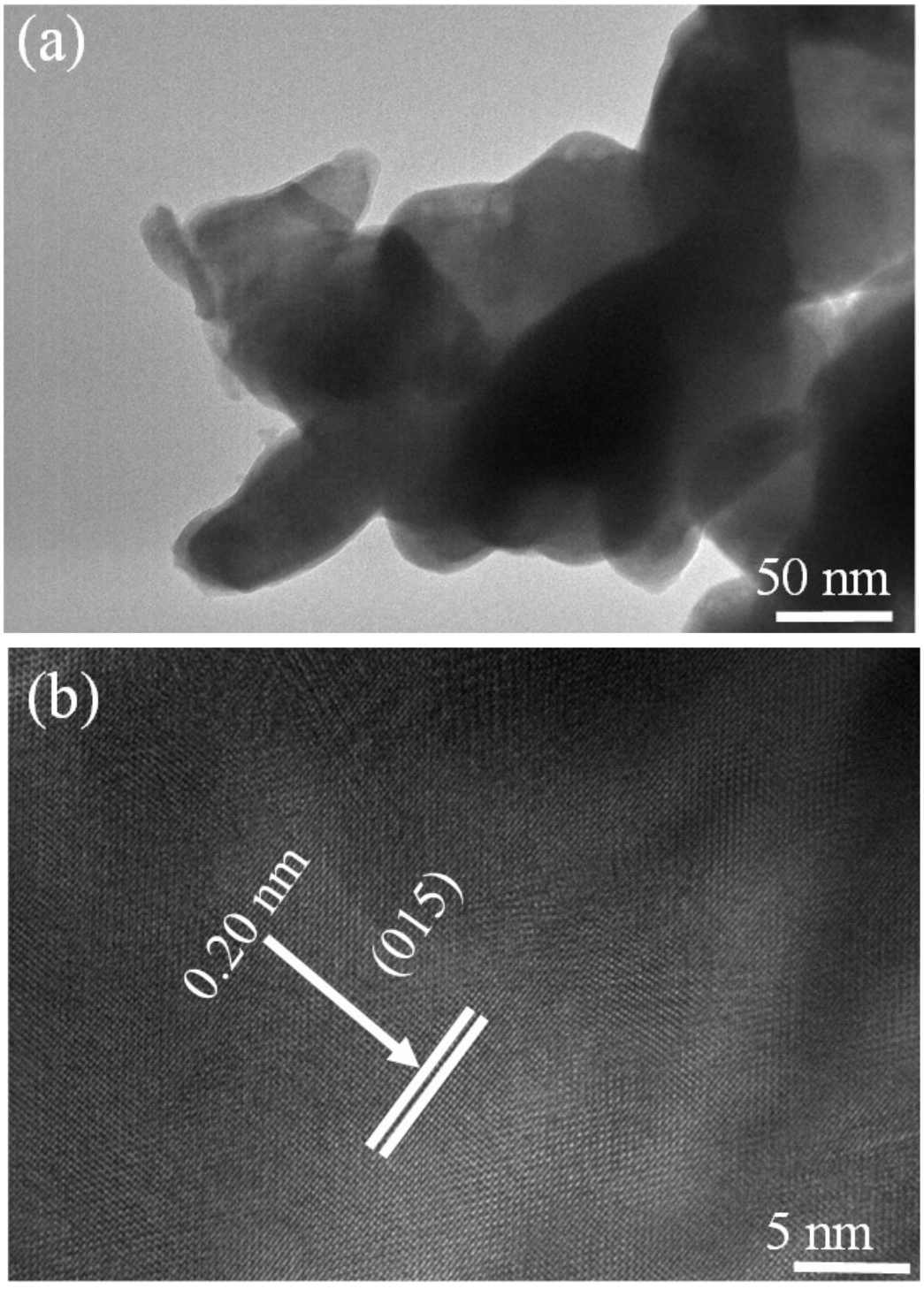


Figure S6: (a) TEM image of individual synthesized metallic Bi^0 and (b) d-spacing between (015) planes of Bi^0.

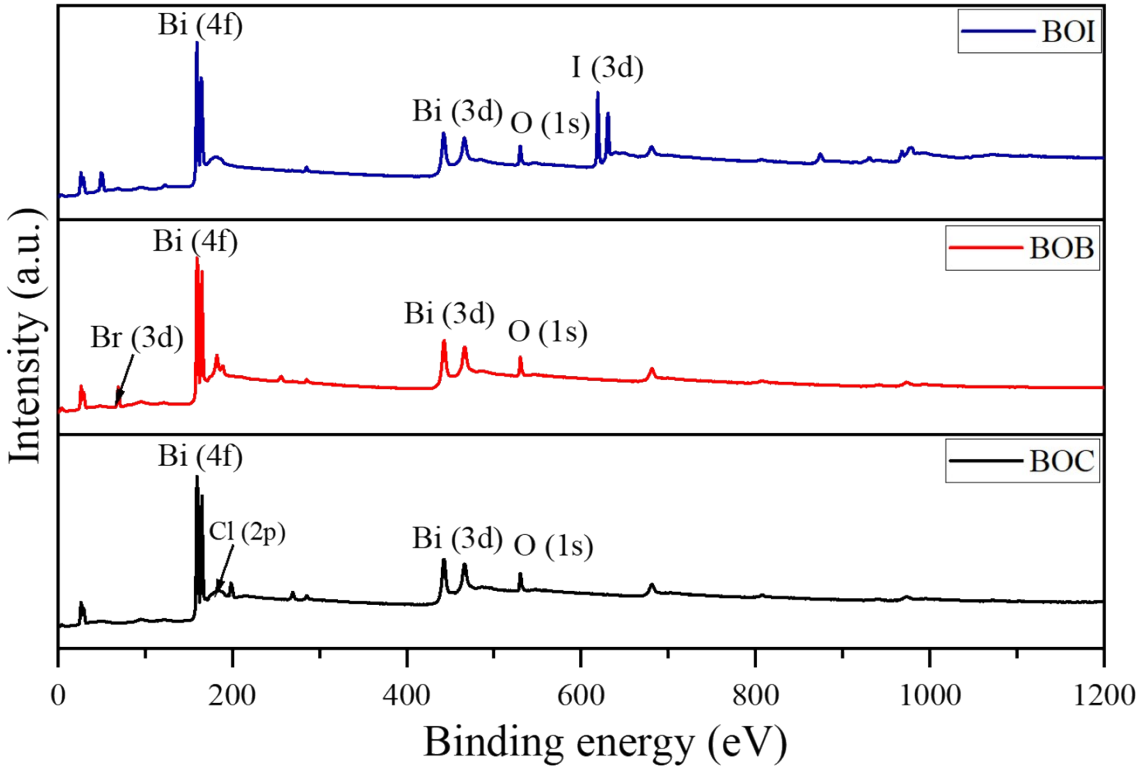


Figure S7: XPS survey spectrum of BOC, BOB, and BOI.

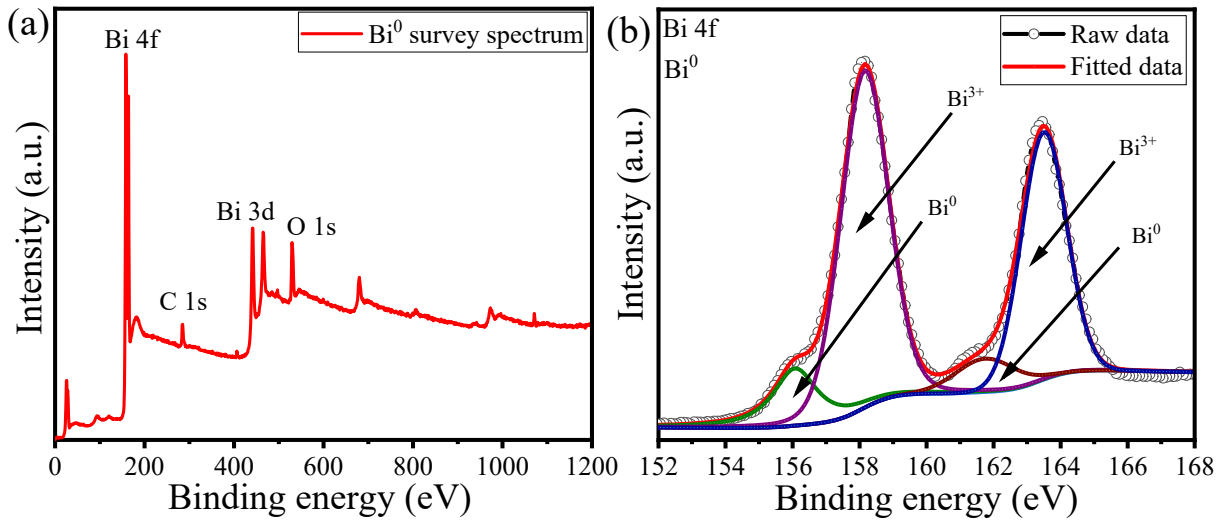


Figure: S8 (a) XPS survey spectrum of individual synthesized metallic Bi^0, and (b) high-resolution XPS spectrum of Bi 4f.

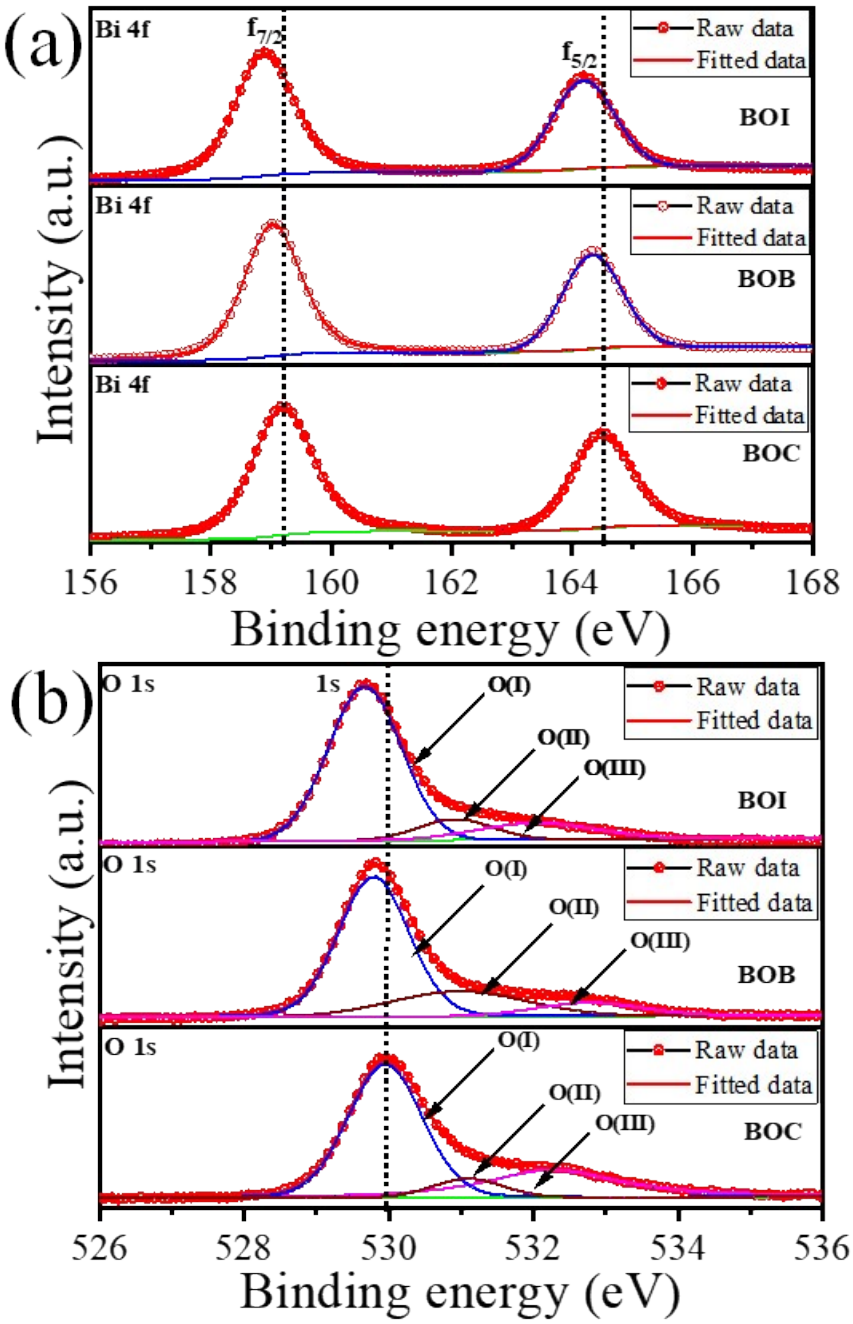


Figure S9: (a) comparison in the binding energy of High-resolution Bi 4f XPS spectrum of BOC, BOB, and BOI samples, and (b) comparison of the binding energy of O 1s XPS spectrum of BOC, BOB, and BOI samples.

Catalysts			Activity factor (AF) = *k*/catalyst weight	References
Active metals	Weight of catalyst (mg)	Rate constant (min^{-1})	($min^{-1} \cdot mg^{-1}$)	
Bi^0-BOI Bi^0-BOB Bi^0-BOC Individual Bi^0 particles	4 4 4 4	0.529 0.098 0.095 0.007	0.132 0.025 0.023 0.0015	This work
Dodecanethiol capped Bi NPs	3.5	0.233	0.066	2
Ni/SG-SWCNTs	15	0.083	0.0056	56
Nickel/Gold Nanostructures	8	0.08	0.01	57
Cu-Ni/GP	10	0.36	0.036	58
Au NCs	6	0.126	0.021	59

Table S2: Comparison of catalytic activity of BiOX (Cl, Br, and I) with different catalysts.

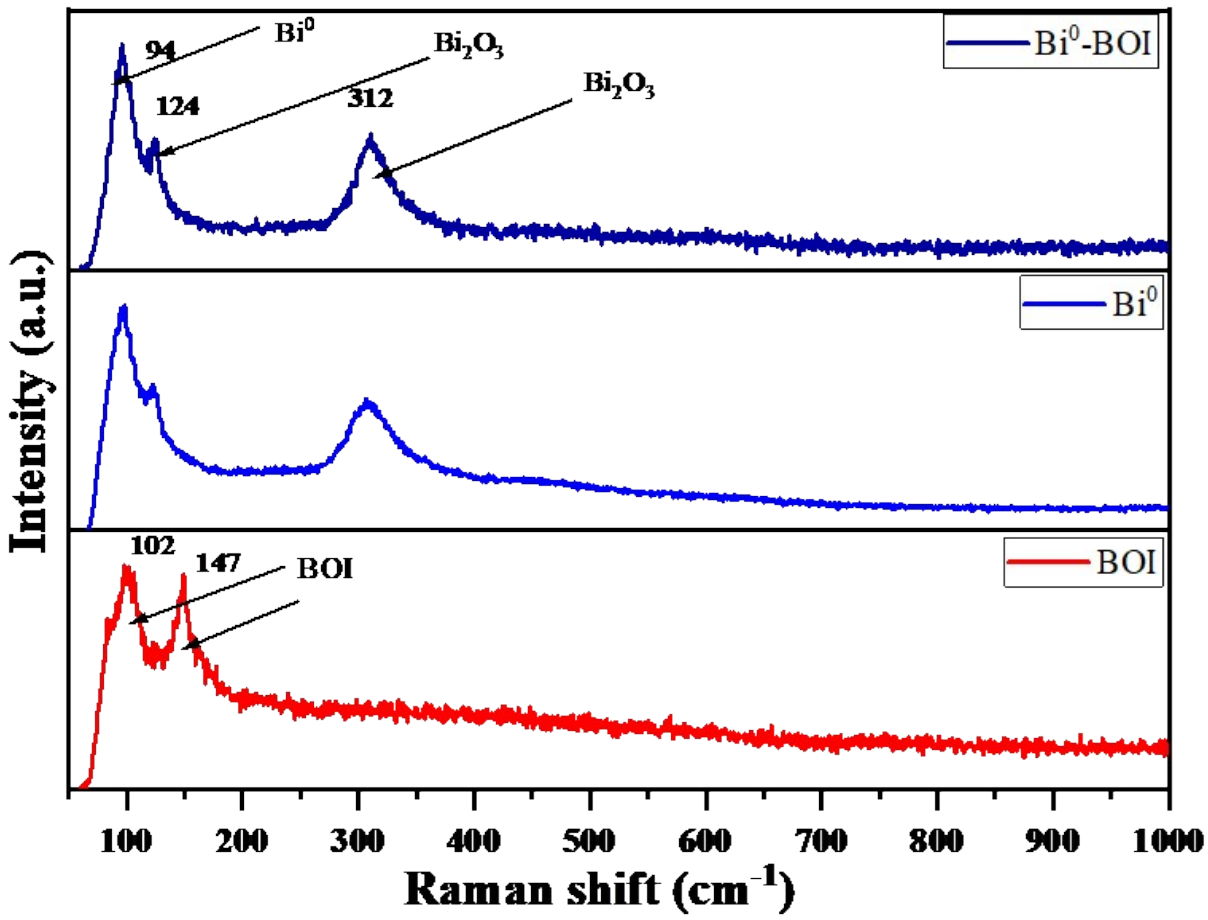


Figure S10: Raman spectrum of BOI, individually synthesized Bi^0, and in situ Bi^0-BOI.

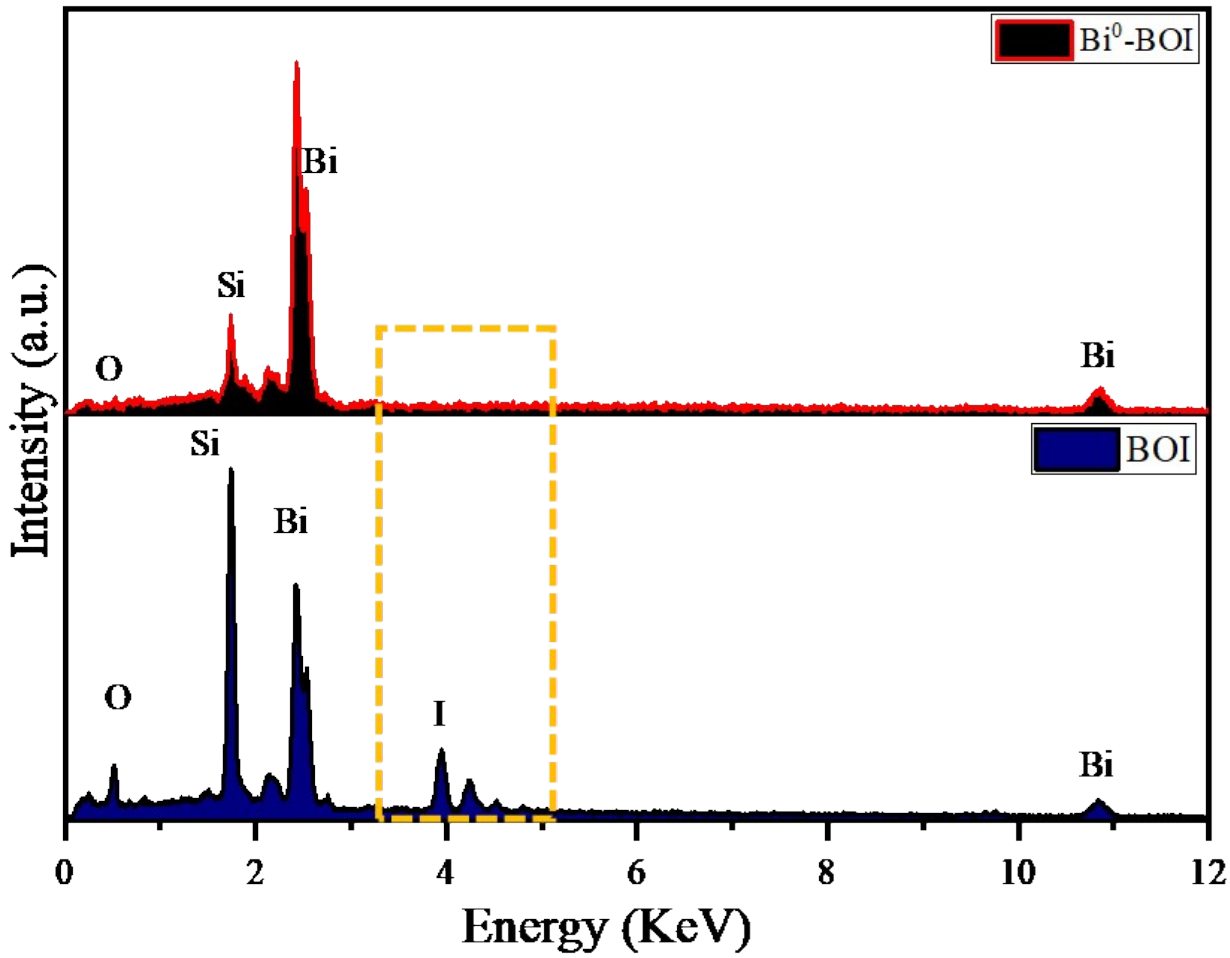


Figure S11: EDAX spectrum of BOI and Bi^0-BOI.

Figure S12: Color changes of BOC, BOB, and BOI samples before and after 4-NP reduction.

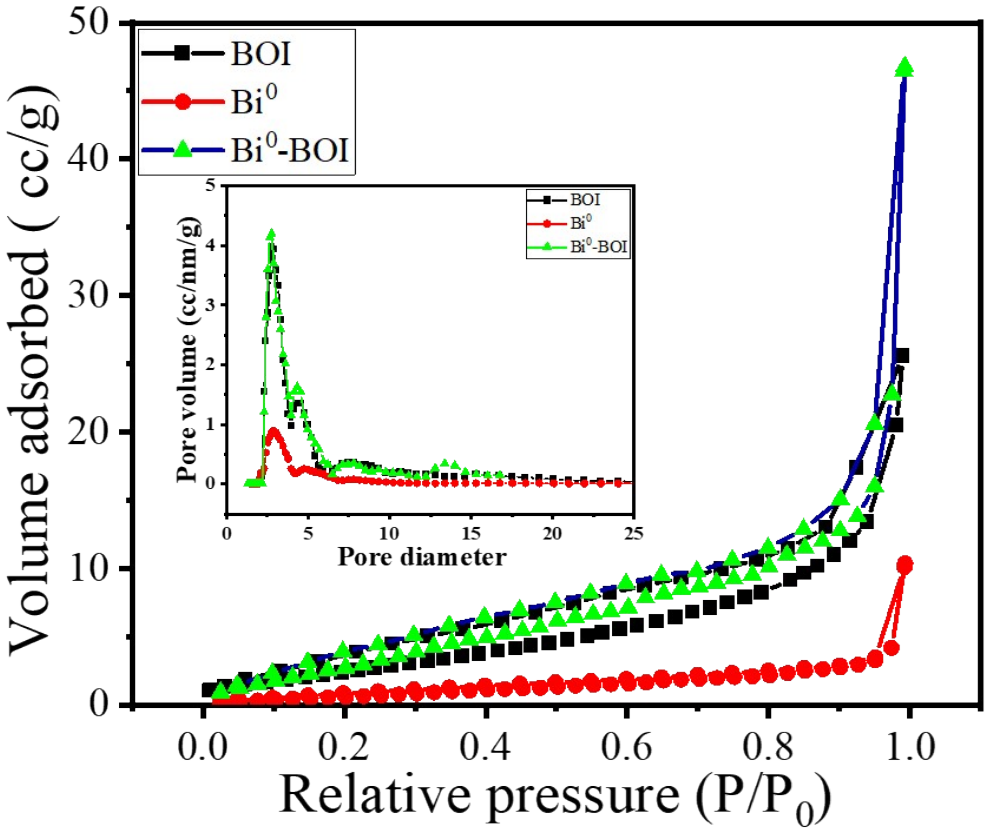


Figure S13: Adsorption and desorption isotherm of BOI, pristine Bi^0, and in situ Bi^0-BOI catalysts.

Samples	**Surface area (m^2/g)**	**Pore volume (cc/g)**
BOI	8 m^2/g	0.025 cc/g
Bi^0	3 m^2/g	0.008 cc/g
Bi^0-BOI	14 m^2/g	0.042 cc/g

Table S13: Texture parameters of BOI, Bi^0, and Bi^0-BOI calculated by the DFT method.