Electronic Supplementary Material (ESI) for Analyst.

PBA–MoS_2 Nanoboxes with Enhanced Peroxidase Activity for Constructing a Colorimetric Sensor Array for Reduction Substances Containing Catechol Structure

Xiangwei Liu,[a] Yunpeng Zhang,[a] Zhenchao Liu,[a] Guang Lu,*[a] Gaochao Fan,[b] Xia Kong,[a] Guijiang Li,*[a] and Qingyun Liu*[a]

2.2 Characterization

The morphology of PBA-MoS_2 nanoboxes as peroxidase-like nanozymes were characterized by transmission electron microscopy (TEM, FEI Tecnai G2 F20 operation at 200 kV) and scanning electron microscopy (SEM, FEI, APREO, USA). The phase and composition of of PBA-MoS_2 nanoboxes were confirmed by the powder X-ray diffractometer (XRD, Cu-Kα, λ = 1.54178 Å, 2θ = 5- 80°, 8°/min) together with the X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi, Al Kα). The absorption spectra of different reaction systems were recorded on a UV-Vis spectrophotometer (UV-8000PC, Puxi, China).

Preparation

Ni-Co PBA nanocubes: Uniform Ni-Co PBA nanocubes with a size of 400 nm were synthesized by a simple method of precipitation.An aqueous solution containing 1.745 g $Ni(NO_3)_2 \cdot 6H_2O$, 2.647 g sodium citrate and 200 mL DI water was quickly added into the aqueous solution of 1.329 g potassium hexacyanocobaltate (III) and 200 mL DI water. Then the mixed solution was under magnetic stirring for 1 min and aged at room temperature for 18 h. The precipitation was collected by centrifugation, washed with DI water and ethanol, and dried overnight at 70℃.

PBA@MoS_2 nanoboxes: 30 mg of Ni-Co PBA nanocubes and 10 mg of ammonium thiomolybdate were dissolved in 30 mL N, N-dimethylformamide (DMF) with constant ultrasound for 15 min. Then the mixture was transferred into a 50 mL autoclave, and reacted at 200 ^oC for 12 h. The final products were collected by

centrifugation, and washed with DI water and ethanol, before drying at 70 °C overnight.

Peroxidase-like activity of PBA@MoS_2

The peroxidase-like activity of PBA@MoS_2 was assessed by the colorimetric reaction. In general, peroxidase mimics catalyze H_2O_2 to oxidize the TMB, producing a blue ox-TMB which has the maximum absorption at 652 nm. Initially, the effects of reaction temperature (15–65 °C) and pH of the buffer (2.0–8.0) on the catalytic activity of PBA@MoS_2 were studied to achieve the optimal working conditions. Typically, 200 μL of 0.3 mg mL^{-1} PBA@MoS_2 suspension, 200 μL of 0.25 M H_2O_2 and 200 μL of 1 mM TMB solution were sequentially added into 1400 μL buffer solution (pH 4.0). After reacting for 2 min, the absorbance of the reaction solution was determined by the UV-vis spectrometer at 652 nm.

The steady-state kinetic experiments were carried out by changing the concentration of one substrate and keeping that of another one a constant.

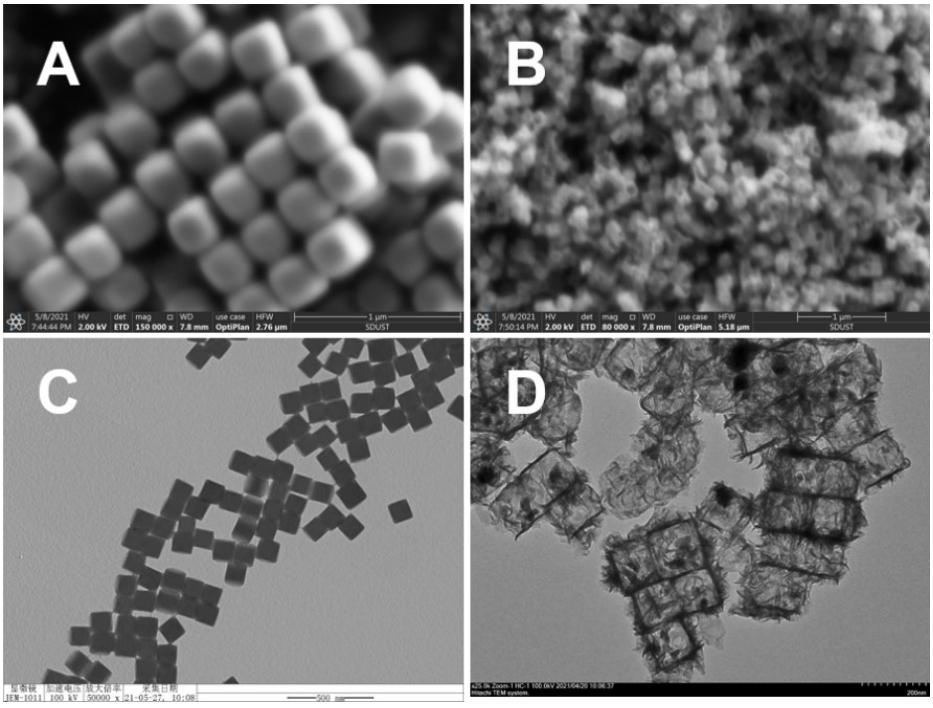

Fig. S1 SEM images of PBA (A) and PBA-MoS_2 (B), respectively. TEM images of PBA (C) and

PBA-MoS_2 (D).

XRD characterization

From Fig. S2, the XRD pattern of PBA matches well with the pure cubic $Ni_3(Co(CN_6))_2 \bullet 12H_2O$ structure (JCPDS 89-3738), and there is no additional peak of impurities.[28] According to the recent study[29], two peaks near the low-angle region (9° and 18°) correspond to (001) and (002) diffractions, respectively. It seemingly indicates the existence of a new unsolved MoS_2 phase. Two peaks located at 44° and 49.5° of the as-synthesized product with PBA templates may be assigned to nickel sulfide (NiS) and no peaks from metal oxides are detected (Fig. S3). Compared to standard MoS_2 cards (JCPDS 37-1492), the diffraction peaks of the as-synthesized product with PBA NCs templates shift toward lower diffraction angles, demonstrating the enlargement of the interlayer distance of MoS_2.[30] The expanded interlayer spacing may be attributed to the intercalation of Ni, Co, or DMF into the MoS_2 layers.[27,29,30]

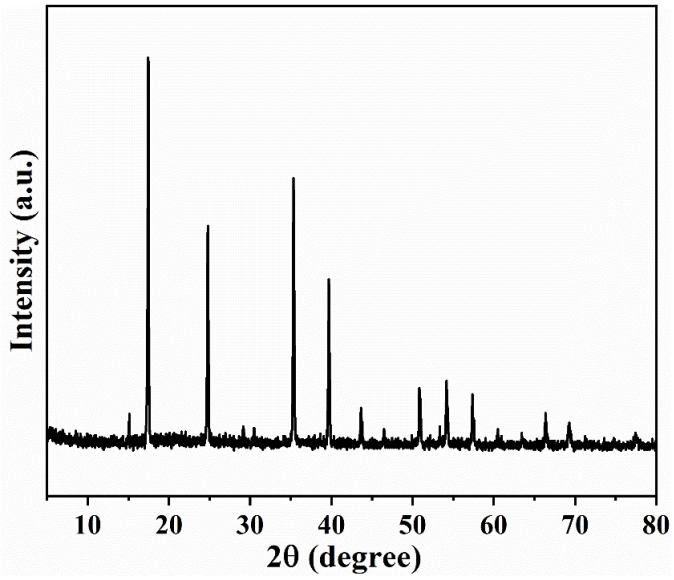

Fig. S2 XRD pattern of PBA nanocubes.

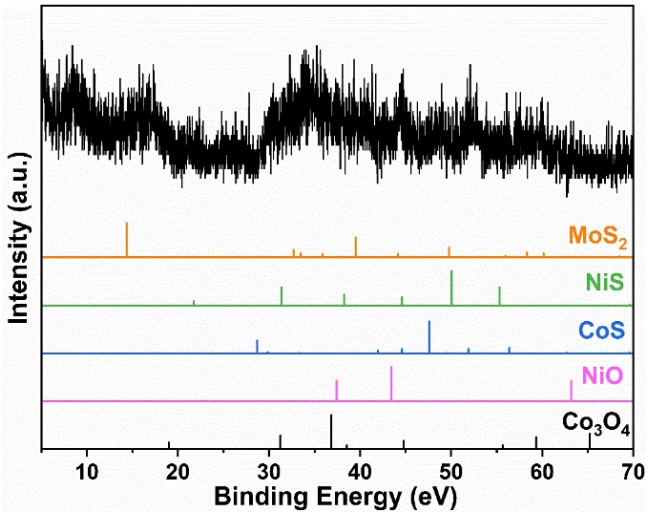

Fig. S3 XRD patterns of PBA-MoS_2 nanoboxes.

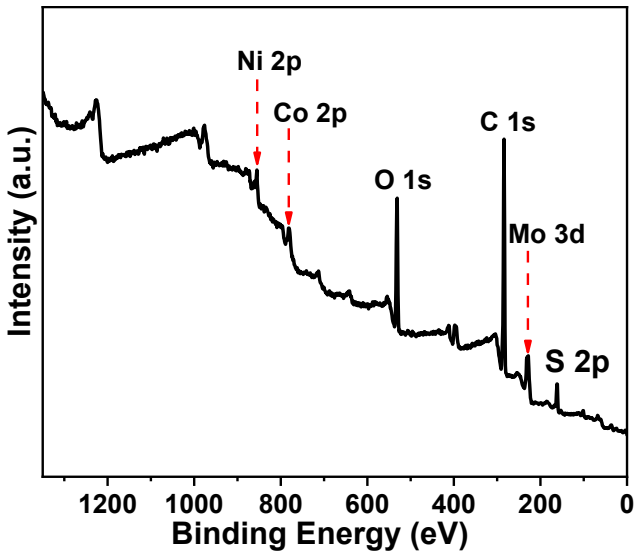

Fig. S4 XPS survey spectrum of PBA-MoS_2 Nbs.

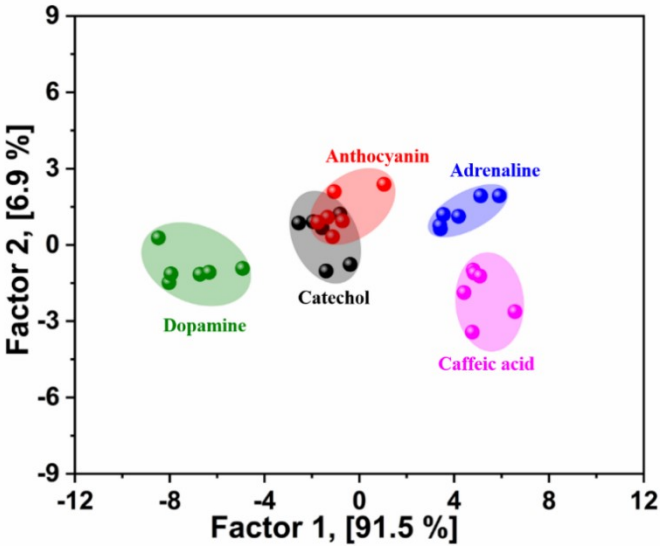

Fig. S5 LDA score diagram concentration of the measured substance (Catechol, Anthocyanin, Adrenaline, Caffeic acid, Dopamine) with a concentration of 1 μM.

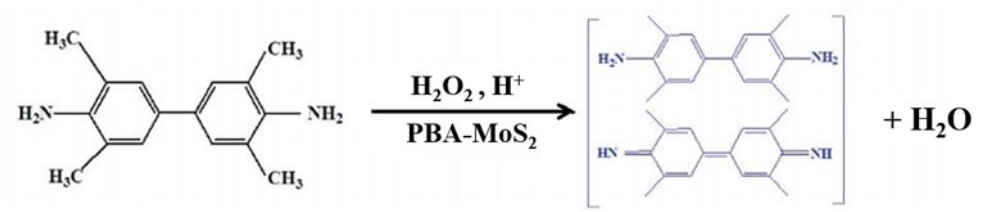

Fig. S6 The reaction principle of PBA-MoS_2 catalyzing the oxidation TMB by H_2O_2.

Table S1 The training matrix of the colorimetric response patterns against the measured substance (Catechol, Anthocyanin, Adrenaline, Caffeic acid, Dopamine) at the concentration of 1 μM using this sensor assay.

	1 min	2 min	3 min	4 min	5 min
Catechol	0.326	0.407	0.47	0.517	0.554
Catechol	0.376	0.461	0.527	0.576	0.613
Catechol	0.411	0.5	0.572	0.627	0.665
Catechol	0.417	0.508	0.58	0.633	0.671
Catechol	0.402	0.482	0.554	0.606	0.645
Anthocyanin	0.431	0.506	0.575	0.626	0.664
Anthocyanin	0.427	0.513	0.583	0.637	0.678
Anthocyanin	0.411	0.505	0.575	0.627	0.666
Anthocyanin	0.414	0.503	0.573	0.626	0.666
Anthocyanin	0.417	0.506	0.576	0.628	0.667
Adrenaline	0.409	0.491	0.553	0.6	0.636
Adrenaline	0.413	0.495	0.559	0.604	0.643
Adrenaline	0.413	0.481	0.54	0.586	0.622
Adrenaline	0.428	0.514	0.578	0.625	0.663
Adrenaline	0.438	0.517	0.578	0.623	0.66
Caffeic acid	0.435	0.511	0.572	0.612	0.642
Caffeic acid	0.406	0.493	0.556	0.599	0.63
Caffeic acid	0.397	0.48	0.542	0.584	0.615
Caffeic acid	0.382	0.478	0.533	0.574	0.604
Caffeic acid	0.379	0.462	0.523	0.565	0.596
Dopamine	0.365	0.459	0.53	0.584	0.626
Dopamine	0.353	0.443	0.517	0.572	0.614
Dopamine	0.338	0.427	0.502	0.557	0.601
Dopamine	0.358	0.448	0.522	0.577	0.618
Dopamine	0.337	0.422	0.496	0.552	0.595