N-Doped TiO$_2$–Carbon Composites Derived from NH$_2$-MIL-125(Ti) for Electrochemical Determination of tert-Butylhydroquinone

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Abstract
Electrochemical determination of tert-butylhydroquinone (TBHQ) is vital to food safety due to negative health effects; however, bare electrode of traditional electrochemical sensors generally has a narrow linear range and low sensitivity, limiting their practical application. Accordingly, the nano-architecture fabricated with N-doped TiO$_2$–carbon nano-composites (TiO$_2$/NC) is prepared by the thermolysis of NH$_2$ functionalized MIL-125(Ti) metal–organic frameworks (NH$_2$-MIL-125(Ti)). TiO$_2$/NC composites are firstly developed as the electrochemical material for electrochemical determination of TBHQ. The TiO$_2$/NC composites with a highly porous structure, excellent conductivity and electron transportation, and large surface area show remarkable electrochemical oxidation ability for TBHQ. Under optimal conditions, TiO$_2$/NC composite-modified electrode presents a broader linear response to TBHQ concentration of 0.05–100 μM with the detection limit as low as 4 nM (S/N = 3). Finally, the sensor platform is implemented directly to determine TBHQ in edible oil for evaluation of its practical application. TiO$_2$/NC composites sensor fabricated perform larger linear range with high sensitivity and anti-interference properties, which can be used as a potential for electrochemical determination of TBHQ.

Keywords NH$_2$-MIL-125(Ti) · TiO$_2$ · N-Doped · Carbon · Tert-Butylhydroquinone

Introduction

tert-Butylhydroquinone (TBHQ) is one of the common preserving additives in edible oils due to its low price, non-toxicity, and high chemical stability (Sanidad et al., 2016; Almeida et al., 2011). Howbeit, many health studies have shown that its oxidative product is toxic. Excessive use of TBHQ may induce negative health effects like stomach tumors and liver damage (Negar et al., 2007; Eskandani et al., 2014), carcinogenesis (Hirose et al., 1998), and underdevelopment of the reproductive system (Jeong et al., 2005). Therefore, many regions (such as European Union, the USA, and China) have legislated laws and permitted the maximum allowable concentration in food of 200 mg kg$^{-1}$ (Li et al., 2017). Summarizing the mentioned above, effective measurement of phenolic antioxidants is meaningful for quality control procedures.

Until now, different types of analytical techniques have been widely used in the determination of TBHQ. Electrochemical methods are more suitable than capillary electrophoresis (Boyce et al., 1999) and chromatography (Farajmand et al., 2017) in terms of low cost, fast speed, easy operation, and accuracy. A variety of electrochemical modified materials, including carbon nanotubes (Caramit et al., 2013; Ziyatdinova et al., 2015; Tang et al., 2022), polymers (Tang et al., 2016), and metal oxide nanoparticles (Gan et al., 2016; Cao et al., 2019; Monteiro et al., 2016), have been done to increasing the sensitivity and selectivity for TBHQ.

In some research, transition metal oxides (e.g., TiO$_2$ and ZnO) as electrochemical materials show facile electron transfer, high biocompatibility, and considerable stability (Arif et al., 2016; Lu et al., 2021; Mahadik et al., 2017). However, the bulk and aggregation of nanostructured TiO$_2$ during the electrochemical process leads to the decrease of active sites and affects the catalytic performance (Liu et al., 2013). Therefore, it is greatly important to find a suitable supports; carbon materials including carbon nanofiber, porous carbon, carbon nanotubes,
and graphene (Zeng et al., 2013; Tang et al., 2021; Qiu et al., 2014; Chen et al., 2011), having advantages of high surface area and electrical conductivity, have been applied as supports to prevent the agglomeration and increase the conductivity and chemical stability of TiO₂ nanomaterials. The interaction between TiO₂ and carbon materials is relatively weak when the TiO₂/C composites are fabricated by separate steps, because of their relatively low ions/electron transfer (Li et al., 2012; Li et al., 2008). Moreover, nanostructured metal oxides–carbon hybrid composites can be obtained via the solid-state pyrolysis of suitable metal–organic frameworks (MOFs) templates with unique thermal behavior. Metal–organic frameworks (MOFs) are one-, two-, or three-dimensional structures consisting of metal ions or clusters of coordinated organic ligands (Rowsell et al., 2004; Li et al., 2020; Wang et al., 2019). Typical Ti-based MOF, MIL-125(Ti) was firstly fabricated by Dan-Hardi et al. (Dan-Hardi et al., 2009) with high porous, low toxicity, and good stability. Some researchers have developed the application of TiO₂/C composite through pyrolysis of MIL-125(Ti) in Na-ion batteries and microwave absorption (Shi et al., 2016; Ma et al., 2017). Meanwhile, introducing heteroatoms like nitrogen and sulfur into metal/metal oxide or carbon matrices can increase chemical stability, adsorptive ability, and electrocatalysis activity (Li et al., 2013). It can be easily realized by direct pyrolysis of MOFs with designable organic linkers with specific functional groups or elements such as amidogen and sulfhydryl (Gu et al., 2016). To our best knowledge, N-doped TiO₂–carbon nano-composites derived from Ti-based MOFs for electrochemical sensors are reported rarely.

Bearing these facts in mind, amino-functionalized titanium MOF (NH₂-MIL-125(Ti)) was synthesized firstly, and then, a porous nitrogen-doped TiO₂–carbon hybrid composites (TiO₂/NC) was fabricated via one-step solid-state pyrolysis in an Ar atmosphere. Based on TiO₂/NC as electrode material, a new electrochemical sensor was constructed for the high-sensitive detection of TBHQ. The schematic illustration of the TiO₂/NC/GCE fabrication process was given in Scheme 1. The TiO₂/NC composites with the highly porous structure, excellent conductivity, and electron transportation, high surface area exhibited remarkable electrochemical oxidation ability for TBHQ. In addition, the composite electrode was successfully applied to recognize and determine TBHQ in edible oil.

### Experimental

#### Reagents and Apparatus

Titanium tetraisopropanolate, tert-butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA), and 2-aminoterephthalic acid (H₂BDC-NH₂) were achieved from Aladdin Industrial Corporation (China). N,N-Dimethylformamide (DMF) and
other chemicals were provided by Sinopharm Chemical Reagent Co., Ltd. Phosphate buffer solution used in this manuscript was prepared by mixing NaH₂PO₄·2H₂O (0.1 M) and Na₂HPO₄·12H₂O (0.1 M). All reagents were used without further purification and the solutions were prepared by the hyperpure water with 18.2 MΩ·cm.

Electrochemical experiments were carried out via a CHI 660E electrochemical workstation (Shanghai CH Instruments, China), in which a three-electrode cell was used with the bare or modified GCE (diameter 3 mm; CH104), the saturated calomel electrode (SCE), and the platinum wire as the working electrode, the auxiliary electrode, and the reference electrode. The morphologies of materials were studied using a JSM-7100F scanning electron microscope and a JEM-100CX electron microscope (JEOL, Japan). Powder X-ray diffraction (XRD) was collected on a Bruker D8-ADVANCE (Bruker, Germany) by using Cu Ka radiation. N₂ adsorption/desorption isotherms were performed at 77 K on an ASAP 2020 analyzer (Micromeritics, Norcross, GA, USA). X-ray photoelectron spectroscopy (XPS) was examined using a K-Alpha spectrometer (Thermo Fisher Scientific Inc., UK).

Fabrication of NH₂-MIL-125(Ti)

Amino-functionalized Ti-based MOF with (Ti₈O₆(OH))₆(bdc-NH₂)₆ (NH₂-MIL-125) was presented by Kim et al. (Kim et al., 2013). A solution of 2-aminoterephthalic acid (2.54 g) in 60 mL of DMF-CH₃OH (9:1, v/v) mixture was described as follows: firstly, the bare glassy carbon electrode (GCE) was carefully polished with 0.05 μm alumina powder. Subsequently, GCE was cleaned with ethanol and ultrapure water for 1 min successively. Finally, it was dried with nitrogen at room temperature. Four milligrams of TiO₂/NC composites was dispersed in 2 mL DMF by sonication to obtain a homogeneous suspension. Nine microliters of the above suspension was dropped onto the bare GCE surface and dried at room temperature to obtain TiO₂/NC/GCE. In contrast, NH₂-MIL-125(Ti)-modified electrode was prepared in a similar process.

Preparation of Nitrogen-Doped TiO₂–Carbon Hybrid Composites (TiO₂/NC)

For the TiO₂/NC composite preparation, the as-obtained NH₂-MIL-125(Ti) was firstly pre-carbonized at 300 °C for 2 h in a tube furnace and then further carbonized at 900 °C for 2 h with a speed of 2 °C/min under Ar atmosphere to make the material fully carbonized. The black powder of TiO₂/NC composites was collected.

Preparation of the Modified Electrode

The detailed preparation of the TiO₂/NC-modified electrode was described as follows: firstly, the bare glassy carbon electrode (GCE) was carefully polished with 0.05 μm alumina.
Fig. 1  SEM images of NH2-MIL-125(Ti) (a) and TiO2/NC composites (b); TEM image of TiO2/NC composites (c), the bright-field TEM image (d), and e–i EDS mapping images of the C (red), N (green), O (cyan), and Ti (purple) (scale bar 250 nm)

Fig. 2  The a XRD patterns of NH2-MIL-125(Ti) and TiO2/NC composites, XPS spectra of the synthesized TiO2/NC composites; b survey spectrum and c Ti 2p, d BET analyses of TiO2/NC composites, inset: BJH pore size distribution

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binding energy of the pyrrolic nitrogen (Casanovas et al., 1996). Figure 2d showed the nitrogen adsorption—desorption isotherms of TiO$_2$/NC. The isotherm exhibited a type IV isotherm curve, indicating the TiO$_2$/NC was a typical mesoporous material. The carbonized sample TiO$_2$/NC showed the BET surface area of 287.9 m$^2$·g$^{-1}$ and pore diameters of 2.95 nm. Therefore, TiO$_2$/NC showed a relatively large surface area and pore diameter. Basically, porous materials with larger pores have excellent advantages for catalysis due to their active sites which rapidly are accessed by any substrate for high reactivity (Corma et al., 1996).

Characterization of TiO$_2$/NC-Modified Electrode

Electrochemical characterization of the TiO$_2$/NC-modified electrode was also studied by the cyclic voltammetric (CV) technique. As seen in Fig. 3a, the CV curves of 5.0 mM [Fe(CN)$_6$]$^{3−/4−}$ containing 0.1 M KCl over bare GCE, NH$_2$-MIL-125(Ti)/GCE, and TiO$_2$/NC/GCE. A pair of oxidation—reduction peaks appeared at the bare GCE with the anode peak current $I_{pa}$ about 48.56 μA. On NH$_2$-MIL-125(Ti) coated on the surface of GCE, the peak currents obviously increased owing to the high surface area with the anode peak current value of 72.06 μA. Moreover, on TiO$_2$/NC/GCE, a pair of well-defined peaks appeared with an $I_{pa}$ (81.76 μA) of almost 2 times higher than bare GCE, indicating that the TiO$_2$/NC sensor had a fast electron transfer rate because of the highly porous structure, excellent conductivity and electron transportation, large surface area of the TiO$_2$/NC composites.

As shown in the inset of Fig. 3a, the peak currents of three different electrodes increased linearly related to the square root of the scan rate. According to Randles–Sevckik equation:

$$I_p = 2.69 \times 10^5 n^{3/2} A D_0^{1/2} C_0 v^{1/2}$$  \hspace{1cm} (1)

where $I_p$, $n$, $A$, $C_0$, $D_0$, and $v$ are the peak current, the number of transfer electrons ($n=1$), the electrochemically active area, the concentration of the reactant, the diffusion coefficient of the [Fe(CN)$_6$]$^{3−/4−}$ (about 7.6 × 10$^{-6}$ cm$^2$·s$^{-1}$), and the scan rate, respectively. The slopes were 69.39, 157.3, and 230.2 of the three lines at bare GCE, NH$_2$-MIL-125(Ti)/GCE, and TiO$_2$/NC/GCE, respectively. According to the slopes of the linear equations, the electroactive surface areas of bare GCE, NH$_2$-MIL-125(Ti)/GCE, and TiO$_2$/NC/GCE were calculated to be 0.026 cm$^2$, 0.070 cm$^2$, and 0.086 cm$^2$, respectively. Their results clearly indicated that TiO$_2$/NC could effectively enlarge the electroactive area and more reactive sites.

The impedance spectroscopy of the different electrodes (bare GCE, NH$_2$-MIL-125(Ti)/GCE, and TiO$_2$/NC/GCE) in 5.0 mM [Fe(CN)$_6$]$^{3−/4−}$ containing 0.1 M KCl was depicted in Fig. 3b. The impedance of the bare GCE was relatively large with the value of 500 Ω. The electrode prepared after coated NH$_2$-MIL-125(Ti) exhibited lower impedance (almost 200 Ω) attributed to the porous structure of NH$_2$-MIL-125(Ti), which can improve the charge transfer efficiency. Again, corresponding to the TiO$_2$/NC/GCE, the impedance value was further reduced to only 10 Ω. This change implied that the charge transfer rate was obviously increased after the carbonization of NH$_2$-MIL-125(Ti), thereby making enhancement in conductivity of this TiO$_2$/NC sensor.

Electrochemical Behaviors of TBHQ

The electrochemical responses of TBHQ (100 μM) were investigated individually applying CV over bare GCE, NH$_2$-MIL-125(Ti)/GCE, and TiO$_2$/NC/GCE. The CV curves were documented in Fig. 4a. In well-defined redox peaks obtained at bare GCE and various modified electrodes, bare GCE exhibited the lowest peak currents ($I_{pa}$ = 1.32 μA) with the largest peak-to-peak separation ($ΔE_p = 182$ mV). Furthermore, at NH$_2$-MIL-125(Ti)/GCE, high redox peak currents ($I_{pa}$ = 4.08 μA) with $ΔE_p$ of 88 mV were found, due to the porous structure of NH$_2$-MIL-125(Ti) with enhanced surface areas. Additionally, at TiO$_2$/NC/GCE, the oxidation current ($I_{pa}$ = 30.58 μA)
μA) further increased 23.2 times that of bare GCE. Meanwhile, the ΔE_p (55 mV) of TBHQ on TiO_2/NC/GCE was much smaller than those on the other electrodes, suggesting that TiO_2/NC/GCE had the best electron transfer kinetics for the redox of TBHQ. Thus, TiO_2/NC composites enabled excellent electrochemical catalytic activity for TBHQ oxidation.

Optimization of the pH Value

The effect of the supporting electrolyte pH value (varied from 4.0 to 9.0) in the electrochemical reaction of TBHQ on the TiO_2/NC sensor applied using CV was depicted in Fig. 4b. The oxidation peaks of TBHQ (50 μM) in phosphate buffer solution (0.1 M) shifted to the negative potential signal as the pH increased (Fig. 4c), due to the protons involved in the electrochemical reactions of TBHQ (Ziyatdinova et al., 2020). A good linear relationship between pH and anodic potential was revealed in Fig. 4c, E_p = 0.3869–0.0554 pH (R^2 = 0.991). The slope was 55.4 mV per pH closed to the theoretical value (59 mV per pH at 298 K), indicating that the number of electrons was equivalent to the number of protons involved in the redox process of TBHQ (Ziyatdinova et al., 2020). Moreover, the acidity of phosphate buffer solution also had a remarkable effect on peak current values of TBHQ. The oxidation peak currents increased with the increase of pH values until they reached the maximum pH value of 7.0 and then decreased when the pH value was further increased. The maximum peak current of TBHQ was achieved at a neutral solution owing to the proton groups of TBHQ which contributed to the reduction of the hydroxyl bond energies so as to improve electron transfer through O–H⋯N (Ding et al., 2005). Therefore, the pH value of the phosphate buffer solution was set to 7.0.
**Kinetics Studies**

The CV curves of TiO$_2$/NC/GCE (Fig. 4d) were investigated at various scan rates (20–400 mV·s$^{-1}$) to analyze the kinetic process. As seen in Fig. 4e, it is clear that both $I_{pa}$ and $I_{pc}$ of TBHQ increased gradually with scan rates ranging from 20 to 400 mV·s$^{-1}$, and the equations satisfy: $I_{pa} (\mu A) = 1.5299 v^{1/2} (V·s^{-1}) − 2.9653(R^2 = 0.998)$ and $I_{pc} (\mu A) = −1.3797 v^{1/2} (V·s^{-1}) + 3.4657 (R^2 = 0.997)$. In addition, the logarithm of anodic peak current ($lg_{I_{pa}}$) vs the logarithm of $v$ ($lg v$) (the inset of Fig. 4e) was linear. The linear equation was $lg_{I_{pa}} (\mu A) = 0.524 lgv (V·s^{-1}) + 0.0157 (R^2 = 0.997)$ with the slope value of 0.54, which was close to 0.5. The results manifested that the electrochemical behavior on the surface of TiO$_2$/NC/GCE was controlled by the diffusion of TBHQ (Chen et al., 2021).

Additionally, the anodic ($E_{pa}$) and cathodic ($E_{pc}$) peak potential vs the natural logarithm of $v$ ($lg v$) of TBHQ (Fig. 4f) were linear ranging from 120 to 400 mV·s$^{-1}$ and obtained the slope values of 0.0747 and −0.0531, according to the following equations (Laviron, 1979):

$$E_{pa} = E^0 + \frac{2.3RT}{(1-\alpha)nF}lgv$$

(2)

$$E_{pc} = E^0 - \frac{2.3RT}{anF}lgv$$

(3)

where $R$-molar gas constant (J mol$^{-1}$ K$^{-1}$), $T$-the absolute temperature (K), and $F$-the Faraday’s constant (C mol$^{-1}$). Thus, the electron transfer number ($n$) and the transfer coefficient ($\alpha$) were calculated to be 1.87 (close to 2) and 0.58, respectively. The result denoted that the two-proton and two-electron process was involved in the electro-oxidation of TBHQ on TiO$_2$/NC/GCE.

The electron transfer rate constant ($k_e$) was calculated based on Eq. (4):

$$lgk_e = a lg(1-\alpha) + (1-\alpha)lag - \frac{lgRT}{nFv} - \alpha(1-\alpha) \frac{nF\Delta E_p}{2.303RT}$$

(4)

**Table 1** Comparison of analytical performances of TiO$_2$/NC/GCE with the reported sensors for the determination of TBHQ

| Sensor            | Linear range (µM) | LOD (µM) | Ref                   |
|-------------------|-------------------|----------|-----------------------|
| MIP/AuNPs/GCE     | 0.08–100          | 0.07     | Fan et al. (2018)     |
| MnO$_2$/ERGO/GCE  | 1–300             | 0.8      | Cao et al. (2019)     |
| α-Al$_2$O$_3$/GCE | 0.5–250           | 0.027    | Lima et al. (2018)    |
| MIP/ZC/GCE        | 1–75              | 0.42     | Ma et al. (2021)      |
| AuNPs/GCE         | 1.2–16.8          | 0.48     | Lin et al. (2013)     |
| TiO$_2$/NC/GCE    | 0.05–10, 10–100   | 0.004    | This work             |

where $n$ is electron transfer number of 2, $\nu$ is the scan rate of 100 mV·s$^{-1}$, and $\Delta E_p = 51$ mV. Also, $k_e$ can be calculated as 0.63 s$^{-1}$. The electron transfer rate constant ($k_e$) of TiO$_2$/NC/GCE was larger than the reported electrode (Wang et al., 2021), indicating that this modified electrode had a higher catalytic capacity to promote electron transfer of TBHQ.

**Analytical Performance of TiO$_2$/NC/GCE to TBHQ**

Quantitative analysis was examined to determine TBHQ using the higher sensitive technique of differential pulse voltammetry (DPV) on TiO$_2$/NC/GCE. As shown in Fig. 5a, the DPV curves for various concentrations of TBHQ were given on TiO$_2$/NC/GCE in 0.1 M phosphate buffer (pH 7.0). The catalytic current increased gradually with the concentration of TBHQ in the range of 0.05–100 µM and the linear equations were $I_{pa} (\mu A) = 2.257C (\mu M) + 2.886 (R^2 = 0.993)$, range of concentration was 0.05–10 µM and $I_{pa} (\mu A) = 0.5886C (\mu M) + 19.54 (R^2 = 0.995$, range of concentration was 10–100 µM), respectively. The detection limit (LOD) of 4 nM (S/N = 3) was superior to those of the previously reported TBHQ sensors (Table 1). Hence, such outstanding analytical performance was ascribed to the specific

Fig. 5 a) DPV curves of TiO$_2$/NC/GCE to 0.05 µM, 0.5 µM, 1.0 µM, 2.0 µM, 5.0 µM, 10 µM, 20 µM, 30 µM, 60 µM, 80 µM, 100 µM (a–k) TBHQ in phosphate buffer (pH 7.0); inset: plots of peak currents vs. concentrations ranging from 0.05 to 100 µM. b) I-t curve of TiO$_2$/NC/GCE with subsequent additions of the possible interfering at the potential of 0.05 V
structure and composition of TiO$_2$/NC composites. The TiO$_2$ itself is a good electrocatalyst with the advantage of facile electron transfer. By engineering TiO$_2$ with N-doped carbon material, the large surface area and porous structure would enlarge the electrocatalytic activity towards TBHQ.

Reproducibility, Stability, and Interferences Studies

To measure the reproducibility of TiO$_2$/NC/GCE, five aforementioned TiO$_2$/NC electrodes were used to detect 10-μM TBHQ by the DPV method. The reasonable relative standard deviation (RSD) of peak currents about 2.5% was exhibited, concluding that TiO$_2$/NC sensor had excellent reproducibility.

Also, the long-term stability of the TiO$_2$/NC sensor was checked by intermittent detection of TBHQ. The peak currents for 10 μM TBHQ were maintained at 98.3% and 97.9% of the initial current after 5 days and 15 days, verifying the prominent long-term stability of the modified electrode.

The selectivity of the TiO$_2$/NC/GCE was further evaluated, the impacts of some organic analytes (tenfold concentration of glucose, twofold concentration of L-aspartic acid and ascorbic acid, onefold concentration of butylated hydroxyanisole), and various ions (50-fold concentration of K$^+$, Na$^+$, Mg$^{2+}$, Cu$^{2+}$) on the current signals of TBHQ was investigated by the I-t method with the 10 μM TBHQ. Furthermore, twofold concentrations of hydroquinone were selected as interference to evaluate selectivity owing to its similar structure with TBHQ. Although hydroquinone had a high electrochemical response, its oxidation potential differed from TBHQ on TiO$_2$/NC/GCE. As shown in Fig. 5b, these additives did not affect the amperometric current response of TBHQ, implying that TiO$_2$/NC/GCE was suitable for the selective determination of TBHQ.

Analysis in Real Sample

To assess the practical potential of the proposed method, the TiO$_2$/NC/GCE was applied to detect TBHQ in edible oil (soybean oil and colza oil). Briefly, 5.0 g of the samples were dissolved in 50 mL of ethanol and centrifuged at 3000 rpm for 20 min; then, the extract procedure was repeated four times. Two hundred microliters of soybean oil or sesame oil samples was respectively diluted to 10 mL of 0.1 M phosphate buffer (pH 7.0) and analyzed by a standard addition method (n = 3) using the DPV technique. The results were listed in Table 2. The recoveries were ranged from 98.5 to 101.2% with the RSD values below 5%. Meanwhile, the obtained results matched well with the HPLC method. All results validate the TiO$_2$/NC/GCE can be applied in the measurement of TBHQ in edible oil samples.

Table 2 Determination of TBHQ in edible oil samples (n = 3)

| Sample       | Spiked (μM) | Found (μM) | RSD$^a$ (%) | Recovery$^b$ (%) | HPLC method (μM) |
|--------------|-------------|------------|-------------|------------------|------------------|
| Soybean oil  | 0           | 0.95±0.03  | 3.1         | -                | 0.87±0.02        |
|              | 10          | 10.79±0.45 | 4.2         | 98.5             | 10.98±0.48       |
|              | 20          | 21.08±0.67 | 3.2         | 100.6            | 20.65±0.86       |
|              | 0           | 1.21±0.03  | 2.5         | -                | 1.12±0.04        |
|              | 10          | 11.34±0.32 | 2.8         | 101.2            | 11.43±0.67       |
|              | 20          | 20.96±0.76 | 2.8         | 98.8             | 21.44±0.73       |

$^a$Relative standard deviation for 3 successive measurements. $^b$Recovery (%) = (Cfound/Ctotal) × 100

Conclusion

We have successfully constructed N-doped TiO$_2$–carbon nano-composites by the pyrolysis of NH$_2$-MIL-125(Ti). The novel TiO$_2$/NC sensor exhibited enhanced electrocatalytic ability towards TBHQ oxidation with a low detection limit and large detection range. The excellent performance of TiO$_2$/NC composites benefited from synergistic advantages of the highly porous structure, large surface area, excellent conductivity, and electron transportation. Moreover, the constructed TiO$_2$/NC sensor has been efficiently used to monitor TBHQ in real oils. This facile strategy may provide a valuable reference to fabricate other MOF-based material sensors.

Author Contribution Jing Tang: conceptualization, investigation, formal analysis, methodology; writing—original draft, funding acquisition; Jie Li: methodology, writing—original draft; Tianna Liu: data curation; Wenjing Tang: methodology; Nali Li: data curation; Shengbiao Zheng: formal analysis; Jiahao Guo: writing—review and editing; Changchun Song: conceptualization, investigation, formal analysis, methodology.

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Data Availability The authors declare that all data supporting the findings of this study are available within the article and its supplementary information file.
Declarations

Ethical Approval This article does not contain any studies with human participants or animals performed by any of the authors.

Consent to Participate Informed consent is not applicable in this study.

Conflict of Interest Jing Tang declares that she has no conflict of interest. Jie Li declares that he has no conflict of interest. Tianna Liu declares that she has no conflict of interest. Shengbiao Zheng declares that he has no conflict of interest. Jiazhao Guo declares that he has no conflict of interest. Changchun Song declares that he has no conflict of interest.

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