

**Recyclable magnetic NiFe₂O₄/C yolk-shell
nanospheres with excellent visible-light-Fenton
degradation performance of tetracycline
hydrochloride**

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Materials

All analytical reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and they were used without further purification.

Preparation of PAA-NH₄ nanospheres

In a 1000 mL flask, 1 mL of PAA (0.2g/ mL) and 1 mL of NH₃·H₂O were firstly added to 100 mL of deionized water under magnetic stirring for 30 min. Then, 400 mL of isopropyl alcohol was slowly dropped into the above solution. Finally, a milk-white color of PAA-NH₄ nanosphere solution was obtained, which was stored at room temperature for further experiments.

Preparation of NiFe₂O₄/C nanospheres

Briefly, different amount of FeCl₂·4H₂O (1, 1.5, 3mmol) and NiCl₂·4H₂O (0.5, 0.75, 1.5mmol) were respectively dissolved into the as-prepared PAA-NH₄ solution under vigorous stirring for 12 h. The resulting suspension was centrifuged at 6000 rpm for 10 min to separate the solid, and then washed with deionized water for several times. Subsequently, the solid sample was dried for 12 h in O₂ atmosphere at 60 °C for 10 h. Finally, the as-prepared sample was heated at 400 °C for 2 h with a rate of 2 °C min⁻¹ in N₂ atmosphere and then cooled to room temperature. The as-obtained samples with different content of Fe²⁺ and Ni²⁺ cations in the raw materials were labeled as (0.5:1) NiFe₂O₄/C, (0.75:1.5) NiFe₂O₄/C and (1.5:3) NiFe₂O₄/C, respectively. The pure NiFe₂O₄ was prepared without the addition of PAA-NH₄ nanospheres.

Characterization

X-ray diffraction (XRD) measurements were carried out by an X-ray powder diffractometer (Rigaku, Japan) equipped with a Cu K α source ($\lambda = 0.15418$ nm). X-ray photoelectron spectroscopy (XPS) was performed using a JEOL2010F instrument. The morphologies and microstructures of the samples were observed by scanning electron microscopy (SEM; S-4800, Hitachi), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM; JEM-2100, Japan). The Brunauer-Emmett-Teller (BET) specific surface areas (SBET) of the samples were measured through nitrogen adsorption by Micromeritics (ASAP 2020M, USA). UV-Vis diffuse reflectance spectra were obtained using UV-3600 UV-Vis spectrophotometer.

Photocatalytic Performance Measurements

The photocatalytic activities of the obtained samples were evaluated by the degradation of tetracycline hydrochloride in the presence of H₂O₂ under visible-light irradiation supplied by an 800 W Xe-lamp (Phchem III, Beijing NBET Technology Co., Ltd, $\lambda > 420$ nm). Typically, 5 mg of as-obtained sample was dispersed in 50 mL of TC (20 mg/L) solution. Before light irradiation, the suspensions were magnetically stirred for 30 min in darkness to ensure the establishment of an adsorption-desorption equilibrium, and then a certain amount of 30 wt% of H₂O₂ was added to the above suspensions. During the photocatalytic test, 3 mL of the suspension was taken out every 10 min and magnetically separated to remove the catalyst completely. The concentration of TC was measured by a UV-Vis spectrophotometer (UV-3600, Shimadzu) at $\lambda_{\text{max}} = 357$ nm. The catalytic activities were calculated by the formula $E = C_0 - C_t / C_0 \times 100\%$, where C_0 and C_t represent the adsorption equilibrium absorbance of TC and the desired time intervals, respectively. To detect the major active species in the photo Fenton-like process, radical-trapping experiments were conducted. The hydroxyl radical ($\cdot\text{OH}$) scavenger, superoxide anion radical ($\cdot\text{O}_2^-$), and hole (h^+) scavenger can usually be trapped by isopropanol (IPA), 4-hydroxy-TEMPO, and triethanolamine (TEOA), respectively. Typically, different scavengers were dispersed into the suspension solutions before the photocatalytic tests, and the following procedure was similar to the TC degradation process.

Table 1. The corresponding physicochemical properties of as-prepared samples

| Sample | Average crystal size [nm] (standard deviation) | S_{BET} [m ² g ⁻¹] | Pore volume [cm ³ g ⁻¹] |
|-------------------------------------|---|---|---|
| NiFe ₂ O ₄ | 21.32 | 22.59 | 0.12 |
| NiFe ₂ O ₄ /C | 10.27 | 72.23 | 0.17 |

Table 2. The comparison of TC degradation activity of NiFe₂O₄/C with previous literatures

| Photocatalyst | Concentration (mg L ⁻¹) | Dosage (g L ⁻¹) | Time (min) | Removal (%) | Light source | Reference |
|--|--|--------------------------------|---------------|----------------|--------------------------------------|-----------|
| 2.5% Ag/AgIn ₅ S ₈ | 10 | 0.3 | 120 | 95.3 | 300 W Xe lamp; $\lambda > 400$ nm | 1 |
| 10% Ag@AgI/V ₁ - BOI | 20 | 0.3 | 60 | 86.40% | 300 W Xe lamp; $\lambda > 420$ nm | 2 |
| Au-TiO ₂ /pDA/PVDF | 10 | — | 120 | 92 | 300 W Xe lamp; $\lambda > 420$ nm | 3 |
| N-TiO ₂ /rGO | 10 | 1.0 | 60 | 98 | 300 W Xe lamp; | 4 |

| | | | | | | |
|---|----|-----|-----|-------|---|-----------|
| | | | | | $\lambda > 400$ nm | |
| N-CNT/mpg-C ₃ N ₄ | 20 | 1.0 | 240 | 67.1 | 300 W Xe lamp; $\lambda \geq 400$ nm | 5 |
| CQDs/g-C ₃ N ₄ | 10 | 0.5 | 240 | 78.6 | 250 W Xe lamp; $\lambda > 420$ nm | 6 |
| GQDs/mpg-C ₃ N ₄ | 20 | 1.0 | 120 | 65 | 300 W Xe lamp; $\lambda \geq 400$ nm | 7 |
| h-BN/g-C ₃ N ₄ | 10 | 1.0 | 60 | 79.7 | 300 W Xe lamp; $\lambda \geq 400$ nm | 8 |
| NiFe ₂ O ₄ /C | 20 | 0.1 | 60 | 97.25 | 800 W Xe lamp; $\lambda \geq 400$ nm | This work |

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