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Investigation of photoelectrocatalytic activity of Cu₂O nanoparticles for p-nitrophenol using rotating ring-disk electrode and application for electrocatalytic determination

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ABSTRACT

A cuprous oxide (Cu₂O) nanoparticles modified Pt rotating ring-disk electrode (RRDE) was successfully fabricated, and the electrocatalytic determination of p-nitrophenol (PNP) using this electrode was developed. Cu₂O nanoparticles were obtained by reducing the copper–citrate complex with hydrazine hydrate (N₂H₄·H₂O) in a template-free process. The hydrodynamic differential pulse voltammetry (HDPV) technique was applied for in situ monitor the photoelectrochemical behavior of PNP under visible light using nano-Cu₂O modified Pt RRDE as working electrode. PNP undergoes photoelectrocatalytic degradation on nano-Cu₂O modified disk to give electroactive p-hydroxylamino phenol species which is compulsive transported and can only be detected at ring electrode at around 0.05 V with oxidation signal. The effects of illumination time, applied bias potential, rotation rates and pH of the reaction medium have been discussed. Under optimized conditions for electrocatalytic determination, the anodic current is linear with PNP concentration in the range of 1.0×10^{-5} to 1.0×10^{-3} M, with a detection limit of 1.0×10^{-7} M and good precision (RSD = 2.8%, n = 10). The detection limit could be improved to 1.0×10^{-8} M by given illumination time. The proposed nano-Cu₂O modified RRDE can be potentially applied for electrochemical detection of p-nitrophenol. And it also indicated that modified RRDE technique is a promising way for photoelecrocatalytic degradation and mechanism analysis of organic pollutants.

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1. Introduction

p-Nitrophenol is one of the priority pollutants included in the US environmental protection Agency (EPA) due to their toxic effects on humans, animals and plants [1]. Generally, there have been some methods for degradation of p-nitrophenol including biodegradation [2], photocatalytic destruction [3], microwave assisted oxidation [4], electrocatalytic oxidation [5] and photoelectrocatalytic degradation [6]. At present, various methods have been developed for detection of p-nitrophenol and intermediates of PNP degradation, such as liquid chromatography and GC-MS methods [7] are commonly used. For detection of p-nitrophenol, electroanalytical techniques based on various chemically modified electrodes [8–10] have been proposed for direct PNP determination, with the analytical signal being derived from the 4-electron reduction of the nitro group. Several applications and electroanalytical methodologies employing microelectrode as working electrode for indirect quantification via the hydroxylamine absorbed product of PNP were recently reported, such as multiwall carbon nanotube [11], nanoporous gold [12] and zircomia (ZrO₂) nanoparticles [13]. However, no publication has reported on using bare ring nano-Cu₂O modified disk Pt RRDE for determination of PNP via monitoring the intermediates of photoelectrocatalytic degradation.

As a p-type semiconductor with a band gap of 2.17 eV [14], Cu₂O is a promising material with potential applications in solar conversion [15], catalysis [16], and sensing [17]. Besides, Cu₂O has a great potential application in photocatalytic degradation of organic pollutants under visible light [18–20]. Some electrocatalytic behaviors of Cu₂O have also been investigated [21,22]. Our previous work [23] has proved that Cu₂O exhibited potential photoelectrocatalytic property. The rotating ring-disk electrode technique has become one of the important tools for detection of reaction intermediates and study of electrode reaction mechanism since Frumkin and Nekrasov proposed in 1957. This is a good "Occurred – collection" technology to use ring electrode to monitor the intermediates formed on disk electrode. Our group has investigated the photoelectrocatalytic degradation behavior of PNP with nano-TiO₂ modified film at rotating ring-disk electrode under UV light [24].

In this study here, we employed a nano-Cu₂O modified Pt RRDE for photoelectrocatalytic degradation of p-nitrophenol, and found the electrode also could be applied for electrocatalytic determination of p-nitrophenol via monitoring the intermedi-

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ates. The Cu₂O nanoparticles were obtained by reducing the copper-citrate complex with N₂H₄·H₂O under alkaline conditions. The morphology of the Cu₂O was observed using scanning electron microscope (SEM). The structure and the chemical composition of the Cu₂O nanoparticles were characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The results showed that p-nitrophenol was photoelectrocatalytic degraded to p-hydroxylamino phenol on nano-Cu₂O modified disk; the intermediate was simultaneously collected and detected at bare Pt-ring electrode due to its further oxidation signal at about 0.05 V. And we found this signal could be applied for electrocatalytic determination of p-nitrophenol. The present work firstly revealed that nano-Cu₂O has photoelectrocatalytic ability for degradation and in situ determination of PNP. And it also indicated that modified RRDE technique could be considered as an important way to investigate the mechanism of the photoelectrocatalytic degradation of organic pollutants.

2. Experimental

p-Nitrophenol (analytical standard) and nafion-117 (5 wt.%) was purchased from Aldrich reagent company. All of the other compounds were AR grade and used without further purification. Milli-Q water was used throughout.

The Cu₂O nanoparticles were synthesized by reducing copper–citrate complex with N_2H_4 · H_2O under alkaline condition at room temperature, with template-free and non-surfactant. In a typical procedure, 200 mL of 0.05 M CuSO₄· $5H_2O$ and 0.1 M C₆H₅Na₃O₇· $2H_2O$ (Na₃Cit), the pH was set to 12.00, adjusted by additions of 4M NaOH solution. Then 2.0 mL N₂H₄· H_2O was added dropwise into the above solution with magnetic stirring for 1 h. The orange yellow power thus obtained. They were collected and washed with Milli-Q water several times and then dried in a vacuum oven at 50 °C for 12 h.

The photoelectrochemical measurements were carried out at room temperature in a quartz glass reactor using 50 mL of 0.1 M Na_2SO_4 (pH 5.8) as the electrolyte; a rotating ring-disk electrode system (Pine Instrument Co.) and a CHI 7101c electrochemical workstation (Shanghai Chenhua Instrumental Co., China) in a fourelectrode system. A daylight lamp (24 W, Shanghai, China) was located about 50 mm far off the bottom of quartz glass reactor as visible light source. Solution was purged with N_2 for 25 min before the experiments and a weak stream of N_2 was maintained during the experiments. A fan cooler system was also employed.

A Pt-ring (i.d. and o.d., 7 and 8.6 mm, respectively) electrode served as working electrode. About 15 μ L of nafion-Cu₂O mixing solution in ethanol, which was composed of 0.5 wt.% Nafion and 15 mg mL⁻¹ Cu₂O by ultrasonic mixing for 1 h, was dropped carefully onto the clean Pt-disk electrode (6 mm diameter) and dried in air. The schematic of working electrodes is shown in Scheme 1. The counter electrode was a Pt wire, and an Ag/AgCl electrode (saturated KCl) served as a reference electrode. HDPV experiments were performed with rotation of the working electrode at 1600 rpm and at a scan rate of 20 mV s⁻¹. The DPV parameters were 50 mV pulse amplitude and 50 ms pulse width.

3. Results and discussion

3.1. Characterization of the Cu₂O nanoparticles

Fig. 1a shows the typical top-view SEM image of the asobtained Cu₂O nanaparticles by reducing copper–citrate complex with N₂H₄·H₂O. As can be seen, Cu₂O nanaparticles were uniformly dispersed, with diameter of 80–120 nm. Fig. 1b shows the highmagnification of the Cu₂O nanaparticles, we could observe that



Scheme 1. The schematic of RRDE and the electrode reaction mechanism of pnitrophenol occurred on it during photoelectrocatalysis.

they exhibit rough surface composed of smaller nanoparticles. No impurities were attached to the surface, attributed to the method fabricated in a template-free process and without any surfactant.

The XRD pattern is displayed in Fig. 2a. All diffraction peaks in the pattern can be perfectly indexed as the cubic phase Cu₂O (JCPDS File No. 05-0667). No other diffraction peaks arising from possible impurities such as Cu and CuO are detected, indicating that the products are pure Cu₂O. The peaks with 2θ values of 29.68°, 36.54°, 42.46°, 61.62°, 73.86° and 77.12° correspond to the crystal planes of 110, 111, 200, 220, 311 and 222 of crystalline Cu₂O, respectively.

XPS was used to further investigate the chemical composition of the Cu₂O nanoparticles. The core level Cu₂p photoemission spectrum is presented in Fig. 2b. It can be clearly observed that two peaks assigned to Cu₂p_{1/2} and Cu₂p_{3/2} appear at 952.62 and 932.77 eV, respectively, which is corrected with reference to C1s (284.6 eV). In combination with the main peak appears at 332.66 eV in the Auger spectrum, it can be confirmed that Cu₂O nanoparticles are highly pure. The result is in good agreement with data observed for Cu₂O [25].

3.2. Photoelectrochemical behavior of PNP on nano-Cu₂O modified Pt RRDE

Fig. 3 shows the DPV on bare ring electrode with nano-Cu₂O modified disk and non-modified disk in the absence and presence of PNP, using 0.1 M Na₂SO₄ as the electrolyte. For the non-modified Pt RRDE, the DPV in the absence and presence of 1×10^{-4} M PNP were recorded as curves a and b. The peak located at about -0.1 V was related to O₂, the inset shows electrochemical behavior of Pt ring electrode in blank solution with different time of purged N₂. While for the nano-Cu₂O modified Pt RRDE, curve c represents the DPV performance of Pt ring electrode without PNP, which indicates that the peak appeared at about +0.3 V is attributed to the electrochemical reaction of Cu₂O and comes from the formation of CuO layer. When PNP was added (curve d), an obvious anodic peak was observed at around 0.05 V, which has been well-defined as an oxidation signal of generated hydroxylamine to nitroso species [26].

3.3. Effect of the illumination time

Fig. 4 shows the corresponding DPV photoelectrochemical responses in $0.1 \text{ M} \text{ Na}_2 \text{SO}_4$ solution containing $1 \times 10^{-4} \text{ M} \text{ PNP}$ with different illumination time. The Pt disk electrode modified with nano-Cu₂O retained the bias potential of 0.2 V herein. At the very start without illumination, the anodic peak at 0.004 V was observed remarkably. The peak current is much larger than that



Fig. 1. SEM images of Cu₂O nanoparticles obtained by reducing copper-citrate complex with N₂H₄·H₂O: (a) at low magnification and (b) at high magnification.

obtained in Fig. 3d (without applied potential), which indicated that the applied bias potential enhanced the catalytic performance of Cu_2O nanoparticles. The obvious increase of the peak currents with the more illumination time during 20 min (curves a–e) can be attributed to the cumulative effects of the intermediate product. Whereafter, the anodic peak currents decreased gradually with more illumination time during the following 40 min (e–i). The results imply that the further degradation of p-hydroxylamino phenol occurs during the process. Apparently, the p-hydroxylamino phenol was electrochemically oxidized to p-nitrosophenol.

3.4. Effect of bias potential

Fig. 5 shows the dependence of the anodic peak current at the Pt ring electrode on continuous illumination time in 0.1 M Na₂SO₄ solution containing 1×10^{-4} M PNP. Different bias potentials ranging from -0.1 to 0.5 V were applied on the nano-Cu₂O modified Pt disk electrode. As shown in Fig. 5, at -0.1, 0, or 0.1 V, the peak current reached the max in 30 min and then decreased gradually. While at 0.2, 0.3, 0.4 or 0.5 V, the peak current reached the max in 20 min, which indicated that the increased positive potential has more forceful effect on the nano-Cu₂O, especially at +0.3 V. The photocatalytic performance at 0 V of the Cu₂O for the degradation of PNP is relatively slow and ineffective compared with the photoelectrocatalytic process. The response current at +0.3 V increased sharply but its change was inconspicuous when decreased, so the photoelectrocatalytic degradation at +0.2 V is more effective. This is because when the bias potential E > 0.2 V, Cu₂O may be partially



Fig. 3. DPV obtained at bare ring with non-modified (a, b) and nano-Cu₂O modified disk (c, d) Pt RRDE; solutions: (a, c) 0.1 M Na₂SO₄, (b, d) 0.1 M Na₂SO₄ + 1 × 10⁻⁴ M PNP. Solutions were purged N₂ for 25 min. Inset: non-modified Pt RRDE ring electrode in 0.1 M Na₂SO₄ with different time of purged with N₂: 0 min, 10 min and 25 min.

oxidized to CuO which grows according to a high field mechanism; Strehblow et al. reported that Cu₂O composition was found with a Cu (II) oxide overlayer at E > 0.2 V [27]. Thus +0.2 V is the optimal bias potential to applied on Cu₂O modified Pt disk. The result



Fig. 2. (a) XRD pattern and (b) XPS spectrum of the as prepared Cu₂O nanoparticles.



Fig. 4. The DPV responses of 0.1 M Na₂SO₄ solution containing 1×10^{-4} M PNP at bare ring nano-Cu₂O modified disk Pt RRDE with different visible light illumination time $(a \rightarrow i) 0, 2, 5, 10, 20, 30, 40, 50$ and 60 min. Applied potential: 0.2 V; rotation rate: 1600 rpm.

exhibited at -0.1 V is not as good as that at 0 V, which reflected that the negative bias potential applied on the nano-Cu₂O modified Pt disk electrode has counteracted effects on direct photolysis. When negative bias potential applied, although it can play a promote role on the electron movement, but it also increase the recombination probability of the electron-hole pairs and lessen the effective holes.

3.5. Influence of rotation rates and solution pH

Fig. 6a shows the DPV responses of 1×10^{-4} M PNP present for various rotation rates recorded at bare ring electrode when the disk electrode was modified with nano-Cu₂O and had an applied potential of 0.2 V. This was operated without illumination as illumination time has effect on peak current. The data was analyzed using the Koutecky–Levich equation [28], plotted as peak current versus $\omega^{1/2}$, and the result is shown in Fig. 6b.

$$\frac{1}{I_{\rm lim}} = \frac{1}{I_{\rm Lev}} + \frac{1}{I_K} \tag{1}$$

where

$$I_{\text{Lev}} = 0.62nFAC_0 D_0^{2/3} \gamma^{-1/6} \omega^{1/2}$$
⁽²⁾

The parameter *I* is the measured limiting current, ω is the rotation rate, *n*, *D*₀ and *C*₀ are the electron number, the diffusion



Fig. 5. The dependence of the oxidation peak currents at Pt ring electrode on continuous illumination time under different disk bias potential (a) -0.1 V, (b) 0 V, (c) +0.1 V, (d) +0.2 V, (e) +0.3 V, (f) +0.4 V and (g) +0.5 V.

coefficient and the PNP concentration, respectively, and γ is the kinetic viscosity of the electrolyte solution. As shown in Fig. 6b, the anodic peak current is linear with $\omega^{1/2}$, defined *k* as the slope, thus,

$$k = 0.62nFAC_0 D_0^{2/3} \gamma^{-1/6} \tag{3}$$

The linear regression equation was $I_{pa} = -0.6127 + 0.3963\omega^{1/2}$, with a correlation coefficient of 0.9997, indicating that the electrode progress is controlled by diffusion [28]. The electrons transfer number was calculated to be 1.8 (approximately 2), demonstrating that p-hydroxylamino phenol was transferred to p-nitrosophenol by two-electron-transfer process. The parameters used in this calculation were the following: diffusion coefficient $D = 4.32 \times 10^{-5}$ cm² s⁻¹, concentration of PNP $C_0 = 1 \times 10^{-4}$ M, kinetic viscosity $\gamma = 0.01$ cm² s⁻¹, rotating ring area A = 0.196 cm².

The electro-reduction of PNP is a proton-participating reaction, so the effect of pH on E_p and I_p was examined in an electrolyte composed by 0.1 M Na₂SO₄ + 1 × 10⁻⁴ M PNP. The disk electrode modified with nano-Cu₂O had an applied potential of 0.2 V, operating under visible light illumination. The successive DPV responses at different pH value were displayed in Fig. 7a, the magnification of line groups 3, 4 and 5 was displayed in Fig. 7b. The pH was adjusted using 0.1 M H₂SO₄ or NaOH. The results showed that the potentials shifted negatively with the increase of solution pH, indicating that protons take part in the electrode reaction process. The anodic peak potential is proportional with the solution pH. The linear regression equation was E_{pa} = 0.320–0.054 pH, the value of slope demonstrated that the electrode process is equal proton-electron transfer involved in the p-hydroxylamino phenol oxidation. The peak current decreased sharply with the pH increasing. At low pH (line groups 1 and 2), the currents were high but the electrode become unstable, the peak currents were decreased much with scan times. This may be ascribed to that electroreduction of PNP and redox of its intermediates proceed easily at low pH values than those of alkaline and neutral conditions [12,29], which results in the high current. On the other hand, Cu₂O was disproportionate easily at acid condition. When pH was 5.8, we found the peak currents were increased with scan times, which attributed to the influence of the visible light. A new peak II appeared at about 0.1 V, which also existed at low rotation rate in Fig. 6a. We preliminarily speculate that this peak is related with adsorption. At pH > 6 (line groups 4 and 5), the peak currents were too low, and the interference of peak II was serious. Therefore, pH 5.8 was chosen as the optimal value.



Fig. 6. (a) DPV responses of 1×10^{-4} M PNP at bare ring Cu₂O modified disk Pt RRDE with various rotation rates. (b) Plots of peak current versus $\omega^{1/2}$. Curve numbers represent rpm rotation rates of: (a) 500, (b) 700, (c) 900, (d) 1200, (e) 1400, (f) 1600 and (g) 1800 rpm. Applied potential: 0.2 V; without visible light illumination.



Fig. 7. (a) Successive DPV responses of 1×10^{-4} M PNP at bare ring nano-Cu₂O modified disk Pt RRDE at different pH value (1) 4.15, (2) 5.05, (3) 5.8, (4) 6.48 and (5) 7.25. Inset shows variation of potential versus pH. Bias potential: +0.2 V, under visible light; rotation rate: 1600 rpm; (b) the magnification of (3) 5.8, (4) 6.48 and (5) 7.25.

3.6. Electrode reaction mechanism of p-nitrophenol on Pt RRDE

On nano-Cu₂O modified disk, PNP undergoes photoelectrocatalytic degradation to give a p-hydroxylamino phenol species, the intermediate product is compulsive transported and detected simultaneously at bare Pt ring electrode at about 0.05 V as oxidation signal. The schematic of RRDE and possible reaction mechanism is shown in Scheme 1. The reduction of the nitro group to hydroxylamine (reaction (1)) had been established with the successive $2e^-$ steps [30]. The calculated value of electrode process of p-hydroxylamino phenol oxidation is $2e^-$ and $2H^+$. The probable electrochemical oxidation reaction of p-hydroxylamino phenol on Pt ring electrode was described as reaction (2).



Fig. 8. (a) DPV responses of increasing PNP concentration, from $a \rightarrow j$, 2, 8, 16, 30, 40, 50, 60, 70, 80, 90, 100×10^{-5} M, respectively. (b) The dependence of I_{pa} on PNP concentration.

3.7. Electrocatalytic determination of PNP

Fig. 8 displays the DPV responses of the Pt ring electrode in increasing concentrations of PNP solution, with nano-Cu₂O modified disk retained the bias potential of 0.2 V. At low concentrations two peaks are evident, one at 0.05 V and the other at 0.15 V. At higher concentrations, the peak at 0.05 V dominates. One possible explanation of this phenomenon is that the peak at 0.15 V is comparable to the postwave adsorption peak first studied by Brdicka [31] and later by Wopschall and Shain [32]. They observed a diffusive peak from the bulk solution and a postwave adsorption peak from the species adsorbed to the surface of the electrode. The current phenomenon we observed is much analogous, so the peak at 0.15 V is identified as the oxidation of adsorbed p-hydroxylamino phenol species on the Pt ring electrode surface. The peak at 0.05 V is controlled by diffusion. As stabilized by the adsorption energy [33], the oxidation of the adsorbed species requires a high energy and occurs at a more positive potential.

The dependence of I_{pa} on PNP concentration was given in Fig. 8b. The results showed that I_{pa} was proportional to concentration of PNP in the range of 1.0×10^{-5} to 1.0×10^{-3} M. The linear regression equation being I_{pa} (μ A) = 64.1127 + 1.3964C, with a correlation coefficient of 0.9985. The detection limit was 1.0×10^{-7} M, it could be improved to 1.0×10^{-8} M if given illumination time. The relative standard deviation of 10 successive scans was 2.8% for 5.0×10^{-5} M PNP, indicating excellent reproducibility of the nano-Cu₂O modified RRDE. The result showed that bare ring nano-Cu₂O modified disk Pt RRDE technique could be successfully used to monitor pnitrophenol by the oxidation signal of p-hydroxylamino phenol generated from photoelectrocatalytic degradation.

4. Conclusions

In summary, the elecrocatalytic determination of PNP was successfully carried out at bare ring nano-Cu₂O modified disk Pt RRDE, using the oxidation signal of p-hydroxylamino phenol produced by photoelectrocatalytic degradation of PNP. This intermediate could be oxidized at low potential thus avoiding matrix interference. The applied bias potential and visible light enhanced the anodic peak currents compared to that without light and bias potential. The present work shows that Cu₂O nanoparticles are potentially applied for monitor the hazardous pollutant p-nitrophenol ascribed to its photoelectrocatalytic property. Our findings suggest that Cu₂O become a new photoelectrocatalytic material for degradation of organic pollutants in environmental remediation, and the modified RRDE technique is a promising way for monitor the intermediates and study the photoelecrocatalytic degradation mechanism of organic pollutants.

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