Supporting Information

Enhanced Photoelectrocatalytic Reduction and Removal of Atrazine: Effect of Co-Catalyst and Cathode Potential

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Text S1

The Mott-Schottky analysis is a rapid and economical technique to obtain information of the band structure of semiconductor materials. The charge carrier type of the semiconductor can be estimated from the slope of the Mott-Schottky plots. A positive slope demonstrates n-type carrier conduction and a negative slope demonstrates p-type carrier conduction, and Mott–Schottky equation can be used to determine the flat-band potential of the semiconductor. For both electrodes, n-type semiconductor behavior was confirmed from the 1/C_sc^2 vs E plots (M-S plots) (Figure S5B), and the Mott-Schottky relationship is written as:

\[
\frac{1}{C^2} = \frac{2}{N_D\varepsilon_0\varepsilon}(E_s - E_{FB} - \frac{kT}{e})
\]

Where, C is the interfacial capacitance, \(\varepsilon_0\) is the permittivity of vacuum (8.854\times10^{12} F\cdot m^{-1}), \(\varepsilon\) is the relative dielectric constant, \(N_D\) is the donor density, \(E_s\) is the electrode potential, \(E_{FB}\) is the flat band potential, \(e\) is the charge of single electron (1.6\times10^{-19} C), \(T\) is the temperature, and \(k\) is the boltzmann's constant.
Text S2

For calculation of the lifetime of the accumulated electrons on PdQDs@TiO$_2$NTs, open circuit potential delay (OCPD) curves were firstly collected (Figure 5A). As shown in the Figure, the original data were presented as $V_{oc}$ (“Potential” in the Y-axis of Figure 5A) against Time ($t$). The lifetime of the photo-generated electrons was calculated according to the formula of $\tau = \frac{k_BT}{e} \cdot \left( \frac{dV_{oc}}{dt} \right)^{-1}$, where $\tau$ represented the potential-dependent lifetime of photo-generated electrons, $k_B$ represented boltzmann's constant, $T$ was the temperature, and $e$ was the charge of single electron respectively.

Here, $\frac{dV_{oc}}{dt}$ could be obtained by differentiating $V_{oc}$ against Time ($t$). Since that $\tau$ was potential-dependent, in Table 2 the potential was fixed as -0.6 V vs. SCE, and $\frac{dV_{oc}}{dt}$ was calculated to be $1.004 \times 10^{-3}$. Then, $\tau$ could be obtained by the above formula to be 25.6 s for PdQDs@TiO$_2$NTs detected in the solution without atrazine. Accordingly, other $\tau$ values could be calculated.
The surface charge transfer efficiency on PdQDs@TiO₂NTs and TiO₂NTs was determined by PEC tests according to the literatures⁵,⁶.

The transient photocurrent experiments were carried out with a 50 s off-on light cycles at a bias voltage of 0 V vs. SCE. \( J_P \) of TiO₂NTs and PdQDs@TiO₂NTs were tested in 0.1 mol·L⁻¹ Na₂SO₄ aqueous solution and \( J_P \) (H₂O₂) of TiO₂NTs and PdQDs@TiO₂NTs were recorded in 0.1 mol·L⁻¹ Na₂SO₄ aqueous solution containing 0.5 mol·L⁻¹ H₂O₂ as electron scavenger. Since that the electron scavenger H₂O₂ could increase the surface charge transfer efficiency to almost 100%, the surface charge transfer efficiency (\( \eta \)) of TiO₂NTs and PdQDs@TiO₂NTs could be calculated according to the formula: \( \eta = \frac{J_P}{J_P(H_2O_2)} \).
Figure S1. Particle size distribution of PdQDs on the surface of PdQDs@TiO$_2$NTs.
Figure S2

Figure S2. TEM and HR-TEM images of PdQDs@TiO$_2$NTs.
Figure S3

The EDS image of elements distribution and element content on the PdQDs@TiO2NTs electrode surface.

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<td>Ti K</td>
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Figure S4

(A) UV-vis diffuse reflectance spectra (DRS) of TiO$_2$NTs and PdQDs@TiO$_2$NTs; (B) the corresponding Tauc plots.

Figure S4. (A) UV-vis diffuse reflectance spectra (DRS) of TiO$_2$NTs and PdQDs@TiO$_2$NTs; (B) the corresponding Tauc plots.
Figure S5

Figure S5. (A) Nyquist curve of TiO₂NTs and PdQDs@TiO₂NTs electrodes before and after radiation; (B) Mott-schottky curve of TiO₂NTs and PdQDs@TiO₂NTs electrode; (C) Open circuit potential decay curve of PdQDs@TiO₂NTs and TiO₂NTs electrodes (D) the potential dependent lifetime plots for PdQDs@TiO₂ NTs and TiO₂NTs electrodes
Figure S6. The activation energy determination of PEC reduction of atrazine on PdQDs@TiO$_2$ NTs: (A) the Arrhenius plots of $\ln i$ vs. $10^3/RT$; (B) activation energy under different potential.
Figure S7. The evolution of the intermediates in atrazine PEC reduction on PdQDs@TiO$_2$NTs under the potential of -0.9 V (A), -1.3 V (B) and -1.5 V (C); (D) the chemical structures of atrazine and the major intermediates.
Figure S8

![Figure S8](image)

<table>
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<th>Elements</th>
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Figure S8. The EDS image of elements distribution and element content on the surface of PdQDs@TiO₂NTs after usage in PEC reduction.
References