

**Supporting Information**

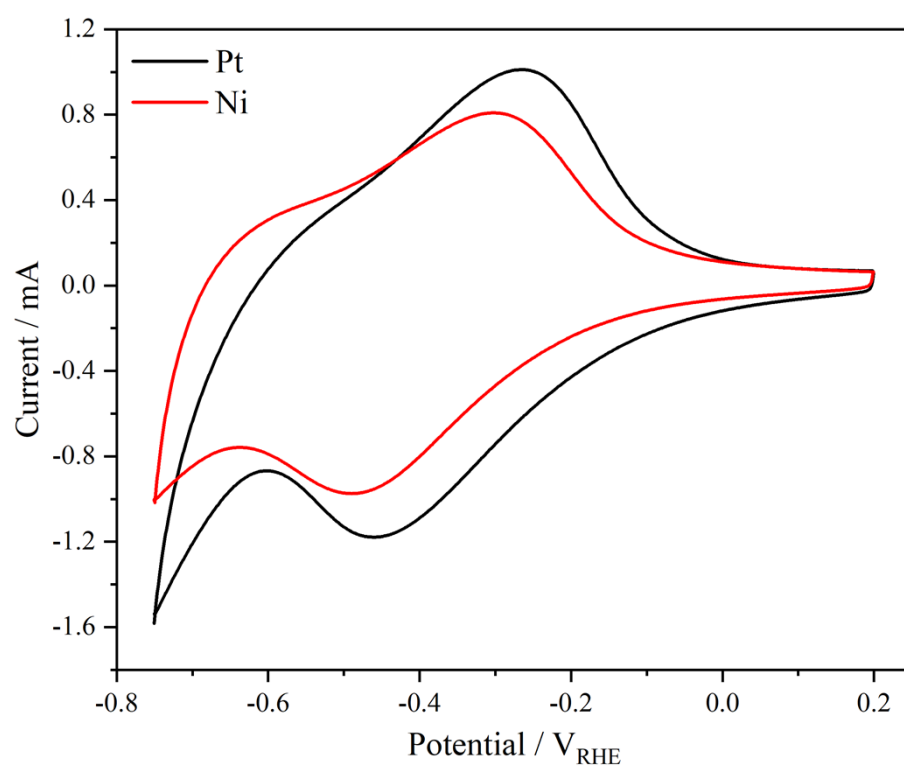
# Tailoring Density of State of Ni(OH)<sub>2</sub> with Ni<sup>0</sup> Towards Solar Urea Wastewater Splitting

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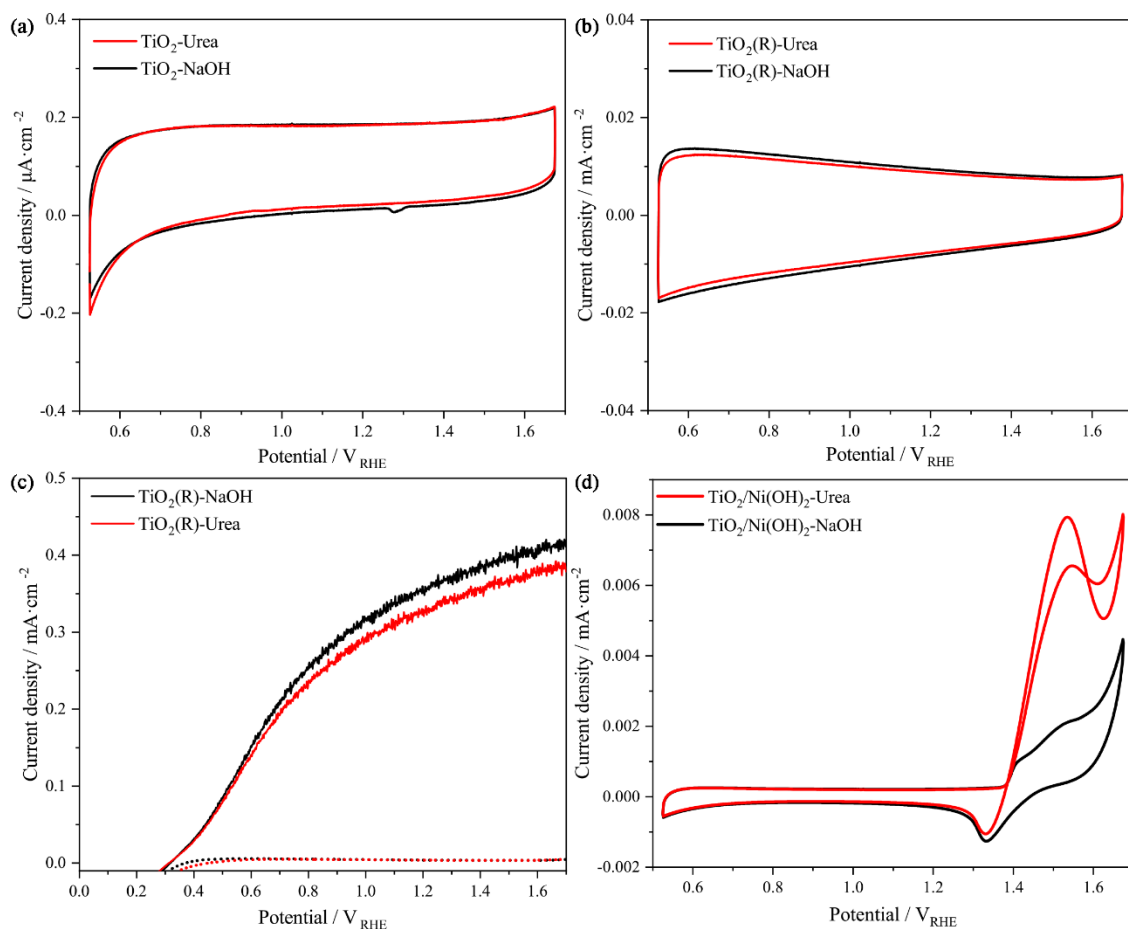
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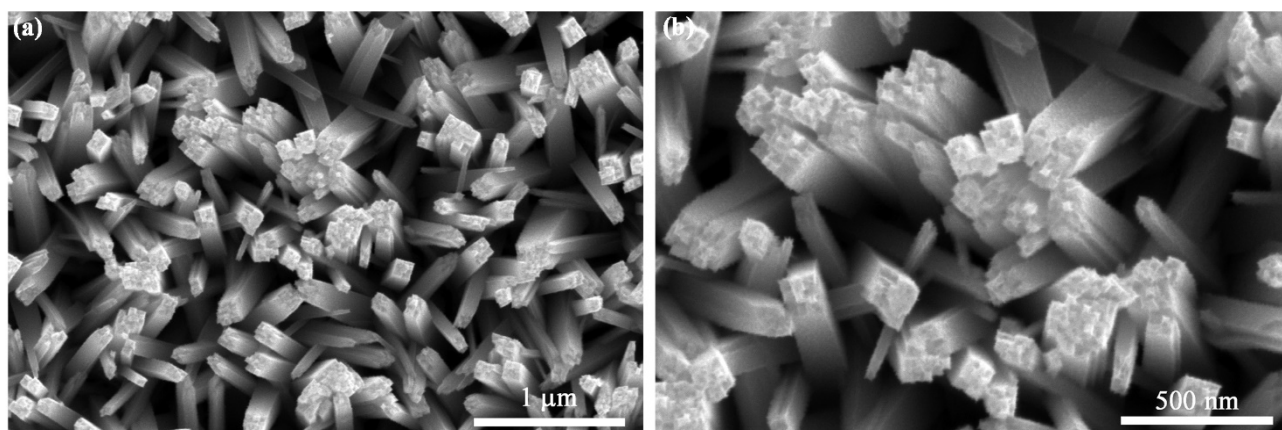


**Figure S1.** CV curves with Pt and Ni counter electrodes in PBS (pH=6.8) at a scan rate of 100 mV s<sup>-1</sup>.

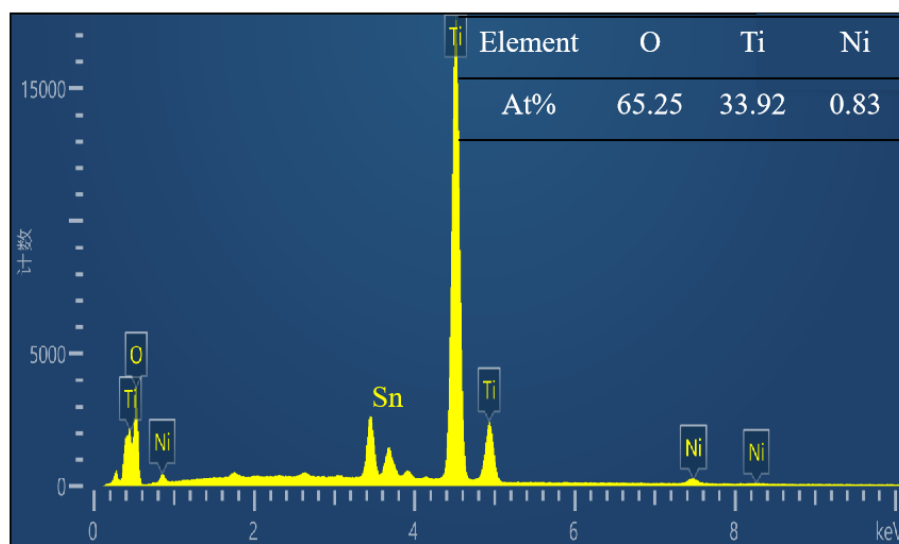
1.



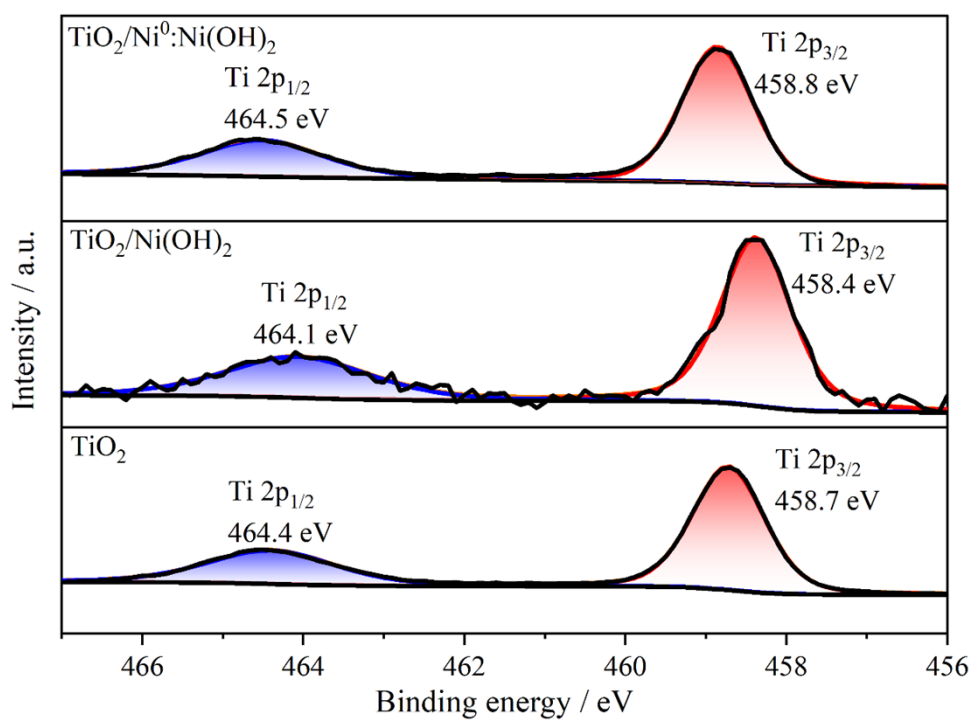
**Figure S2.** (a) CV curves of  $\text{TiO}_2$ . (b) CV curves of the electrochemical reduced  $\text{TiO}_2$  ( $\text{TiO}_2(\text{R})$ ). (c) Dark (dot line) and light (solid line) of  $\text{TiO}_2(\text{R})$ . (d) Dark CV curves of  $\text{TiO}_2/\text{Ni}(\text{OH})_2$ . Test conditions: the electrolyte is 1.0 M NaOH with/without 0.33 M  $\text{CO}(\text{NH}_2)_2$ . The scan rate is 20  $\text{mV s}^{-1}$ .



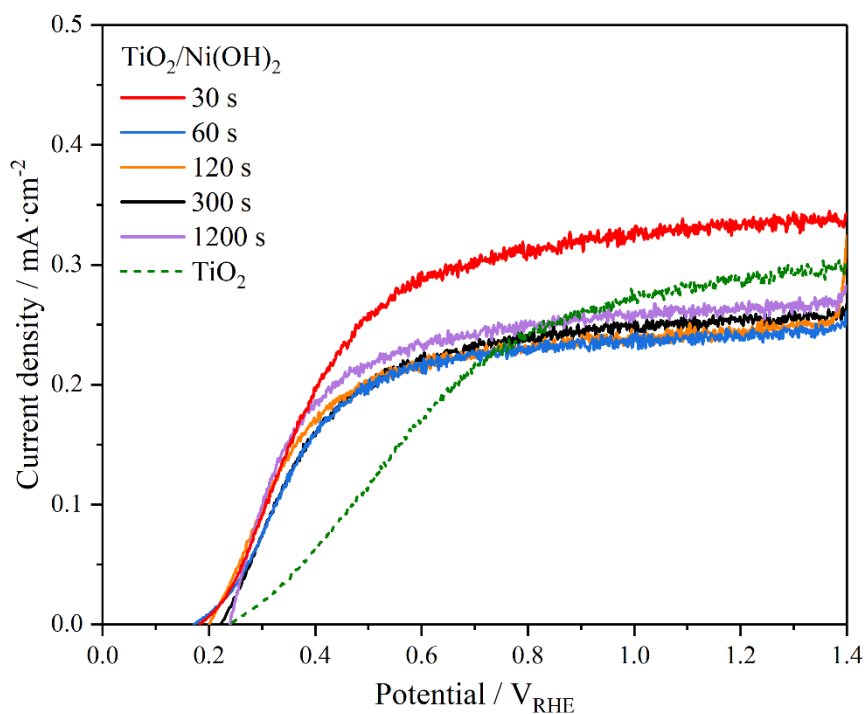
**Figure S3.** SEM images of  $\text{TiO}_2/\text{Ni}(\text{OH})_2$  photoanodes.



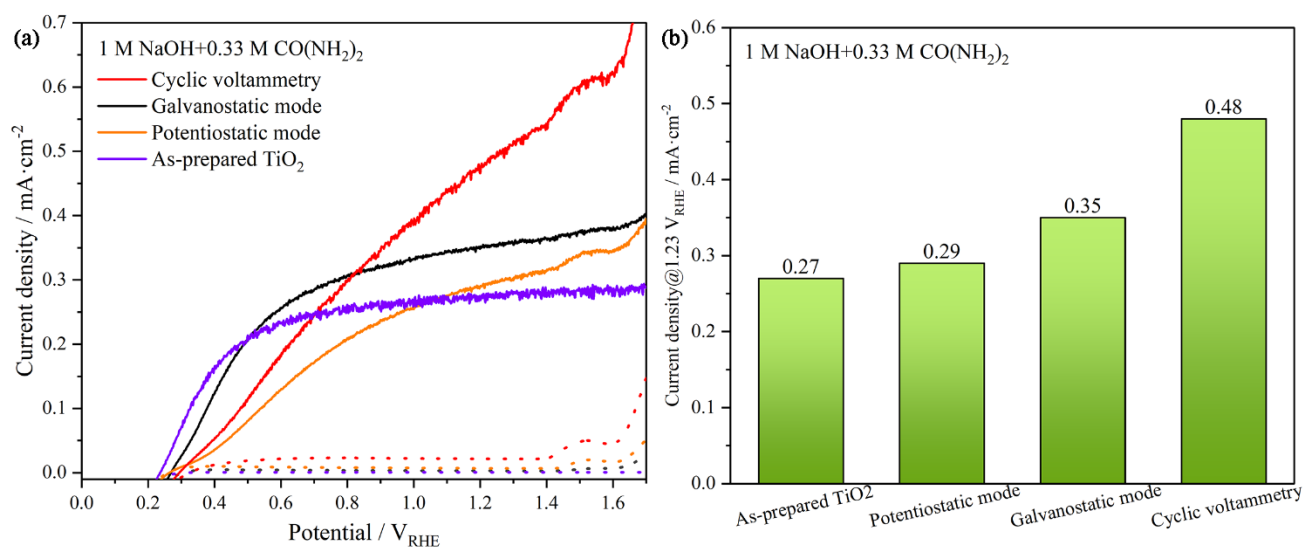
**Figure S4.** EDS pattern of  $\text{TiO}_2/\text{Ni}^0:\text{Ni}(\text{OH})_2$ . The inset is the atomic ratios of O, Ti and Ni elements.



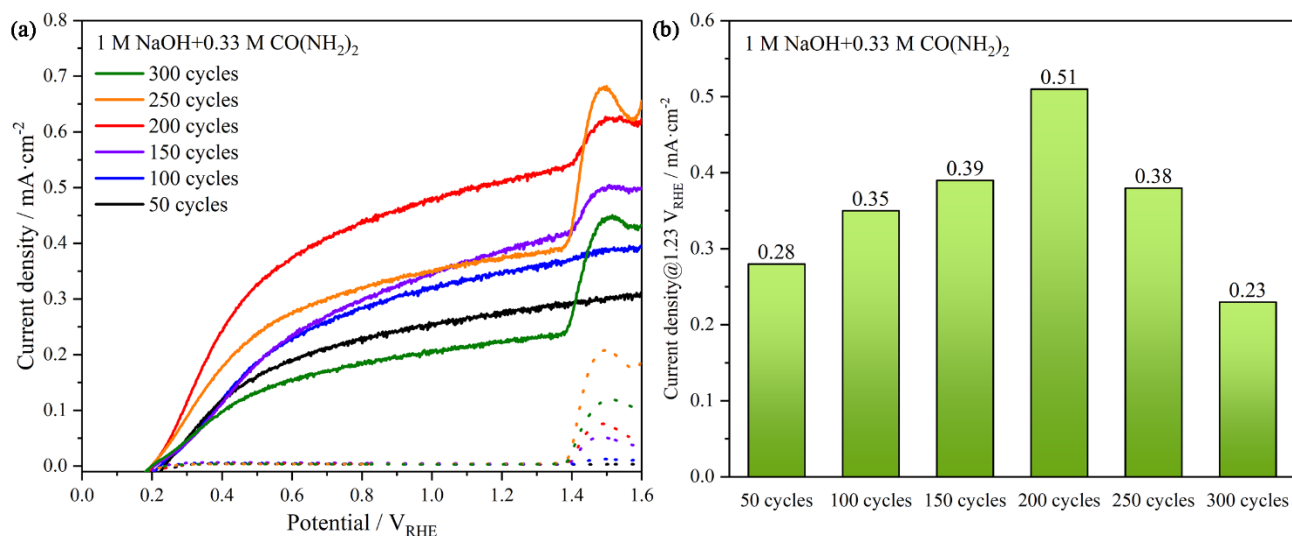
**Figure S5.** Ti 2p XPS spectra of  $\text{TiO}_2$ ,  $\text{TiO}_2/\text{Ni}(\text{OH})_2$ , and  $\text{TiO}_2/\text{Ni}^0:\text{Ni}(\text{OH})_2$  photoanodes.



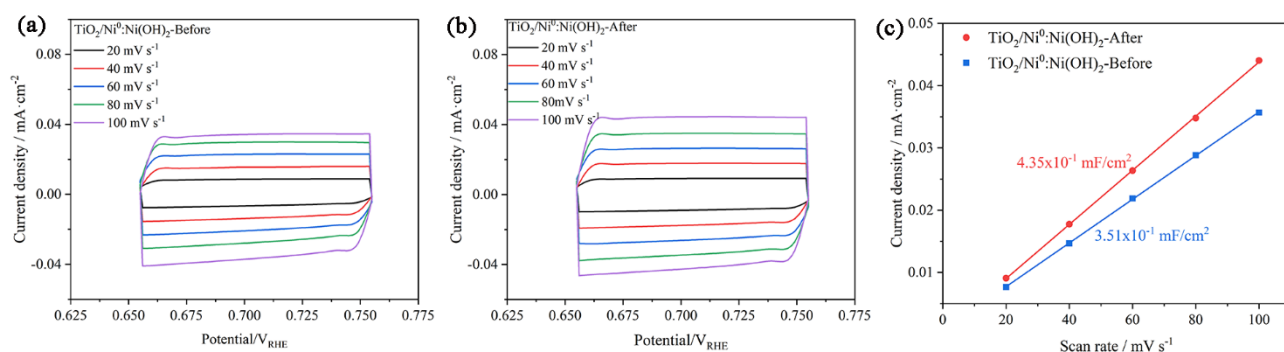
**Figure S6.** LSV curves of  $\text{TiO}_2/\text{Ni}(\text{OH})_2$  photoanodes with different loading of  $\text{Ni}(\text{OH})_2$  measured at a scan rate of  $20 \text{ mV s}^{-1}$  in  $1 \text{ M NaOH}$  and  $0.33 \text{ M CO}(\text{NH}_2)_2$  under AM 1.5G illumination.



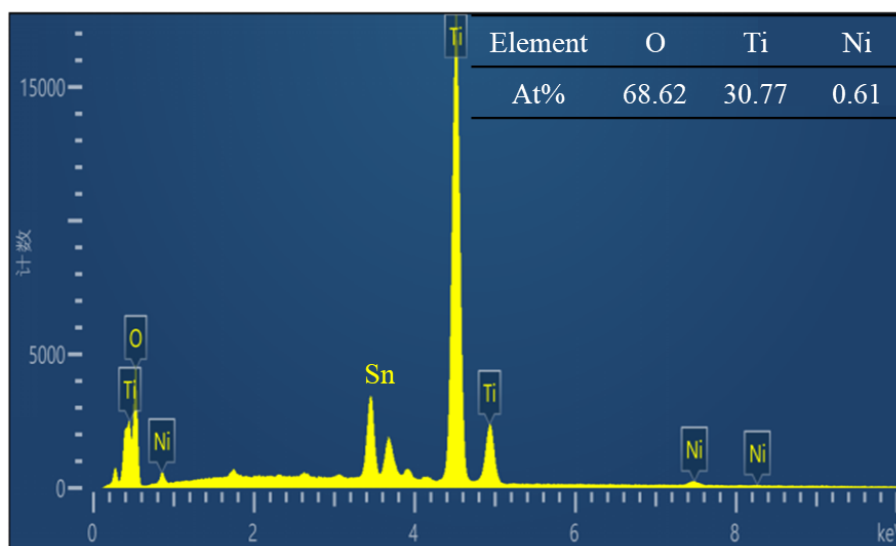
**Figure S7.** (a) LSV curves of  $\text{TiO}_2/\text{Ni}^0:\text{Ni}(\text{OH})_2$  prepared with different electrochemical technologies under AM 1.5G illumination. The dot lines are the corresponding dark LSV curves. Scan rate:  $20 \text{ mV s}^{-1}$ . (b) Photocurrent density of the above  $\text{TiO}_2/\text{Ni}^0:\text{Ni}(\text{OH})_2$  photoanodes at  $1.23 \text{ V}_{\text{RHE}}$ . For the synthesis of  $\text{Ni}^0:\text{Ni}(\text{OH})_2$ , the quantity of electric charge during these three techniques is as same as  $0.37 \text{ C}$ .



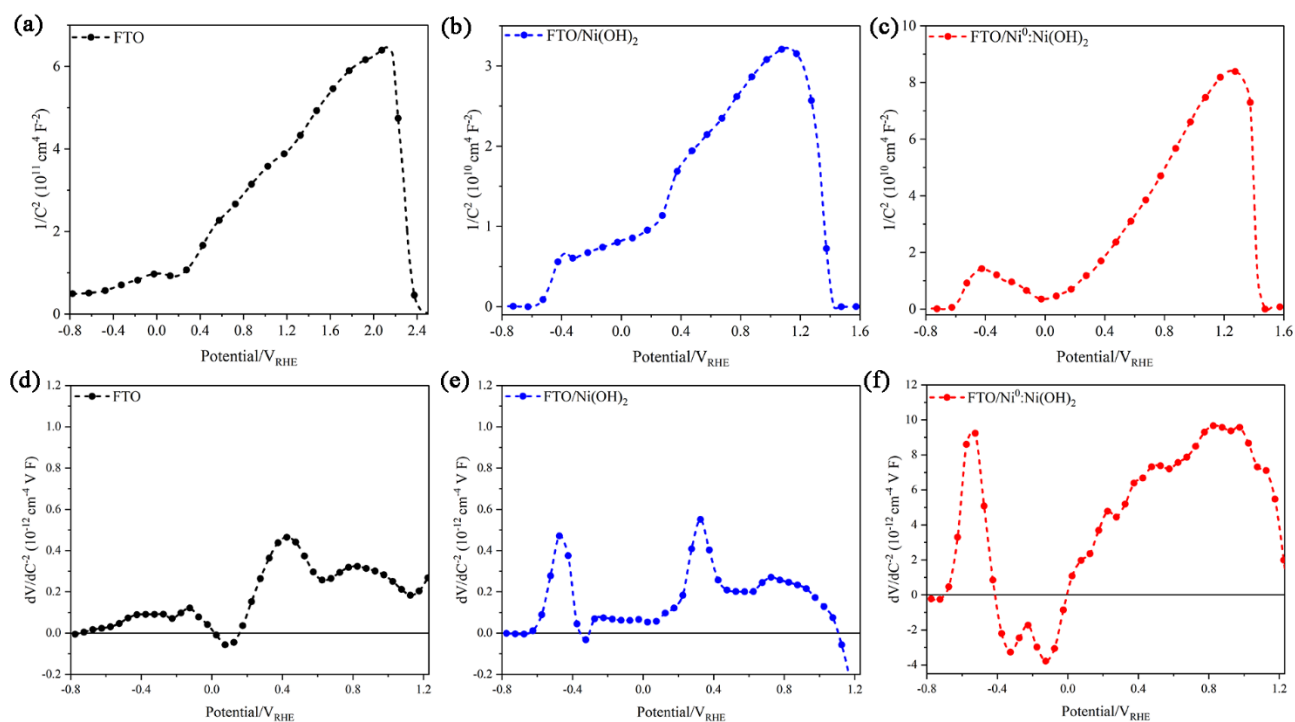
**Figure S8.** (a) LSV curves of  $\text{TiO}_2/\text{Ni}^0:\text{Ni}(\text{OH})_2$  prepared with various CV cycles under AM 1.5G illumination. The dot lines are the corresponding dark LSV curves. Scan rate:  $20 \text{ mV s}^{-1}$ . (b) Photocurrent density of the above  $\text{TiO}_2/\text{Ni}^0:\text{Ni}(\text{OH})_2$  photoanodes at  $1.23 \text{ V}_{\text{RHE}}$ .



**Figure S9.** (a) CV curves of  $\text{TiO}_2/\text{Ni}^0:\text{Ni}(\text{OH})_2$  before the stability test. (b) CV curves of  $\text{TiO}_2/\text{Ni}^0:\text{Ni}(\text{OH})_2$  after the stability test. (c) Capacitances of the above electrodes. Test conditions: the electrolyte of  $1.0 \text{ M NaOH}$  and  $0.33 \text{ M CO}(\text{NH}_2)_2$ .



**Figure S10.** EDS pattern of  $\text{TiO}_2/\text{Ni}^0:\text{Ni}(\text{OH})_2$  after stability testing. The inset is the atomic ratios of O, Ti and Ni elements.



**Figure S11.** MS plots of (a) FTO, (b)  $\text{FTO}/\text{Ni}(\text{OH})_2$  and (c)  $\text{FTO}/\text{Ni}^0:\text{Ni}(\text{OH})_2$ . The derivative of the nonlinear MS plots of (d) FTO, (e)  $\text{FTO}/\text{Ni}(\text{OH})_2$  and (f)  $\text{FTO}/\text{Ni}^0:\text{Ni}(\text{OH})_2$ .

**Table S1.** Summary the PEC performances of the reported photoanodes for urea oxidation reaction.

| Cocatalyst                 | Photoanode                          | Electrolyte                                                                  | PEC performance                                                     | Ref. |
|----------------------------|-------------------------------------|------------------------------------------------------------------------------|---------------------------------------------------------------------|------|
| Ni(OH) <sub>2</sub>        | TiO <sub>2</sub> (hydrogenated )    | 1 M NaOH+0.33 M CO(NH <sub>2</sub> ) <sub>2</sub>                            | $J_{ph}=2.51 \text{ mA cm}^{-2}$ , $E_{on}=0.2 \text{ V}_{Ag/AgCl}$ | 1    |
| Ni(OH) <sub>2</sub>        | TiO <sub>2</sub> /CdS               | 1 M NaOH+0.33 M CO(NH <sub>2</sub> ) <sub>2</sub>                            | $J_{ph}=0.81 \text{ mA cm}^{-2}$ , $E_{on}=1.23 \text{ V}_{RHE}$    | 2    |
| Ni(OH) <sub>2</sub>        | Ti:α-Fe <sub>2</sub> O <sub>3</sub> | 1 M NaOH+0.10 M CO(NH <sub>2</sub> ) <sub>2</sub>                            | $J_{ph}=1.57 \text{ mA cm}^{-2}$ , $E_{on}=1.30 \text{ V}_{RHE}$    | 3    |
| Ni(OH) <sub>2</sub> /Au/Co | α-Fe <sub>2</sub> O <sub>3</sub>    | Human urine                                                                  | $J_{ph}=7.51 \text{ mA cm}^{-2}$ , $E_{on}=1.33 \text{ V}_{RHE}$    | 4    |
| Co-Pi                      | SnO <sub>2</sub> /BiVO <sub>4</sub> | 0.1 M PBS+2% CO(NH <sub>2</sub> ) <sub>2</sub>                               | $J_{ph}=3.44 \text{ mA cm}^{-2}$ , $E_{on}=1.23 \text{ V}_{RHE}$    | 5    |
| Ni/SiO <sub>x</sub>        | Si                                  | 1 M KOH+0.33 M CO(NH <sub>2</sub> ) <sub>2</sub>                             | $J_{ph}=10.00 \text{ mA cm}^{-2}$ , $E_{on}=1.50 \text{ V}_{RHE}$   | 6    |
| CoOOH/NiOOH                | BiVO <sub>4</sub>                   | 0.5 M Na <sub>2</sub> SO <sub>4</sub> +2 % CO(NH <sub>2</sub> ) <sub>2</sub> | $J_{ph}=4.93 \text{ mA cm}^{-2}$ , $E_{on}=1.23 \text{ V}_{RHE}$    | 7    |

**Table S2.**  $V_{fb}$ ,  $N_D$ ,  $W_{SCL}$  of TiO<sub>2</sub> based photoanodes.

| Photoanode                                             | $V_{fb} / \text{V}_{RHE}$ | $N_D / \text{cm}^{-3}$ | $W_{SCL}@0.8 \text{ V}_{RHE} / \text{nm}$ |
|--------------------------------------------------------|---------------------------|------------------------|-------------------------------------------|
| TiO <sub>2</sub>                                       | 0.12                      | $2.63 \times 10^{17}$  | 169.10                                    |
| TiO <sub>2</sub> /Ni(OH) <sub>2</sub>                  | 0.2                       | $6.98 \times 10^{19}$  | 9.75                                      |
| TiO <sub>2</sub> /Ni <sup>0</sup> :Ni(OH) <sub>2</sub> | -0.16                     | $1.21 \times 10^{22}$  | 0.90                                      |

**Table S3.**  $R_s$ ,  $R_{bulk}$ ,  $CPE_{bulk}$ ,  $R_{ct}$ ,  $CPE_{trap}$  of TiO<sub>2</sub> based photoanodes.

| Photoanode | $R_s / \Omega$ | $R_{bulk} / \Omega$ | $CPE_{bulk} / \text{F}$ | $R_{ct} / \Omega$ | $CPE_{trap} / \text{F}$ |
|------------|----------------|---------------------|-------------------------|-------------------|-------------------------|
|------------|----------------|---------------------|-------------------------|-------------------|-------------------------|



|                                                        |       |         |                       |                      |                       |
|--------------------------------------------------------|-------|---------|-----------------------|----------------------|-----------------------|
| TiO <sub>2</sub>                                       | 25.03 | 113.40  | 7.10×10 <sup>-6</sup> | 1.18×10 <sup>4</sup> | 3.25×10 <sup>-5</sup> |
| TiO <sub>2</sub> /Ni(OH) <sub>2</sub>                  | 24.68 | 1447.00 | 3.79×10 <sup>-7</sup> | 1.09×10 <sup>4</sup> | 2.51×10 <sup>-6</sup> |
| TiO <sub>2</sub> /Ni <sup>0</sup> :Ni(OH) <sub>2</sub> | 25.24 | 104.80  | 6.24×10 <sup>-6</sup> | 0.87×10 <sup>4</sup> | 1.46×10 <sup>-5</sup> |

## References

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