Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information

Fabrication of $Ag/Ag_3PO_4/TiO_2$ heterostructure photoelectrodes for Efficient Decomposition of 2-chlorophenol Under Visible Light Irradiation

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Summary: This document contains 11 pages, including 1 table, 5 figures.

Table Captions:

Table S1. Experimental conditions for the preparation of samples.

Figure Captions:

Figure S1. Mott-Schottky (MS) plots of the different electrodes. The MS plots were obtained at a frequency of 1 kHz in an aqueous solution of Na_2SO_4 (0.01 M).

Figure S2. Top surface SEM view of the prepared $Ag/Ag_3PO_4/TiO_2$ NTs with different concentration of the $AgNO_3$ solution in water under ultrasonication, (a): 0.01 M (sample 1); (b): 0.03 M (sample 2); (c): 0.05 M (sample 3); (d): 0.1 M (sample 4).

Figure S3. I-V curves of the as-prepared $Ag/Ag_3PO_4/TiO_2$ NTs with different concentration of $AgNO_3$ under visible light irradiation.

Figure S4. Top surface SEM view of the prepared $Ag/Ag_3PO_4/TiO_2$ NTs with different cycles during impregnation procedure in 0.03 M $AgNO_3$ solution in water: (a) 5 cycles (sample 5), (b) 10 cycles (sample 2), (c) 15 cycles (sample 6).

Figure S5. I-V curves of the as-prepared $Ag/Ag_3PO_4/TiO_2$ NTs with different times of cycle under visible light irradiation.

Preparation of TiO_2 NTs Electrode

Titanium sheets (0.5 mm thick, 99.7% purity), hydrofluoric acid (48%), and ethyl alcohol (99.9%) were purchased from Aldrich Corp. (Milwaukee, WI). Prior to anodization, Ti samples (2×4 cm^2) were mechanically ground with emery papers, then degreased in an ultrasonic bath in anhydrous ethanol, and deionized (DI) water for 10 and 10 min, respectively. Then they were chemically etched by immersing them in a mixture of HF and HNO_3 acids (HF: HNO_3: H_2O) 1:4:5 in volume for 30 s, followed by rinsing with deionized water. The electrochemical anodization was carried out in a two-electrode electrochemical cell connected to a DC power supply. A Pt foil acted as a counter-electrode. The distance between the two electrodes was maintained at 2 cm. Ti samples were immersed in a 0.5 wt% HF electrolyte .The potential was initially ramped with a sweep rate of 0.5 V s^{-1} from 0 to 20 V and then kept constant for 30 min at room temperature (～25 ℃). After the electrochemical treatment the samples were rinsed with deionized water and dried in air. Subsequently, the resultant amorphous TiO_2 nanotubes were crystallized to anatase TiO_2 by annealing at 500 ℃ in oxygen ambient for 2 h with heating and cooling rates of 2 ℃ min^{-1}.

Activity Test

The $Ag/Ag_3PO_4/TiO_2$ NTs photoanode with an effective area of 4 cm^2

The electrochemical (EC) process of 2-CP was carried out in a round-bottom quartz reactor. All the experiments were performed with magnetic stirring, using 0.01 M Na_2SO_4 as the electrolyte. The initial concentration of the 2-CP aqueous solution was 20 mg L^{-1} during the experiment. Prior to the start of EC experiments, dark (adsorption) experiments were carried out for 30 min under continuous stirring until sufficient adsorption of the 2-CP onto the surface of the catalyst. The applied external potential was 0.6 vs SCE.

The photocatalytic (PC) process of 2-CP was carried out in a round-bottom quartz reactor. All the experiments were performed with magnetic stirring. The initial concentration of the 2-CP aqueous solution was 20 mg L^{-1} during the experiment. Prior to the start of light experiments, dark (adsorption) experiments were carried out for 30 min under continuous stirring until sufficient adsorption of the 2-CP onto the surface of the catalyst. The working electrode was irradiated by visible light (420 nm $< \lambda$) through a UV-cutoff filter from a high-pressure xenon short arc lamp (a Phillips 500 W Xe lamp).

The direct photolysis (DP) process of 2-CP was carried out in a round-bottom quartz reactor. The experiment was performed with magnetic stirring. The initial concentration of the 2-CP aqueous solution was 20 mg L^{-1} during the experiment. The light source was a high-pressure xenon short arc lamp (a Phillips 500 W Xe lamp) through a UV-cutoff filter.

Effect of the Concentration of $AgNO_3$ solution

Figure S2a shows the surface SEM images of the sample that the concentration of $AgNO_3$ solution is 0.01 M. It can be seen that just a few Ag nanoparticles have been deposited on the surface of the TiO_2 NTs. In addition, Figure S2b shows the surface SEM images of the sample 3 which the concentration of $AgNO_3$ solution is 0.03 M. It is clearly demonstrated that the deposition of Ag nanoparticles was successfully promoted. Figure S2c shows the surface SEM images of the sample that the concentration of $AgNO_3$ solution is 0.05 M. It can be seen that there are more Ag nanoparticles deposited on the surface of the TiO_2 NTs. Figure S1d shows that a thick layer of Ag nanoparticles covered the TiO_2 NTs that the concentration of $AgNO_3$ solution was 0.1 M (sample 5). Moreover, as shown in Figure S3, the photocurrent density is strongly dependent on the concentration of $AgNO_3$ solution. It can be seen that the photocurrent density of $Ag/Ag_3PO_4/TiO_2$ NTs increases with the concentration of $AgNO_3$ solution (from 0 to 0.03 M), but dramatically decreases when the concentration is further increased to 0.05 M and 0.1 M. Therefore, the maximum photocurrent density of the $Ag/Ag_3PO_4/TiO_2$ NTs could be observed when the concentration of $AgNO_3$ solution is 0.03 M. These results confirm that the quantity of the Ag/Ag_3PO_4 nanoparticles deposited on the surface of the TiO_2 NTs affect the photocurrent density of the electrode significantly.

Effect of the Repeating Cycles

Figure S4a shows the surface SEM images of the sample 6 where the number of repetitions is 5. It can be seen that just a few Ag nanoparticles have been deposited on the surface of the TiO_2 NTs. Figure S4b shows the surface SEM images of the sample 3 which the number of repetitions is 10. But the ordered structure of the TiO_2 NTs was not damaged during the deposition process. Additionally, Figure S4c shows the surface SEM images of the sample which the number of repetitions is 15. It can be clearly observed that the particles cover the top surface of the TiO_2 NTs significantly. The photocurrent density of the samples was displayed in Figure S4. The maximum photocurrent density of the $Ag/Ag_3PO_4/TiO_2$ NTs was obtained when the number of repetitions is 10. These results confirm that the quantity of the Ag/Ag_3PO_4 nanoparticles deposited on the surface of the TiO_2 NTs affect the photocurrent density of the electrode significantly.

Table S1

No.	**Electrode**	**Concentration of $AgNO_3$ (M)**	**Cycles (time)**
1	TiO_2 NTs	--	--
2	$Ag/Ag_3PO_4/TiO_2$ NTs	0.01	10
3	$Ag/Ag_3PO_4/TiO_2$ NTs	0.03	10
4	$Ag/Ag_3PO_4/TiO_2$ NTs	0.05	10
5	$Ag/Ag_3PO_4/TiO_2$ NTs	0.1	10
6	$Ag/Ag_3PO_4/TiO_2$ NTs	0.03	5
7	$Ag/Ag_3PO_4/TiO_2$ NTs	0.03	15

Figure S1.

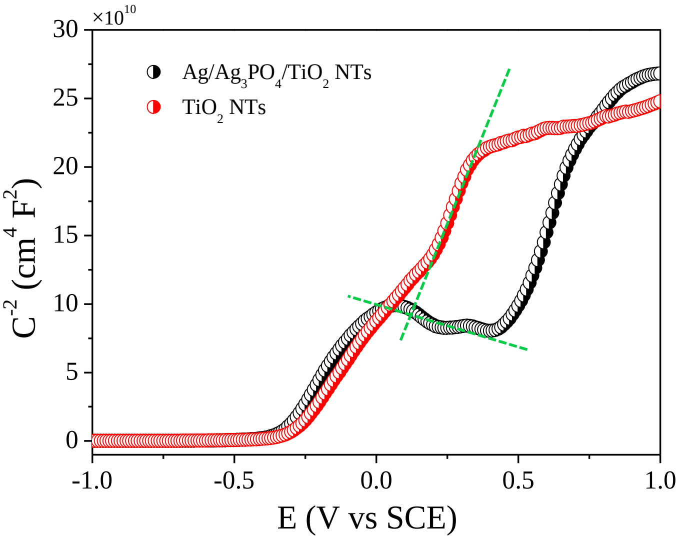

×10^10
30
25
20
15
10
5
0
C^-2 (cm^4 F^2)
-1.0
-0.5
0.0
0.5
1.0
E (V vs SCE)
Ag/Ag3PO4/TiO2 NTs
TiO2 NTs

Figure S2.

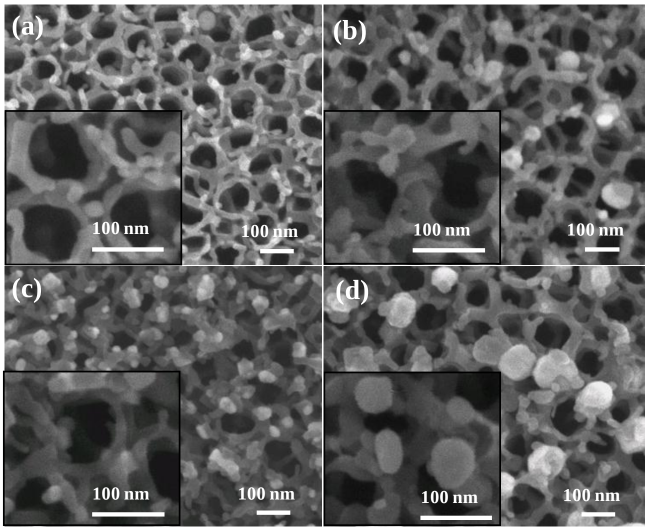


Figure S3.

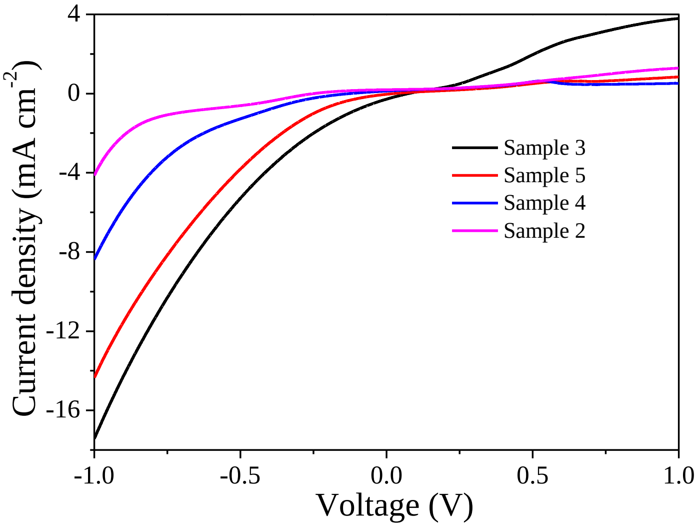

4
0
-4
-8
-12
-16
Current density (mA cm^{-2})
-1.0
-0.5
0.0
0.5
1.0
Voltage (V)
Sample 3
Sample 5
Sample 4
Sample 2

Figure S4.

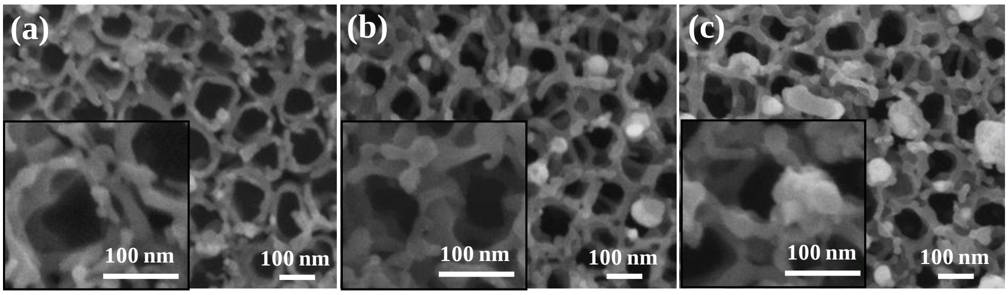
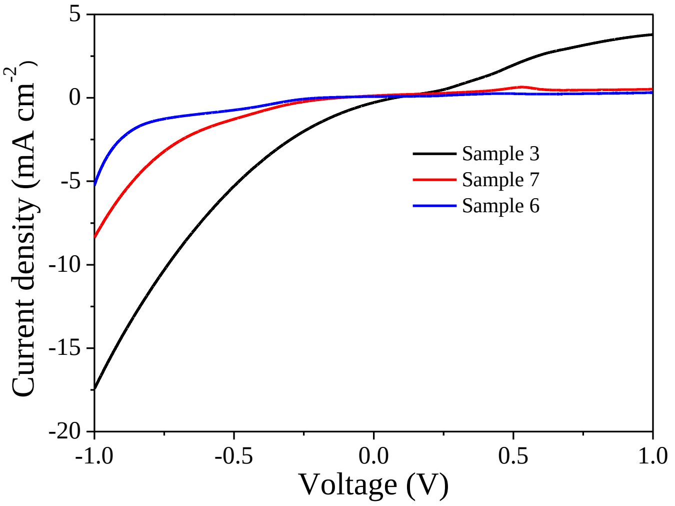


Figure S5.


5
0
-5
-10
-15
-20
Current density (mA cm^{-2})
-1.0
-0.5
0.0
0.5
1.0
Voltage (V)
Sample 3
Sample 7
Sample 6