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ORIGINAL ARTICLE

Enhancement. Photoelectrocatalytic Degradation. of All EDCs A. Peroxymonosulfate Activated by a $CO_3O_4/BiVO_4$ Composite Photoanode

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Abstract: A nanostructured $Co_3O_4/BiVO_4$Composite photoanode. synthesized using a facile electrospinning method, applied. photoelectrochemical(PEC)Degradation. of all EDCs(BPA). Assistance. peroxymonosulfate(PMS).REsults show, PMS obviously enhanced. photoelectrocatalytic degradation. BPA. $Co_3O_4/BiVO_4$Composite photoanode.When at 0. 25 V bias potential, Visible Light Irradiation. 2 mmol in L^{-1}PMS Addition96%. BPA. removed within 2 h, Corresponding Kinetic Constant. 0. 471 4 min^{-1}.. Effects. initial PMS concentration, bias potential. BPA degradation..REsults show, BPA could. efficiently degraded at lower PMS concentrations, lower bias Potentials.$SO^{In}{}_4^-$, In OH. identified as. primary free radicals using an electron spin resonance Spectrometer.Free Radical Quenching experiments. carried out, The photogenerated hole$SO^{In}{}_4^-$, In OH proved. responsible. BPA oxidation.There. no metal ion leaching detected. solution after. ReactionsWhich means. secondary pollution could. avoided.

KeyWords: $BiVO_4$;$CO_3O_4/BiVO_4$Photoanode;Photoelectrocatalytic;Peroxymonosulfate;Of all EDCs

Water in organic of pollutants has concentration high,Toxicity and can be biochemical of poor characteristics traditional of water treatment methods such as physical adsorption,Chemical oxidation and biological degradation and it is difficult to implement pollution water Of effective Purification.Photoelectric catalytic technology is a kind of biodegradable and remove the water in toxic organic pollutants of superior oxidation methods in recent years Increasingly get attention.It The photocatalytic oxidation and electrochemical oxidation method combined with to produce collaborative effect effective oxidation degradation pollutants at the same time overcome the powder light catalyst for follow-up separation of Problem[5].However because photoelectric catalytic reaction for multi-phase catalytic process its Mass Transfer Rate Limited,The activity free radical quantity low so its[67] Oxidation Removal Organic Pollutants efficiency to be further improve .

A sulfate (PMS)Can be activation sulfate radical have free radical $SO^{In}{}_4^-$)[8].Sulfate free radical has oxidation reduction potential high,PHApplicable range and wide advantages and can andH_2OOrOH$^-$Reaction Base oxidation phase combined with the Collaborative effect can efficient Catalytic Degradation Organic To improve system free radical content to effective improve organic pollutants of degradation efficiency.

$CO_3O_4/BiVO_4$Composite catalyst visible light response activity good and hasP-nHeterojunction photo electronic-Hole of separation efficiency than single

Before most$CO_3O_4/BiVO_4$Composite catalyst Degradation Organic Pollutants of Research Limited to powder catalyst of Photocatalytic Oxidation Process few will use it as a photoelectric very Catalytic Degradation Organic Matter of reports.This paper willCO_3O_4Nano-particles Dispersion in$BiVO_4$Precursor body in by electrostatic spinning legal system by$CO_3O_4/BiVO_4$Composite Electrode.The method is simple and easy repeatability strong.BisphenolA(Of all EDCs-BPA)Is a kind of frequent was detection to of Phenolic estrogen in Water Environment in residual and

Preparation$CO_3O_4/BiVO_4$Composite Electrode for light anode in PMSAuxiliary role under carry out the photoelectric Catalytic Degradation bisphenolAOf Study.

1. Material and Methods

1.1 Experimental Equipment and main drug

Rivers of cobalt nitrate [$CO(NO_3)_2$In 6 H_2O>98%],Five hydration bismuth nitrate($BiNO_3$In 5 H_2O>98%),Vanadyl acetylacetonate $C_{15}H_{21}O_6V$>98%)Were purchased in Japanese Tokyo into Industrial Co., Ltd..Ammonia (NH_3In H_2O),Anhydrous sodium sulfate (Na_2SO_4),. Potassium bisulfate ($Khso_5$),Concentrated sulfuric acid ($H_2SO_4$98%),Hydrogen Sodium oxide(NaOH),Tert-butyl alcohol($C_4H_{10}O$)And anhydrous ethanol C_2H_6O)Were purchased from Chinese medicine group chemical reagent limited the company;55-Dimethyl-1-Pyrrole Phenanthroline-N-Oxide (DMPO)Purchase self-Sigma Aldrich the company.The purchasing of reagent are pure "with before without further purification.FTOConductive Glass purchased in Shenzhen crystal Waite the company size10 cm × 2. 5 cm × 0. 2 cm.

Electrochemical workstation (CHI660EShanghai, lvcheng instrument limited the company)Xenon lamp light source (PLS-SXE300, Beijing, Park Philae Science and Technology Limited the company power500 WWith420 nmThe filter)Quartz Glass electrochemical reactor (Specifications5 cm × 5 cm × 6 cm)Magnetic stirrer (Germany IKA Instrument Equipment limited the company).Electrode of micro-morphology using field emission scanning electronic microscope(SEMSU-8020Japanese Hitachi the company)And transmission electronic microscope (TEMH-7500Japanese Hitachi the company)The Characterization crystal structure and functional groups respectivelyXRay diffraction (XRDX 'Pert PRO MPD.Netherlands PANalytical analysis instrument limited the company) Observation.

1.2 Experimental Methods

5 mLAmmonia (Quality score28%)In160Insulation5 H;After Will product washing,Dry muffle furnace in450Calcination3 H.

Certain quality the preparationCO_3O_4Nano-particles Dispersion mLAcetic acid in join270 mg $BiNO_3$In 5 H_2OAnd195 mgVanadyl acetylacetonate stirring uniform placed syringe in the electrostatic spinning.Will cleaning cleanFTOGlass placed receive Device.Spinning device as shown in Figure1Shown in.Spinning Conditions:Voltage7/VReceive Distance LengthReceive Temperature180Promote speed0. 01mm in S^{-1}.Spinning Silk after get load inFTOGlass of precursor body film will its placed muffle furnace in450Calcination3 HAfter get pure$BiVO_4$Electrode and 2 $CO_3O_4/BiVO_4$Composite Electrode(Below writingCO/BIV).$CO_3O_4/BiVO_4$Composite Electrode of micro-morphologySEM,HRTEM

Degradation experiment in Three-Level polar body in:To$CO_3O_4/BiVO_4$Composite Electrode as an anode platinum wire as an electrode saturated calomel electrode as an REFERENCE ELECTRODE.Will100 mlConcentration5 mg in L^{-1}Of bisphenolASolution join to quartz glass reactor in XELamp Light Source (λ>420 nm)Irradiation under the degradation experiment.In fixed time sampling0. 5 mLJoin0. 5 mLMethanol quenching agent using high performance liquid chromatography Concentration Analysis.

2. Results and discussion

2.1 $CO_3O_4/BiVO_4$Composite Electrode of Physical Chemical Characterization

TheSEMAndHRTEMObserve$CO_3O_4/BiVO_4$Composite Electrode of micro-morphology.From low powerSEM[Figure2(A)] In can see film continuous complete distribution uniform show that by electrostatic spinning method success InFTOGlass on the load.$CO_3O_4/BiVO_4$Composite Thin Film.By high SEM[Figure2(B)] The Thin Film Micro Structure for loose of nano-porous structure show that by electrostatic spinning method the preparation of electrode for Micro nano structure of Thin Film Electrode.HRTEM[Figure2(C)] Can Clear to observe the$CO_3O_4/BiVO_4$Composite Electrode of lattice striped which,0. 238 nmFor$BiVO_4$(2 1 1)CRYSTAL PLANE OF LATTICE SPACING,252 nmForCO_3O_4(2 2 2)Crystal plane of lattice spacing the results 8Of Li Jiang such:$CO_3O_4/BiVO_4$Composite anode activation. A sulfate strengthen photoelectric Catalytic Degradation bisphenolA 3715 Peak corresponding monoclinic phase$BiVO_4$Of (0 1 1),(1 2 1),(2 1 1)CRYSTAL PLANE.BecauseCO_3O_4Doped of low and dispersion high so The,$CO_3O_4/BiVO_4$Composite Electrode of visible light absorption threshold happened red mobile in visible light regional enhanced absorption attributedCO_3O_4Of CharacteristicsSPRAbsorption.CO_3O_4Can as an good of electronic receptor in photoelectric catalytic process in thereCO^2AndCO^3Of valence transformation; so more of photo electronic can fast$BiVO_4$Conduction band further improve photo electronic hole right of Separation Efficiency

2.2 Degradation of Bisphenol in different systems and different photoelectric ConditionsAEfficiency Comparison

4.Bisphenol A in different systemsADegradation effect.By
Figure shows, do not joinPMSTime,$Bivo_4$.Electrode andCO_3O_4./$Bivo_4$.Composite Electrode in2
hNaypyidawADegradation efficiency
13%And19%;When joiningPMSTime,$Bivo_4$.Electrode and
CO_3O_4./$Bivo_4$.Composite Electrode in2 hNaypyidawADegradation efficiency increased49%And96%.The results show that in the photoelectric catalytic system,PMSThe addition of bisphenolADegradation efficiency; meanwhile,CO_3O_4./$Bivo_4$.The degradation efficiency of composite electrode was significantly better than that $Bivo_4$.Electrode, descriptionCO_3O_4./$Bivo_4$.Composite electrode activationPMS
Than alone.$Bivo_4$.This further indicates that the composite electrode has a higher carrier migration efficiency..

5.Given the different photoelectric ConditionsCO_3O_4./$Bivo_4$.Composite electrode activationPMSDegradation of bisphenolAEffect.From the figure, in2.

Solution Organic Pollutants.In ontology systemCO_3O_4In Electrode in content very low (Quality score0. 02%)And uniform distribution in electrode body phase and Surface.So separateCO_3O_4ActivationPMSAbility Limited.In addition separate electrocatalytic process in electric oxidation can remove a small amount bisphenolA[19].When separate and light when bisphenolAOf degradation main attributedCO_3O_4/$BiVO_4$Composite Electrode of photocatalytic role.At the same time photoelectric body
Department of under bisphenolAThe degradation efficiency greater than separate Photocatalytic and separate electric oxidation sum show that the system light electrocatalytic has collaborative role.

2.3 Influence Factors

6(A)ForPMSConcentration2 mmol in L^{-1}Visible Light (λ
420 nm)Irradiation under plus bias of bisphenolAThe degradation effect.
It's concluded that when plus bias respectively0,0. 25,0. 5And1. 0
V When bisphenolAIn2 hIn the degradation efficiency respectively55%,
96%,98%And71%.When electrode applying a lower bias (0. 25
Or0. 5 V)When bisphenolAThe degradation efficiency significantly up shows that
Applying a lower bias can be significantly increaseCO_3O_4/$BiVO_4$Composite Electrode of photo electronic-Hole Separation Efficiency.When the bias voltage is high when(1 V)BisphenolAThe degradation efficiency has decreased this is due to bias. High lead to electrode damage electrode integrity Influence
CO_3O_4/$BiVO_4$Catalytic Activity of Composite Electrode.In addition, bisphenolADegradation efficiency in0. 25 VWith0. 5 VDegradation efficiency, and the lower the voltage, the lower the energy consumption,0. 25 VFor the optimal bias voltage of the system.

5 mg · L^{-1}.Double PhenolAAs the target pollutant,CO_3O_4./$Bivo_4$.Composite Electrode Area13 cm^{2}, Electrode LoadCO_3O_4./$Bivo_4$.Composite catalyst content is6 mg, Pollutant solution volume is
100, Systematic study ofPMSAdded amountCO_3O_4./$Bivo_4$.
Photocatalytic Degradation of bisphenol with Composite ElectrodeAPerformance impact.As shown in Fig.6.
B)As shown when the system is not joinedPMSBisphenolAIn2 hOf
Removal rate is16%;WhenPMSAdded amount is0. 5,1. 0And2. 0 mmol · L^{-1}.BisphenolAIn2 hThe removal rate99%, 100%And96%.Visible,PMSWithCO_3O_4./$Bivo_4$.The composite electrode has a synergistic effect under photoelectricPMSSignificant increase in bisphenolAPhotoelectric Catalytic Degradation efficiency.When the system is not joinedPMSDue to the low amount of catalyst
0. 06g · L^{-1}.)And therefore, aloneCO_3O_4./$Bivo_4$.Photoelectric degradation of bisphenol with Composite ElectrodeALimited effect.When the system joinsPMSTime, light
Raw electrons can be activatedPMSProduction$So^{\cdot}_4^{-}$,$So^{\cdot}_4^{-}$Can be converted· OHSo in the system$So^{\cdot}_4^{-}$And· OHCan significantly improve the bisphenolAOf

2.4 Activity Species Identification Analysis

The electronic spin resonance spectroscopy instrument (ESR)ToDMPOFor
Free Radical capture agent the system of free radical the determination.As shown in figure7/Shown in visible light irradiation under separatePMSOf signal very weak show that separatePMSIn visible light irradiation under it is difficult to produce free radical;SeparateCO_3O_4/$BiVO_4$Composite Electrode Photoelectric System not joinPMSWhen,ESRSpectrum shown in not observe the to free radical signal show that at this time system in almost did not produce free radical;WhenCO_3O_4/$BiVO_4$Composite Electrode Photoelectric System in joinPMSWhen can at the same time observe the$SO^{In\ \cdot}_4^{-}$(Black Diamond dimension)AndIn OH(White triangle dimension)Two free radicals andIn OHFree Radical signal is strong show that in the system in,PMSWas activation produce$SO^{In\ \cdot}_4^{-}$.In addition according to reported,$SO^{In\ \cdot}_4^{-}$Can andH_2OReaction generatedIn OH. So Optical System in joinPMSWhen,In OHSignal High Strength in separate photoelectric Catalytic System.

In order to further explore the reaction mechanism on reaction system the quenching experimental.Methanol (MeOH)For QuenchingIn OH[K = 9. 7/×2NaAnd benzoquinone (P-BQ)As an hole (H_{VB}^{+})And oxide self-ADegradation of suppression performance followEDTA-2Na>TBA>MeOH>P-BQOf Order show thatH_{VB}^{+},$SO^{In\ \cdot}_4^{-}$AndIn OHThe double
AOf degradation the main role.Which$O^{In\ \cdot}_2^{-}$Of role limited and$SO^{In\ \cdot}_4^{-}$,In OHAndH_{VB}^{+}Is System in main of oxide.

3. Conclusion

By electrostatic spinning legal system by$CO_3O_4/BiVO_4$Composite Film Electrode the preparation methods simple made thin film electrode uniform complete will use it as light anode inPMSAuxiliary under on water double

OfAPollutants has efficient degradation Performance.When plus bias

25 VVisible Light(λ>420 nm)Irradiation under plus2 mmol in L^{-1}PMSWhen bisphenolAIn2 hIn the removal efficiency 96%.ESRShow that the system in main activity species$SO^{In}{}_4^-$AndIn OHTwo free radicals.In addition, the system has is high stability no metal ion dissolution avoid the secondary pollution.

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