Ag@AgCl修饰的锐钛矿相 TiO₂ 纳米管的制备及其光催化性能

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摘要: 首先采用水热合成法和双氧水处理制备了具有锐钛矿相的 TiO₂ 纳米管, 然后通过沉淀和光化学反应将 Ag@AgCl 纳米粒子负载于其上, 从而制得 TiO₂ 纳米管负载的表面等离子体光催化剂. 结果表明, 经 Ag@AgCl 纳米粒子修饰后, 锐钛矿相 TiO₂ 纳米管因表面等离子共振效应而对可见光具有明显的响应, 光生电子-空穴对更容易分离, 因而 TiO₂ 纳米管的可见光催化活性提高. 该催化剂对亚甲基蓝分子具有很强的吸附能力, 可见光下照射 1 h 后即可完全降解脱色. 另外, 该光催化剂重复使用 5 次后, 亚甲基蓝脱色率仍保持在 90% 以上.

关键词: 银; 氯化银; 二氧化钛; 纳米管; 表面等离子共振; 可见光响应; 光催化; 亚甲基蓝

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Preparation and Photocatalytic Activity of Ag@AgCl Modified Anatase TiO₂ Nanotubes

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Abstract: The combination of TiO₂ nanotubes and a surface plasmon resonance (SPR) photocatalyst used their large adsorption capacity and wide visible light response, respectively, and a synergistic effect to enhance photocatalytic activity under visible light irradiation. Anatase TiO₂ nanotubes were prepared by hydrothermal synthesis, a hydrogen peroxide treatment, and calcination at 400 °C. AgCl nanoparticles were then loaded onto the TiO₂ nanotubes by a precipitation reaction, and some of the AgCl particles were reduced to Ag particles under halogen tungsten lamp irradiation. This gave a visible light SPR photocatalyst of Ag@AgCl/TiO₂ nanotubes that exhibited high photocatalytic activity, which was due to its large adsorption capacity, wide visible light response due to the SPR effect, fast separation of photogenerated electron-hole pairs, and strong oxidizing ability of Cl⁰ generated by combining Cl⁻ ions with photoexcited holes. Methylene blue dye was thoroughly decolorized within 1 h in the presence of this photocatalyst under visible light irradiation. In addition, the photocatalyst was stable after recycling the photocatalytic reaction five times.

Key words: silver; silver chloride; titanium dioxide; nanotube; surface plasmon resonance; visible light activation; photocatalysis; methylene blue

TiO₂ 是一种常用的光催化剂, 具有催化活性高、化学和光稳定性好、安全无毒和廉价易得等优点, 因而广泛用于有机污染物降解、消毒灭菌和自清洁等领域. 但是, 作为一种 n 型半导体, TiO₂ 能带隙较宽, 使其只能被仅占太阳光 3%~5% 的紫外光所激发, 因而大大限制了 TiO₂ 光催化技术的实际应用. 为了将 TiO₂ 光响应范围扩展至可见光区, 人们对其

进行了各种改性和修饰, 如贵金属沉积、半导体复合、离子掺杂、光敏化以及表面还原处理等. 同时, TiO₂ 纳米管具有比其纳米粉体更大的比表面积, 更强的吸附能力和表面活性, 因此可望显著增强 TiO₂ 的光催化性能. 自 TiO₂ 纳米管被 Kasuga 等^[1]采用水热法合成以来, 它被广泛用于光催化领域, 并通过掺杂或负载其他离子^[2,3]和半导体量子点^[4,5]等方法

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来进一步提高 TiO₂ 纳米管的光催化活性。

近年来, 贵金属纳米粒子因具有表面等离子共振效应而成为研究热点。一些等离子体体系被应用到光催化降解有机染料等领域, 其中以 Ag 及 Ag 与卤化银复合纳米粒子为等离子体光催化剂的研究相对较多。Wang 等^[6]以 AgMoO₄ 和 HCl 为原料, 采用离子交换和光致还原法合成了不同形状的 Ag@AgCl 等离子体光催化剂。作者认为, Ag@AgCl 共振体中的 Ag 粒子强烈吸收可见光, 阻止了光生电子与 Ag⁺的结合, 同时 Cl⁻与光生空穴结合形成具有强氧化性的 Cl⁰ 自由基。人们进一步将等离子体负载在 TiO₂ 上以促进光生电子-空穴对的分离, 将 TiO₂ 的光响应范围扩大到可见光区。Hu 等^[7]以十六烷基甲基溴化铵 (CTAB), P25 (TiO₂, Degussa) 和 AgNO₃ 为原料, 采用浸渍法制备了 Ag@AgBr/TiO₂ 可见光催化剂, 用来降解偶氮染料和破坏细菌。在碱性条件下, CTAB 可吸附到 TiO₂ 表面上, 使得 AgBr 分布均匀。循环使用 5 次后, 样品催化效果依然良好, 说明其光稳定性很好。Li 等^[8]用 LiI, AgNO₃ 和钛酸四丁酯为原料制得具有核/壳纳米结构的 AgI/TiO₂ 可见光催化剂。在该催化剂的作用下, 结晶紫在可见光照射 120 min 后完全脱色。Yu 等^[9]通过钛片的阳极氧化生成多形貌的 TiO₂ 纳米管阵列, 再将 AgCl 负载于其上, 最后通过光照将 AgCl 中的一部分 Ag⁺还原成 Ag⁰, 得到了负载 Ag@AgCl 等离子体的 TiO₂ 纳米管阵列。AgCl 本身的光响应范围在紫外区, 然而获得一个光子后, 激发的电子与 AgCl 中的 Ag⁺结合形成 Ag⁰, 形成的 Ag 纳米簇由于表面等离子共振效应可使 AgCl 的光响应范围扩大到可见光区。尽管有关 TiO₂ 纳米管和银/卤化银等离子体光催化剂的研究较多^[10~18], 但关于具有锐钛矿型 TiO₂ 纳米管的合成鲜见报道, 而通常锐钛矿相 TiO₂ 光催化活性比其它晶相的高。将 Ag@AgCl 等离子体与锐钛矿相 TiO₂ 纳米管复合后, 可以充分发挥锐钛矿相 TiO₂ 纳米管的光催化性能, 以及 Ag@AgCl 表面等离子体的可见光响应和光生激子的分离能力, 从而进一步提高该类光催化剂活性。

本文首先采用水热合成法和双氧水处理制得具有锐钛矿相的 TiO₂ 纳米管 (TiO₂-NTs), 再以 AgNO₃ 和 HCl 通过沉淀反应和光还原法得到 Ag@AgCl/TiO₂-NTs 等离子体光催化剂, 采用 X 射

线衍射 (XRD)、透射电镜 (TEM) 等技术对样品进行了表征, 并考察在可见光下样品光催化降解亚甲基蓝 (MB) 的性能。

1 实验部分

1.1 催化剂的制备

称取 2 g TiO₂ 粉末 (Degussa P25), 与 70 ml 10 mol/L 的 NaOH 溶液 (96%, AR, 上海试剂四厂) 混合, 在室温搅拌 10 min 后, 倒入高压水热釜中, 密封。在 150 °C 水热反应 24 h 后, 自然冷却至室温。过滤后, 用去离子水和 0.1 mol/L HCl 溶液 (36%, AR, 上海试剂四厂) 冲洗。然后将粉末与 0.1 mol/L HCl 溶液混合, 在室温搅拌 10 h 后, 过滤, 用水洗涤。重复该过程一次后, 用去离子水洗至 pH = 6.8, 再与 20% H₂O₂ 溶液 (30%, AR, 上海桃浦化工厂) 混合后在 40 °C 回流 4 h, 得到的粉末于 90 °C 干燥 14 h, 再在马弗炉中以 1 °C/min 升至 400 °C, 保温 2 h, 最后以同样速度降至室温, 即得具有锐钛矿相的 TiO₂-NTs。

称取 1 g 制得的 TiO₂-NTs 倒入烧杯中, 加去离子水于室温超声 10 min 后, 再加入 10 ml 0.1 mol/L AgNO₃ 溶液 (99.9%, AR, 上海尚思精细化工厂), 超声 10 min 后于室温搅拌 20 min, 加入 10 ml 0.1 mol/L HCl 溶液后超声 10 min, 室温搅拌 20 min, 过滤。用去离子水洗净, 得到的粉末于 100 °C 干燥 10 h 后, 在卤钨灯 (220 V, 500 W, 广东佛山照明) 下照射 20 min, 使生成的 AgCl 中部分 Ag⁺在光照下还原成 Ag⁰, 得到 TiO₂-NTs 负载 Ag@AgCl 纳米粒子的表面等离子体光催化剂 Ag@AgCl/TiO₂-NTs。

1.2 催化剂的表征

样品的 XRD 测试在日本 Rigaku D/Max-RB 型 X 射线衍射仪上进行, Cu 靶, K_α 辐射, Ni 片滤波, 管电压 40 kV, 管电流 40 mA, 扫描范围 2θ = 10°~80°。采用法国 HORIBA Jobin Yvon 公司 LabRam-1B 型拉曼光谱仪测定固体样品的拉曼光谱 (Raman), 激发光源为氦氖激光器, 波长 632.8 nm, 激发功率 6 mW。采用日本 Shimadzu UV-2450 型紫外可见分光光度计进行固体紫外可见光谱 (UV-Vis) 分析。采用美国 Nicolet 公司 Nexus 870 型红外光谱仪测定样品的红外光谱 (FT-IR), 制样采用 KBr 压片法, 扫描范围 400~4000 cm⁻¹。利用日本 JEOL JEM-100C

II 型 TEM 观察材料形貌.

1.3 催化剂的评价

称取 0.1 g $\text{Ag@AgCl/TiO}_2\text{-NTs}$ 粉末, 放入装有 100 ml 10 mg/L MB 溶液的带冷凝水夹层的玻璃容器内. 将反应器置于搅拌器上, 开动搅拌器, 通冷凝水. 将 500 W 卤钨灯置于反应容器上方约 25 cm 处, 在反应器上方 2~3 cm 处放置日本 Kenko L41 滤光镜 (滤去 410 nm 以下的光), 以确保通过的光为可见光. 先在暗处搅拌 60 min 以使反应体系达到吸附-脱附平衡, 保证染料在催化剂表面被充分吸附, 然后开始光照, 每隔一定时间取混合液 5 ml. 将所取混合液离心分离, 测定上层清液吸光度以确定 MB 的脱色率.

2 结果与讨论

2.1 锐钛矿相的 $\text{TiO}_2\text{-NTs}$ 的形成

图 1 为 $\text{TiO}_2\text{-NTs}$ 的 TEM 照片. 可以看出, 所得样品形状规则, 中空, 末端开口, 管径较大, 管壁较厚, 外径约 10 nm, 内径约 7 nm, 长度几十到上百纳米. 这样的中空管状结构比表面积大, 有利于吸附其他粒径更小的有机及无机纳米粒子, 为负载卤化银等离子体提供了较好的载体平台, 同时也有利于光催化过程中光生载流子的传输.

图 2 为 $\text{TiO}_2\text{-NTs}$ 的 XRD 谱. 可以看出, 样品

图 1 $\text{TiO}_2\text{-NTs}$ 的 TEM 照片

Fig. 1. TEM images of anatase TiO_2 nanotubes ($\text{TiO}_2\text{-NTs}$).

图 2 TiO_2 纳米管及负载 Ag@AgCl 后的 XRD 谱

Fig. 2. XRD patterns of $\text{TiO}_2\text{-NTs}$ (1) and $\text{Ag@AgCl/TiO}_2\text{-NTs}$ (2).

晶相为锐钛矿相 (JCPDS 21-1272), 其中位于 $2\theta = 25.3^\circ$ 处衍射峰最强, 归属于锐钛矿相 (101) 晶面衍射, 峰形尖锐, 说明样品晶型完整. 另外, 样品中未出现相关 Na 化合物或其他物种晶相, 说明所得 $\text{TiO}_2\text{-NTs}$ 样品较纯.

研究表明^[11,19-22], 在水热条件下, TiO_2 纳米管的形成主要分为剥落和卷曲两个过程. 在强碱 NaOH 的作用下, TiO_2 中 Ti-O 键断裂, 形成层状碎片^[19,20], 这是纳米管形成的中间态, 该预处理过程对最终纳米管的化学组成及晶体结构的影响非常大. 层状碎片的主要成分是水合钛酸钠, 在酸洗过程中发生 H^+ 与 Na^+ 之间的交换而得到水合钛酸, 同时, 多层的钛酸钠进一步剥落成为薄层的钛酸钠, 后者再进一步卷曲形成纳米管. 酸洗所用的盐酸浓度不宜太高, 否则易使形成的纳米管变形. 当盐酸浓度大于 0.2 mol/L 时, 纳米管孔径会随着盐酸浓度变大而变小^[19]. 溶液 pH 值对纳米管的最终形成影响也很大, pH 过大时不会卷曲形成纳米管, 在 $\text{pH} < 2$ 或 $\text{pH} \approx 7$ 时都可得到纳米管, 但当 $\text{pH} < 2$ 时, 所得纳米管管壁上存在较多缺陷, 在 $\text{pH} \approx 7$ 时得到的纳米管则更为完整^[20], 所以本文在 $\text{pH} = 6.8$ 下进行相关实验.

在较高 pH 值条件下, 纳米管主要组成是钛酸钠或水合钛酸, 如 $\text{H}_2\text{Ti}_3\text{O}_7$ ^[21,22], $\text{A}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ ^[23,24], $\text{A}_2\text{Ti}_4\text{O}_9 \cdot \text{H}_2\text{O}$ ^[25] (其中 A 为 Na 或 H). 从纳米管的形成机理看, TiO_2 中 Ti-O-Ti 键在 NaOH 的作用下断裂形成 Ti-O-Na 键和 Ti-OH 键^[1], 所以经过酸洗后最终会形成钛酸钠或水合钛酸. 当溶液 pH 值较小时, Ti-O-Na 键中的 Na 则可通过酸洗和水洗过程除掉. 而当溶液 pH 值较高时, 酸洗不充分, 得到的

纳米管中还会残余 Na. 而实验发现, 残余的 Na 很难全部被 H⁺ 置换出来, 因此本文采用 H₂O₂ 处理法以除去残余 Na^[26]. 同时, 在纳米管形成过程中, 其晶面被强碱破坏而留下氧空位, 但经 H₂O₂ 处理而得以修补, 同时激活 TiO₂ 纳米管中的晶格氧^[26]. 样品再经 400 °C 煅烧 2 h, 即可得到具有良好锐钛矿晶型的 TiO₂-NTs. 若煅烧温度太高, 会导致样品晶相由锐钛矿相转变为金红石相, 且破坏纳米管结构^[19]. 结果表明, 与未使用 H₂O₂ 处理的 TiO₂-NTs 样品相比, 经 H₂O₂ 处理过而得到的 TiO₂-NTs 内部变化更小, 所以在化学环境下其表面更稳定, 得到的 TiO₂-NTs 更有规律性, 结晶度更高.

2.2 Ag@AgCl/TiO₂-NTs 的形貌和结构

为了将 Ag@AgCl 纳米粒子负载到 TiO₂-NTs 上, 本文首先将自制的 TiO₂-NTs 与 AgNO₃ 溶液在常温下超声混合, 使 TiO₂-NTs 充分吸附 Ag⁺, 然后用 HCl 溶液处理, 使吸附的 Cl⁻ 与吸附的 Ag⁺ 结合形成 AgCl 而负载于 TiO₂-NTs 上. 在卤钨灯照射下, 吸附在样品中的 AgCl 发生光还原反应而部分生成 Ag⁰, 从而得到 Ag@AgCl/TiO₂-NTs.

图 3 为 Ag@AgCl/TiO₂-NTs 的 TEM 照片. 与 TiO₂-NTs 相比, 负载后样品形状没有发生明显的变化, 说明 Ag@AgCl 的负载对 TiO₂-NTs 结构影响不

图 3 Ag@AgCl/TiO₂-NTs 的 TEM 照片

Fig. 3. TEM images of Ag@AgCl/TiO₂-NTs.

大. 由图可清晰地观察到一些椭圆或圆形的 Ag@AgCl 纳米粒子负载在纳米管的内外表面上. AgCl 纳米粒子粒径在 5 nm 左右, 生成的 Ag 原子则聚积形成纳米晶而沉积在 AgCl 粒子表面上^[9].

由图 2 可见, 负载 Ag@AgCl 后, TiO₂-NTs 的锐钛矿晶相并未改变, 但特征衍射峰变得更加尖锐, 说明其结晶度增加. 这可能与修饰 Ag@AgCl 时的一系列处理过程有关. 另外, Ag@AgCl/TiO₂-NTs 样品中还出现 AgCl 特征峰 (JCPDS 31-1238), 但未见 Ag 衍射峰, 说明生成的 Ag 粒径太小或无定形.

图 4 为 TiO₂-NTs 负载 Ag@AgCl 前后的 Raman 光谱. 可以看出, 负载 Ag@AgCl 后, TiO₂-NTs 的 Raman 振动峰有所位移, 且谱峰变得更宽. 这是由于 Ag@AgCl 粒子的负载使 TiO₂ 晶格产生畸变和缺陷所致. 锐钛矿相 TiO₂ 属于 D_{4h} 点群, 分别在 147, 198, 398, 515 和 637 cm⁻¹ 处有 5 个 Raman 活性振动峰. 负载 Ag@AgCl 后, 样品虽然也出现这几个振动峰, 但还在 245, 830 和 1 120 cm⁻¹ 处出现新的峰, 这是由于 Ag 等离子体的共振效应所致, 表明体系中存在 Ag 纳米粒子.

图 4 TiO₂-NTs 和 Ag@AgCl/TiO₂-NTs 的 Raman 光谱

Fig. 4. Raman spectra of TiO₂-NTs (1) and Ag@AgCl/TiO₂-NTs (2).

图 5 为 Ag@AgCl/TiO₂-NTs 的 UV-Vis 光谱. 可以看出, 与 TiO₂ 原料和 TiO₂-NTs 相比, Ag@AgCl/TiO₂-NTs 不仅在 400 nm 以下有吸收, 而且在可见光区 550~750 nm 也有比较强的吸收. 这是由于 Ag 纳米粒子的等离子共振效应而产生的共振吸收带^[27]. 锐钛矿相 TiO₂ 能带隙为 3.2 eV, AgCl 间接能带隙为 3.25 eV, 两者都只在紫外光区有吸收, 但负载 Ag@AgCl 等离子体后, 由于等离子共振效

图 5 P25, TiO_2 -NTs 和 Ag@AgCl/TiO_2 -NTs 的 UV-Vis 谱
Fig. 5. UV-Vis spectra of P25 (1), TiO_2 -NTs (2), and Ag@AgCl/TiO_2 -NTs (3).

应使得 TiO_2 的光响应范围扩大到可见光区域,从而有利于提高 TiO_2 -NTs 在可见光下的光催化活性.

2.3 Ag@AgCl/TiO_2 NT 的可见光催化性能

图 6 为 Ag@AgCl/TiO_2 -NTs 光催化降解 10 mg/L MB 水溶液的反应结果. 为了比较,在相同实验条件下还进行了 P25 和 TiO_2 -NTs 光催化实验. 可以看出,在 60 min 的暗反应阶段, P25 几乎不吸附 MB, 而 TiO_2 -NTs 吸附染料后, MB 溶液浓度下降了 25%. 负载 Ag@AgCl 后, TiO_2 -NTs 的吸附能力进一步增强, 暗反应 30 min 后, MB 浓度就下降了 65%. 可见, Ag@AgCl/TiO_2 -NTs 样品的吸附能力更强. 在可见光照射阶段, P25 仍无降解 MB 活性,

图 6 Ag@AgCl/TiO_2 -NTs 对亚甲基蓝的光催化降解脱色曲线

Fig. 6. Photocatalytic decolorization of methylene blue (MB) under visible light over different samples. (1) P25; (2) TiO_2 -NTs; (3) Ag@AgCl/TiO_2 -NTs. c_0 is the initial concentration of the dye, and c is the concentration of the dye at time t . Reaction conditions: photocatalyst 0.1 g, 100 ml 10 mg/L MB aqueous solution.

TiO_2 -NTs 虽然使 MB 浓度有所下降, 但光照 60 min 后, TiO_2 -NTs 仍为蓝色, 而没有恢复到原来的白色, 说明它对 MB 仅起吸附作用, 而没有光催化降解作用. 而 Ag@AgCl/TiO_2 -NTs 在光照 30 min 后, MB 溶液基本变成无色, 且光催化剂恢复至原来的灰白色. 这说明 Ag@AgCl/TiO_2 -NTs 对 MB 分子不仅有吸附作用, 而且有光催化脱色效果.

负载 Ag@AgCl 等离子体后, 由于 Ag 纳米粒子的表面等离子共振效应, 使得 TiO_2 -NTs 光响应范围扩大到可见光区域. 在可见光照射下, 在 Ag 纳米粒子上形成光生电子-空穴对, 产生的光生电子跃迁到 TiO_2 导带上^[28], 导致光生电子和空穴有效地分离. 光生电子转移到吸附在催化剂表面上的 O_2 分子上形成 $\cdot\text{O}_2^-$, 还可以进一步形成 $\cdot\text{OH}$. 吸附在催化剂表面上的 MB 分子被这些活性物质氧化降解脱色. 光生空穴则直接将吸附在 Ag 纳米粒子表面上的 MB 分子氧化分解. 同时, 光生空穴也可能与存在于 AgCl 中的 Cl^- 结合形成 Cl^0 自由基^[12], 后者是一个很强的氧化剂, 可氧化分解 MB 分子, 再生成 Cl^- , 这样的循环过程使得催化剂能够稳定存在.

能够满足实际应用的光催化剂不仅需要高的光催化活性, 还必须要有高的光热稳定性. 图 7 为 Ag@AgCl/TiO_2 -NTs 循环使用 5 次的反应结果. 可以看出, Ag@AgCl/TiO_2 -NTs 循环使用 5 次后, 虽然吸附能力有所下降, 但光催化活性变化不大, 对 MB 脱色效果影响很小. 经 5 次使用后, MB 降解脱色率仍能保持在 90%, 说明样品稳定性较好.

图 7 Ag@AgCl/TiO_2 -NTs 的循环使用降解 MB 反应结果
Fig. 7. Photocatalytic decolorization of MB under visible light in the presence of Ag@AgCl/TiO_2 -NTs recycled five times. Reaction condition: photocatalyst 0.1 g, 100 ml 10 mg/L MB aqueous solution.

3 结论

合成了锐钛矿相 TiO₂ 纳米管负载 Ag@AgCl 等离子体光催化剂. 它对 MB 分子具有很强的吸附能力和光催化降解脱色作用, 在可见光照射 60 min 内可完全脱色, 且光催化剂恢复至原来状态. 充分利用纳米管的强吸附能力, 金属纳米粒子的表面等离子共振效应, 以及两者之间的协同作用, 可以大大提高催化剂在可见光下的光催化活性. 由于金属纳米粒子的表面等离子共振效应取决于纳米粒子的种类、大小和形状, 因此, 如果在 TiO₂ 纳米管上负载不同的金属纳米粒子, 有望能进一步增强光催化剂对可见光甚至红外光的吸收, 从而提高光催化剂对太阳光的利用率, 增强其光催化活性.

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英 译 文

English Text

TiO₂ is widely employed as a photocatalyst in the degradation of organic contaminants, disinfection, sterilization, self-cleaning, and other fields due to its high catalytic activity, good chemical stability, non-toxicity, low cost, and abundance. However, TiO₂ is an n-type semiconductor with a wide band gap (3.2 eV for anatase and 3.0 eV for rutile) that can be only excited by ultraviolet light, which is only 3%–5% of solar irradiation. This greatly limits TiO₂ photocatalytic technology in practical applications. In order to extend the optical response of TiO₂ to the visible light region, various approaches have been used to modify TiO₂, including noble metal deposition, semiconductor compositing, ion doping, photosensitization, and surface reduction treatment. TiO₂ nanotubes have a larger surface area, larger adsorption capacity, and surface activity than their nanoparticles, thus it is expected they will have significantly better photocatalytic efficiency. Since TiO₂ nanotubes were synthesized by the hydrothermal method in 1998 [1], they have been widely used in photocatalysis. The photocatalytic activity can be further improved by ion doping [2,3], photosensitization with semiconductor quantum dots [4,5], and other methods.

In recent years, nanoparticles of noble metals such as gold

and silver have become a hot research topic because of their unique optical properties that arise from the localized surface plasmon resonance (SPR) effect. SPR in gold and silver nanoparticles results in strong surface plasmon absorption bands, usually in the visible region, and has been exploited to develop visible light plasmonic photocatalysts. Among these photocatalysts, silver and silver/silver halide coupled systems have been widely investigated. For example, Wang et al. [6] prepared a plasmonic photocatalyst of Ag@AgCl by treating Ag_2MoO_4 with HCl to form AgCl, and subsequently reducing some Ag^+ ions to form Ag nanoparticles on the AgCl surface. They proposed that Ag nanoparticles were photoexcited by the SPR effect under visible light irradiation. The photoexcited electrons were then trapped by the Ag nanoparticles, which reduced the probability of electron-hole recombination. At the same time, the holes migrated to the AgCl surface and reacted with Cl^- ions adsorbed there to form Cl^0 radicals. These plasmonic photocatalysts have been further loaded onto TiO_2 to extend the optical response of TiO_2 to the visible region, and reduce electron-hole recombination by taking advantage of the SPR and synergistic effects. Hu et al. [7] prepared a visible light photocatalyst of Ag@AgBr/ TiO_2 using the deposition-precipitation method, with cetyltrimethylammonium bromide (CTAB), Degussa P25, and AgNO_3 as raw materials, for the photodegradation of azo dyes and inactivation of *E. coli*. Under alkaline conditions, CTAB can be adsorbed on the surface of TiO_2 to limit the number of nucleation sites for AgBr, to result in a homogeneous dispersion of AgBr. Li et al. [8] prepared a visible light photocatalyst of core/shell structured AgI/ TiO_2 with AgNO_3 , LiI, and $\text{Ti}(\text{O}i\text{Bu})_4$ as raw materials. This photocatalyst exhibited very high photocatalytic activity for the photodegradation of crystal violet and 4-chlorophenol under visible light irradiation. A visible light plasmonic photocatalyst of Ag@AgCl/ TiO_2 nanotube arrays was first prepared by Yu et al [9]. The self-organized TiO_2 nanotubes were grown by the anodic oxidation of Ti foils, and then AgCl nanoparticles were deposited onto the self-organized TiO_2 nanotubes. Finally, part of the oxidized Ag^+ ions were reduced to Ag^0 nanoparticles on the surface of AgCl. This photocatalyst exhibited a high photocatalytic activity and good stability under visible light irradiation due to SPR absorption by Ag nanoparticles and the efficient charge separation at the Ag nanoparticles. Although many plasmonic photocatalysts with TiO_2 nanotubes and silver@silver halide systems have been reported [10–18], less work has been carried out with TiO_2 nanotubes with the anatase phase, which showed better photocatalytic activity than the rutile phase. The combination of anatase TiO_2 nanotubes and a plasmonic photocatalyst should be advantageous because of their strong adsorption capacity, SPR absorption in the visible region, and efficient charge separation, that can thereby further enhance their

photocatalytic activity under visible light irradiation.

In this work, anatase TiO_2 nanotubes were prepared by hydrothermal synthesis and a hydrogen peroxide treatment. Then, Ag@AgCl nanoparticles were loaded onto the nanotubes by precipitation and photoreduction reactions with AgNO_3 and HCl to give a visible light photocatalyst of Ag@AgCl/ TiO_2 nanotubes. The structure of this photocatalyst was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), etc, and its photocatalytic performance was studied for the decolorization of methylene blue (MB) under visible light irradiation.

1 Experimental

1.1 Preparation of catalyst

TiO_2 powder (2 g, Degussa P25) and 70 ml of 10 mol/L NaOH solution (96%, analytical pure, 4th Shanghai Reagent Factory) were mixed together. After stirring for 10 min at room temperature, the mixture was heated in a Teflon-lined autoclave at 150 °C for 24 h. After the hydrothermal treatment, the filtered powder was well washed with distilled water and 0.1 mol/L HCl aqueous solution (36%, analytical pure, The Fourth Shanghai Reagent Factory), and subsequently separated from the washing solution. Then, the powder was mixed with 0.1 mol/L HCl solution and stirred for 10 h at room temperature. The filtered powder was washed alternatively with distilled water and 0.1 mol/L HCl solution several times until the pH value of the rinsing solution was 6.8. After that, the synthesized TiO_2 nanotubes were treated by 20% hydrogen peroxide (30%, analytical pure, Shanghai Taopu Chemicals) aqueous solution under refluxing conditions at 40 °C for 4 h. Then, the filtrated powder was washed with distilled water and dried in an oven at 90 °C for 14 h. The dried powder was calcined at 400 °C with a dwell time of 2 h and a heating/cooling rate of 1 °C/min. Finally, anatase TiO_2 nanotubes (TiO_2 -NTs) were obtained.

The synthesized TiO_2 -NTs (1 g) was dispersed in deionized water, ultrasonicated for 10 min at room temperature, and then mixed with 10 ml of 0.1 mol/L AgNO_3 solution (99.9%, analytic pure, Shanghai Shangsi Fine Chemicals). After stirring for 20 min at room temperature, 10 ml 0.1 mol/L HCl aqueous solution was added. The mixture was ultrasonicated for 10 min and stirred for 20 min at room temperature. The filtered powder was washed with deionized water and dried at 100 °C for 10 h. Finally, the dried powder was irradiated with a 500 W halogen tungsten lamp (Guangdong Foshan Lighting) for 20 min to reduce part of the Ag^+ ions in the AgCl particles to Ag^0 species. Finally, the plasmonic photocatalyst of anatase TiO_2 nanotubes modified with Ag@AgCl nanoparticles, named Ag@AgCl/ TiO_2 -NTs, was obtained.

1.2 Characterization of catalyst

The phase identification of all the samples was conducted with a Rigaku D/Max-RB X-ray diffractometer equipped with Ni-filtered Cu K_{α} radiation. The data were collected for scattering angles (2θ) from 20° to 80°. Raman spectra were collected on a HORIBA Jobin Yvon LabRam-1B Raman spectrometer. The excitation source was a helium-neon laser with a wavelength of 632.8 nm and an excitation power of 6 mW. UV-Vis diffuse reflectance spectra were recorded with a Shimadzu UV-2450 solid state UV-Vis spectrophotometer equipped with an integrating sphere diffuse reflectance accessory. Fourier transform infrared (FT-IR) spectra were recorded using a KBr pellet on a Nicolet Nexus 870 spectrophotometer with a range of 400–4 000 cm^{-1} . The morphologies of the TiO₂ nanotubes were observed using a JEOL JEM-100C II transmission electron microscope.

1.3 Evaluation of photocatalytic activity

The decolorization of MB was used to evaluate the photocatalytic activity of the photocatalysts. Photocatalytic experiments were carried out with a homemade reactor that was surrounded with a cooling system to keep the photocatalytic system at room temperature. A 500 W halogen tungsten lamp with a KenKo L41 UV-cutoff filter ($\lambda > 410$ nm) was used as a visible light source. The lamp was placed above the reactor at about 25 cm and the filter was mounted on the top 2–3 cm away from the reactor. The photocatalyst (0.1 g) was suspended in 100 ml of 10 mg/L dye solution by magnetic stirring. The photocatalytic system was kept in the dark for 60 min to establish adsorption-desorption equilibrium before the visible light radiation. The dye concentration was determined based on its characteristic optical absorbance using a UV-1700 UV-Vis spectrophotometer. 5 ml of the dye solution was taken out at regular intervals and the upper clear liquid after centrifugation was used to monitor the change in concentration.

2 Results and discussion

2.1 Formation of TiO₂-NTs

Figure 1 shows TEM images of the pure TiO₂-NTs. The open-ended hollow TiO₂ nanotubes have a uniform shape with length varying from several tens to hundreds of nanometers. They have an average outer diameter of 10 nm and inner diameter of 7 nm. This hollow structure has a large surface area for the adsorption of small organic and inorganic nanoparticles inside the nanotubes, and provides a good platform for the loading of Ag@AgCl nanoparticles. In addition, this structure facilitates the transport of photogenerated

carriers during a photocatalytic reaction.

As shown in Fig. 2, the XRD pattern feature of the TiO₂-NTs was nearly identical to that of anatase TiO₂ (JCPDS 21-1272). The strongest diffraction peak was at a scattering angle (2θ) of 25.3°, corresponding to (101) lattice plane of the anatase phase. This sharp peak indicated good crystallinity of the TiO₂ nanotubes. Other than the anatase phase, no sodium titanate or any other crystalline phase was seen in the XRD pattern of the TiO₂ nanotubes, indicating that pure anatase TiO₂ nanotubes were synthesized in our work.

It was reported in the previous studies [1,19–22] that, under the hydrothermal conditions, the formation of TiO₂ nanotubes includes two processes: exfoliating and rolling. The structure of anatase TiO₂ consists of zigzag chains of distorted TiO₆ octahedra that are linked to each other through shared edges. During the NaOH treatment, the longer axial Ti–O–Ti bonds in the distorted TiO₆ octahedra are attacked by OH[−] ions and break, while the shorter Ti–O–Ti bonds in the horizontal plane do not [23]. As a result, layered titanate flakes are formed and peeled off from TiO₂ crystalline particles. Finally, lamellar sheets are formed with these layered titanates linked with each other with Na⁺ or OH[−] intercalated between them. They are the intermediates in the formation of TiO₂ nanotubes [19,20]. The pretreatment process is crucial for determining the final chemical composition and crystalline structure of the TiO₂ nanotubes.

The rolling of the lamellar sheets into nanotubes occurs during the pickling treatment. The main composition of the lamellar sheets is hydrated sodium titanate. During the pickling, the Na⁺ ions are replaced by H⁺ ions in the layered sodium titanates, forming protonic titanates. Meanwhile, the H⁺ exchange results in further exfoliation of the lamellar sheets to layered titanates, and subsequently these layered titanates roll up into nanotubes. In the acidic washing process, both the HCl concentration and final wash pH value have significant influence on the formation of nanotubes. The concentration of hydrochloric acid should not be too high, as too high a concentration easily makes the nanotubes deform, and even evolve into granules [19]. If the pH value is higher than 12, the layered titanates do not roll up into nanotubes. Nanotubes become the dominant species when the wash pH value is less than 7 [20]. At pH = 1.6, the nanotubes are mainly composed of anatase, but with defects on the walls. At pH = 6.3, the walls are intact, but the composition is mainly hydrated sodium titanates or acid titanates, such as H₂Ti₃O₇ [21,22], A₂Ti₂O₄(OH)₂ [23,24], A₂Ti₄O₉·H₂O [25] (where A is Na and/or H). Based on the formation mechanism of TiO₂ nanotubes, the Ti–O–Ti bonds in the TiO₂ nanoparticles get broken under the effect of concentrated NaOH aqueous solution to form Ti–O–Na and Ti–OH bonds [1]. After the HCl wash, Na⁺ ions are exchanged and even-

tually hydrated sodium titanates or protonic titanates are formed. The sodium species can be eliminated by washing with dilute acid solution and water when the wash pH value is very low. However, the structure of the nanotubes will be destroyed in this case. When the wash pH value is high, the structure of the nanotubes is intact, but the sodium species cannot be eliminated, even by washing many times. In order to get anatase TiO_2 nanotubes with intact walls, the pH value of 6.8 was chosen as the final wash pH value in our current work, and a hydrogen peroxide treatment was employed to thoroughly remove residual sodium species [26]. At the same time, the hydrogen peroxide treatment can improve the crystallinity. During the NaOH treatment, some oxygen vacancies were found in the prepared TiO_2 nanotubes, which was probably due to the presence of sodium. The peroxo species introduced in the H_2O_2 treatment resulted in the removal of oxygen vacancies and activation of lattice oxygen [26].

Finally, the above treated sample was calcined at $400\text{ }^\circ\text{C}$ for 2 h to get highly crystalline anatase TiO_2 nanotubes. The tubular structure was preserved when the calcination temperature was chosen as $400\text{ }^\circ\text{C}$. However, if the calcination temperature was further increased, phase transition from anatase to the rutile phase occurred and the structure of the nanotubes would be destroyed [19]. Our results demonstrated that the final TiO_2 nanotubes have a regular structure and high crystallinity with the anatase phase after acidic wash at pH = 6.8, a further H_2O_2 treatment, and final calcination at $400\text{ }^\circ\text{C}$.

2.2 Morphology and structure of Ag@AgCl/TiO_2 -NTs

In order to deposit Ag@AgCl nanoparticles onto TiO_2 -NTs, TiO_2 -NTs and a AgNO_3 aqueous solution were first mixed and ultrasonicated at room temperature to get Ag^+ ions fully adsorbed by the TiO_2 nanotubes. Then, the filtered powder was treated with HCl aqueous solution to form AgCl nanoparticles. Finally, the AgCl-modified TiO_2 nanotubes was irradiated under a halogen tungsten lamp to get part of the Ag^+ ions reduced to Ag^0 , to get Ag@AgCl/TiO_2 -NTs.

Figure 3 shows TEM images of the Ag@AgCl/TiO_2 -NTs. There was no obvious change in their shape as compared to that of the TiO_2 -NTs displayed in Fig. 1, indicating that the loading with Ag@AgCl nanoparticles had little effect on the structure of the nanotubes. It can be clearly seen in Fig. 3 that some oval or circular Ag@AgCl nanoparticles were deposited in the internal and external surfaces of the TiO_2 -NTs. The size of the Ag@AgCl nanoparticles was about 5 nm, and small Ag nanoparticles were dispersed on the surface of the AgCl particles [9].

As shown in the XRD spectrum of the Ag@AgCl/TiO_2 -NTs in Fig. 2, the crystalline anatase phase in the TiO_2

nanotubes was preserved after the loading of Ag@AgCl nanoparticles. However, the diffraction peaks became more intense, indicating increased crystallinity. This change may be due to a series of processes during the loading of Ag@AgCl nanoparticles. Besides the anatase phase, other diffraction peaks present were indexed to a cubic phase of AgCl (JCPDS 31-1238; highest peak at $2\theta = 32.3^\circ$). However, the diffraction peaks of Ag nanoparticles were not observed, suggesting that the amount or size of the Ag nanoparticles was small in the Ag@AgCl/TiO_2 -NTs.

It is shown in Fig. 4 that the scattering peaks in the Raman spectrum of the Ag@AgCl/TiO_2 -NTs were shifted and became wider as compared with those of anatase TiO_2 . The changes in intensity and position of the scattering peaks were probably associated with distortions and defects in the TiO_2 crystal lattice induced by the loading of Ag@AgCl nanoparticles. Anatase TiO_2 belongs to D_{4h} point group, and has five characteristic Raman active modes at 147, 198, 398, 515, and 637 cm^{-1} . These characteristic Raman peaks were also found in the Raman spectrum of Ag@AgCl/TiO_2 -NTs, but with changes in their intensity. Besides, there were additional peaks at 245, 830, and $1\ 120\text{ cm}^{-1}$, which was associated with the surface enhancement effect induced by the SPR of Ag nanoparticles. This observation proved the existence of Ag nanoparticles in the Ag@AgCl/TiO_2 -NTs.

The UV-Vis diffuse reflectance spectrum of the Ag@AgCl/TiO_2 -NTs is shown in Fig. 5. As compared with P25 TiO_2 and self-made TiO_2 -NTs, Ag@AgCl/TiO_2 -NTs exhibited both an absorption edge near 400 nm corresponding to the interband transition of TiO_2 and a broad absorption band between 550–750 nm in the visible region. The latter band was attributed to the SPR absorption of Ag nanoparticles [27], which further proved that the Ag@AgCl/TiO_2 -NTs contained silver nanoparticles as result of the photochemical decomposition or photocatalytic reduction of AgCl. As anatase TiO_2 has a direct band gap of 3.2 eV and AgCl has an indirect band gap of 3.25 eV, both absorb in the ultraviolet region. After the loading with Ag@AgCl nanoparticles, the absorption by the nanotubes was extended to the visible region due to the SPR effect. This should improve the photocatalytic activity of TiO_2 nanotubes to be active under visible light irradiation.

2.3 Photocatalytic activity of Ag@AgCl/TiO_2 -NTs under visible light irradiation

The photocatalytic decolorization of MB dye was used to evaluate the photocatalytic performance of the Ag@AgCl/TiO_2 -NTs under visible light irradiation. Degussa P25 TiO_2 and pure TiO_2 -NTs were chosen as the reference photocatalysts for comparison. The photocatalytic results are shown in Fig. 6, where c_0 is the initial dye concentration and

c is the dye concentration at time t . Both pure TiO₂-NTs and Ag@AgCl/TiO₂-NTs exhibited strong adsorptive capacities for MB in the dark, while P25 did not. In the dark after 60 min, the dye concentration decreased to 75% of its initial value by the adsorption on pure nanotubes, and to 35% of its initial value by adsorption on the Ag@AgCl/TiO₂-NTs, suggesting that the adsorptive capacity of the nanotubes increased after the loading of Ag@AgCl nanoparticles. Under visible light irradiation, the dye molecules were not degraded in the presence of P25. Although the dye concentration decreased in the presence of pure TiO₂-NTs, the dye molecules were mostly adsorbed by the TiO₂ nanotubes as the color of the photocatalyst changed from white to blue. However, this does not rule out the possibility that part of the dye molecules were degraded by the sensitization effect. As the dye molecules can absorb visible light, their photoexcited electrons can be injected into the conduction band of TiO₂. The dye molecules that lost electrons will decompose if no electron donors are available. The dye solution became nearly colorless in the presence of Ag@AgCl/TiO₂-NTs after 30 min of visible light illumination, and meantime, the photocatalyst recovered its original color of light gray. This result indicated that both the adsorption capacity and photocatalytic ability of the Ag@AgCl/TiO₂-NTs were responsible for the fast decolorization of the dye molecules.

After the loading of Ag@AgCl nanoparticles on the TiO₂ nanotubes, the optical response of the photocatalyst was extended to the visible region due to the SPR effect. After irradiation by visible light, the conduction electrons in the Ag nanoparticles oscillate coherently with the oscillating electric field to give rise to photo-excited electron-hole pairs in the Ag nanoparticles. The photoexcited electrons are then injected into the conduction band of the TiO₂ nanotubes [28], which results in an effective electron-hole separation. The electrons in the conduction band can be transported to the surface of the nanotubes to reduce O₂ molecules adsorbed on the surface to superoxide anion radicals ($\cdot\text{O}_2^-$), and further reduction of these to other reactive oxygen species like $\cdot\text{OOH}$, H₂O₂, and even $\cdot\text{OH}$ radicals. At the same time, the electron-deficient metal would oxidize some reduced species adsorbed on its surface and return to its original metallic state. The direct oxidation of MB molecules is possible, but it is more probable that the hole in Ag nanoparticles would react with H₂O or hydroxide ions to create hydroxyl radicals

($\cdot\text{OH}$), or is transported to the surface of AgCl particles to oxidize Cl⁻ ions to Cl⁰ atoms [12]. Since all these oxygen species are extremely reactive, the dye molecules get degraded and decolorized. As chlorine atoms are also reactive radicals, they can also oxidize the dye molecules and be restored to chloride ions, to regenerate the photocatalyst.

In order to meet the requirements for practical applications, a good photocatalyst should have high photocatalytic activity and good stability. In order to test the photocatalytic stability of the Ag@AgCl/TiO₂-NTs, the photocatalyst was recycled five times under repeated photocatalytic experiments of bleaching dye molecules. It is shown in Fig. 7 that the photocatalytic activity of the photocatalyst was little changed after five runs of photocatalytic reactions, although the adsorption capacity decreased somewhat. This observation indicated that the Ag@AgCl/TiO₂-NTs photocatalyst was stable under repeated photocatalytic runs.

3 Conclusions

Anatase TiO₂ nanotubes were synthesized using hydrothermal synthesis and a hydrogen peroxide treatment. Ag@AgCl nanoparticles were deposited on the internal and external surfaces of the nanotubes by a precipitation reaction and photoreduction reaction to get a plasmonic photocatalyst of Ag@AgCl/TiO₂-NTs. The Ag@AgCl/TiO₂-NTs have a large adsorption capacity and good photocatalytic decolorization activity for MB. Under visible light irradiation, MB molecules were completely bleached and the photocatalyst was restored to its original state after 60 min under our experimental conditions. The photocatalytic activity under visible light irradiation was much improved by the large adsorption capacity of the nanotubes and the SPR effect of the metal nanoparticles, as well as a synergistic effect between the two. Since the SPR effect of noble metal nanoparticles strongly depends on their species, size, and shape, the optical response of the TiO₂ nanotubes can be easily extended to the visible and even the mid-infrared region by different kinds of metal nanoparticles deposited on the TiO₂ nanotubes, thereby enhancing their absorption of sunlight and enhancing their photocatalytic activity.

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