学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Development of high-performance photocatalysts by using graphene and AgCl and/or AgBr nanoparticles as the constitutive elements for the decomposition of chemical pollutants

（グラフェンと塩化銀または臭化銀ナノ粒子を素材として用いた環境浄化用高性能光触媒の開発）

Novel Ag@AgX@Graphene (X = Cl, Br) photocatalysts with high-performance decomposition of chemical pollutants in water were developed by using graphene and AgCl and/or AgBr nanoparticles as the constitutive elements. Graphene, a two-dimensional sheet structure patterned with monolayer carbon atoms, has been the subject of intense study due to its unique morphologies and attractive properties. Graphene is the thinnest sheet-shaped nanomaterial with an ultralarge surface area and superior mechanical and electronic properties, which facilitate the assembly of Ag@AgX@Graphene photocatalysts adapted for wide applications in environmental remediation. Large-scale production of high-quality graphene has been the key to achieving the goal of industrialization. The solution-based chemical oxidation of graphite has long been used for the mass production of graphene oxide (GO), a solution-based precursor of graphene. However, a reduction step is required to convert the GO into graphene. Chemical reduction has been commonly used and this is achieved with hydrazine, sodium borohydride, sodium hydrosulfite and L-ascorbic acid as the typical reductants. As the attractive precursor of graphene, the intrinsic hydroxyl, epoxy, carbonyl and carboxylic functional groups of GO sheets could act as active anchoring sites for the heterogeneous nucleation of metal ions and subsequently grown to nanosized photocatalyst particles via the seeding growth mechanism. In particular, its unique nanostructure and tunable surface properties allow it to be a competitive host substrate for the controlled growth and formation of desired photocatalysts.

The dissertation consists of five chapters. In chapter 1, a brief introduction to the thinnest material ever created with abundant excellent properties was described. In chapter 2, mass production of GO

heavily decorated with oxygen-containing functional groups were introduced by using expanded graphite as the starting material. H_2SO_4 as the main intercalating agent separates the layered structure of expanded graphite with the aid of ultrasonication. A rapid, cost-effective and safer approach to the facile production of graphene that employs thiourea dioxide (TDO) as the green reductant was described. GO was converted into high quality graphene within 30 min with TDO as the reductant under moderate reaction conditions. The C/O ratio of the TDO reduced graphene was ~ 5.9 with the yield of graphene from GO > 99%. This is better than the reduction efficiency under the identical experimental conditions by using L-ascorbic acid as the reductant which required a reaction time of about 48 h. In chapter 3, in order to stabilize the graphene sheets in a single-layered and/or few-layered manner, poly(diallyldimethylammonium chloride) (PDDA), a positively charged polyelectrolyte, was used as the stabilizer to stabilize graphene sheets in the AgCl/Graphene composites. New insights into the unique photocatalytic properties of the PDDA-stabilized AgCl/graphene hybrid nanoparticles were obtained through analysis of the resultant samples by using X-ray photoelectron spectroscopy together with other suitable analytical methods. In chapter 4, novel cubic Ag@AgX@Graphene photocatalysts are facilely manipulated by means of a GO sheet-assisted assembly protocol, where GO act as an amphiphilic template for hetero-growth of AgX nanoparticles. A morphology transformation of AgX nanoparticles from sphere to cube-like shape was accomplished by involving GO. With further UV irradiation, the reduction of GO to graphene and the generation of Ag nanocrystals on AgX occur simultaneously. The as-prepared Ag@AgX@Graphene nanocomposites were employed as stable plasmonic photocatalysts to decompose acridine orange as a typical dye pollutant under sunlight. When graphene was employed in the photocatalysts, the decomposition efficiency was enhanced by ~50%. Compared with the bare quasi-spherical Ag@AgX, such graphene-interfaced Ag@AgX display distinctly higher adsorptive capacity, smaller crystal size and reinforced electron–hole pair separation owing to the interfacial contact between Ag@AgX and graphene components, resulting in an enhanced photocatalytic decomposition performance. This study provides new avenues for the assembly of morphology-controlled plasmonic photocatalysts that utilize sunlight as an energy source. In chapter 5, the overall achievements obtained in the study were summarized and the prospects of graphene –based photocatalysts in the practical applications of environmental remediation were described.

In conclusion, as the functioning element, graphene oxide, shows a key role in the creation of sunlight-driven Ag@AgX@Graphene photocatalysts. Two kinds of novel Ag@AgX@Graphene photocatalysts display enhanced plasmonic photocatalytic activity toward the chemical pollutants. These new findings reported in this dissertation provide new insights into the environmental remediation.