Title:	DESIGN OF HYBRID PLASMONIC NANOSTRUCTURES FOR ENHANCED PHOTOCATALYTIC ACTIVITY
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Abstract: The utilization of gold and silver plasmonic nanostructures has recently emerged as a booming field of research due to their fascinating optical properties attributable to a unique phenomenon known as localized surface plasmon resonance (LSPR). LSPR is defined as the confinement of a surface plasmon in a nanoparticle of size comparable to or smaller than the wavelength of light used to excite the plasmon. After being resonantly excited by the light, the LSP produces a strong electric field that is localized near the metal surfaces. During both the excitation and decay processes of LSP, the electron-hole pairs, the strong electric field, and the heat generated can serve as potential excitation sources for the molecules present in proximity to the metal nanoparticles. LSPR can be tuned by altering the shape and size of plasmonic nanostructures. As a result, the optical properties of these materials can be tailored to accomplish the requirements of a particular application. Tuning plasmon resonance can be achieved with remarkable precision by manipulating the shape of metal nanoparticles. By changing the size of nanoparticle, surface plasmon resonances in spheres can be tuned over a narrow wavelength range (a few tens of nm), but shape anisotropy adds an additional level of flexibility for tuning these wavelengths over a wide range. Due to their one-of-a-kind optical properties, plasmonic nanoparticles have the potential to be utilized in a wide range of areas, including biosensing, SERS, photocatalysis, photothermal therapy, and many others. When two or more distinct types of plasmonic metal nanostructures are combined, they have the potential to produce extraordinary plasmonic capabilities. The integration of two or three different components within the same nanostructure not just adds up the properties of the individual components but also imparts novel properties upon the hybrid nanostructure as a result of the synergistic effect. Enhanced reactivity, product selectivity, and optical sensitivity are all benefits that come from utilizing hybrid plasmonic core-shell type integrated nanostructures. These capabilities make them an attractive candidate for several applications. DNA origami has emerged as a reliable technique for the assembly of a wide variety of nanostructures, allowing for precise control over the position of nanoparticles. Compared to top-down lithographic methods, such assembly methods are simple and cost-effective. This means that nanostructures 1Abstract templated on DNA origami can be used for a wide range of purposes, from sensing to optical applications. In line with the background information provided above, the first part of the thesis consists of an interfacial designing procedure for the fabrication of a class of bimetallic hybrid nanomaterials as a profoundly active photocatalyst for the conversion of para- aminothiophenol (PATP) into 4,4'-dimercaptoazobenzene (DMAB). To accomplish this goal, core-shell nanostars composed of gold (core) and silver (shell) (Au/Ag NSs) have been synthesized which served as both a surface-enhanced Raman scattering substrate and a plasmon driven catalyst when subjected to laser excitation at a wavelength of 532 nm. The surface-enhanced Raman scattering (SERS) efficiency of PATP is shown to be exceptionally high by Au/Ag NSs with sharp tips. Using the SERS technique, we were able to determine that PATP undergoes a rapid transformation into its dimerized product DMAB within a few seconds as a result of a surface photochemical reaction occurring in the Au–Ag heterojunction of core-shell nanostars. Au/Ag NSs with multiple sharp tips exhibit intense LSPR, and these tips also create exceptionally strong electric fields, which enable the generation of hot electrons that are responsible for the rapid conversion reaction. These interfacial bimetallic nanostars could have potential applications in SERS, biosensing, and photoinduced surface catalysis when they were designed and constructed adequately. In the following chapter of the thesis, core-shell nanostructures of silicon oxide@noble metal were synthesized and utilized for enhanced SERS and photothermal effect. These core-shell nanostructures have piqued a lot of researchers' interest due to their unique properties, as well as their low toxicity and remarkable biocompatibility. Plasmonic nanoparticles are being used as a SERS based detection of pollutants and photothermal (PT) agents in cancer therapy. This is possible due to the unique property of localized surface plasmon resonance (LSPR), which plasmonic nanoparticles possess. The synthesis of multifunctional silica core - Au nanostars shell (SiO2@Au NSs) nanostructures using surfactant free aqueous phase method is presented and demonstrated in this chapter. Using Rhodamine B (RhB) dye as a Raman probe, the SERS performance of the as-synthesized anisotropic core-shell NSs was evaluated, and the results showed a 2Abstract significant enhancement factor of 1.37 × 106. In addition, SiO2@Au NSs were utilized in the process of PT killing of breast cancer cells, and these nanoparticles demonstrated a concentration-dependent increase in the intensity of the photothermal effect. The incredible photothermal conversion efficiency of up to 72% has been displayed by the SiO2@Au NSs, which sets a new benchmark. As an outcome, our synthesized NIR active SiO2@Au nanostructures are of pivotal significance to have their dual applications in SERS enhancement and PT effect. Apart from the metal core-metal shell nanostructures and dielectric core-metal shell nanostructures described earlier, the next chapter of the thesis presents nanostructures of the metal core-semiconductor shell type. Due to their enhanced plasmonic fields of plasmonic metal nanoparticles, metal-semiconductor core-shell nanostructures have recently been investigated for their potential to facilitate efficient photocatalytic water splitting. Therefore, we have developed a new type of nanostructure of Au nanostar core ZnO nanopetals composite (Au@ZnO). The as-synthesized Au@ZnO nanocomposites (NCs) were characterized utilizing different spectroscopic and microscopic techniques. Powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) studies clearly confirm the formation of highly crystalline Au/ZnO composite structure. The transmission electron microscopy (TEM) images clearly show that Au is present in the core and ZnO in the surrounding. The fabricated Au@ZnO NCs were used as a catalyst for photocatalytic water splitting. Au@ZnO NCs exhibited hydrogen and oxygen evolution up to 518.36 and 177.86 μmol g−1, respectively. The observed enhanced photocatalytic activity of Au-ZnO NCs is associated with the efficient suppression of the recombination of photogenerated charge carriers in ZnO due to the strong electron scavenging activity of Au nanoparticles combined with the improved sun light utilization capability of Au@ZnO NCs coming from the plasmonic response of Au core surrounded with ZnO nanostructures. In addition to the applications of plasmonic metal nanoparticles based on LSPR that were mentioned earlier, the last part of the thesis covers another unusual application of noble metal nanostructures which is to act as electrocatalyst for Oxygen Evolution Reaction (OER). The kinetically slow anodic OER is a cause for concern when considering the 3Abstract feasibility of large-scale hydrogen synthesis from electrochemical water splitting as a means of producing clean energy that can replace fossil fuels. Hence, the development of highly active electrocatalysts is of immense interest for improving the efficiency of gas evolution. In this chapter, we present the design of a monomer structure of Ag-coated Au nanostars (core-shell-type Au@Ag nanostars) assembled on rectangular DNA origami and investigate their electrocatalytic activities through OER. Our designed DNA origami- templated bimetallic nanostar catalyst showed excellent OER activity and high stability without using any external binder and exhibited a current density of 10 mA cm−2 at a low overpotential of 266 mV, which was smaller than those of ss-DNA-functionalized Au@Ag nanostars and DNA origami templated pure Au nanostars. Our results reveal that DNA origami-assembled core−shell Au@Ag nanostars show better electrocatalytic performance as compared to pure-core Au nanostars immobilized on DNA origami, owing to the presence of a highly conductive Ag layer. Such controlled assembly of bimetallic nanostructures on a DNA origami template can provide additional electrochemical surface area and a higher density of active sites resulting in enhanced electrocatalysis. The research presented in this thesis is part of an ongoing effort to create new plasmonic hybrid nanomaterials with promising photocatalytic, energy, and medical applications. A discussion of potential follow-up studies is included in the investigation as well.

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