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Photo-induced reduction of CO_2 to CO with hydrogen over plasmonic Ag-NPs/TiO_2 NWs core/shell hetero-junction under UV and visible light

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ABSTRACT

Ag-NPs-promoted TiO_2 nanowires (TiO_2 NWs) core/shell hetero-junction with plasmonic properties for selective CO production in photo-induced CO_2-hydrogen system has been investigated. Ag-NPs were photo-deposited over the TiO_2 NWs and characterized by XRD, TEM, N_2-adsorption-desorption, XPS, UV–vis and PL spectroscopy. Ag-NPs in metal-state were successfully coated on the TiO_2 NWs surface, producing core-shell hetero-junction. Ag-NPs coated over TiO_2 NWs exhibited strong absorption of visible light due to localized surface plasmon resonance (LSPR) excitation, trapped electrons and hindered charges recombination rate. The synergistic effect of Ag-NPs coated over TiO_2 NWs for CO_2 conversion was evaluated in a gas-phase system under UV and visible light irradiation. The plasmonic Ag-NPs/TiO_2 NWs demonstrated excellent photoactivity in the reduction of CO_2 into CO, CH_4 and CH_3OH under visible light irradiation. The results show that 3 wt.% Ag-NPs-loaded TiO_2 NWs was found to be the most active, giving the highest CO evolution of 983 μmole-g-catal.$^{-1}$ h^{-1} at selectivity 98%. This amount of CO produced was 23 times more than the TiO_2 NWs and 109 times larger than the yield of CO produced over the pure TiO_2. More importantly, the quantum yield was substantially enhanced for CO evolution. The LSPR excitation and synergic effect of Ag-NPs which can effectively accelerate the charge separation was proposed to be responsible for the enhancement of photocatalytic activity. The photo-stability of Ag-NPs/TiO_2 NWs evidenced in cyclic runs for selective CO production under visible light, yet photoactivity declined over the irradiation time under UV-light. The reaction mechanism to describe the reaction pathways is also presented.

1. Introduction

The energy shortages and increase of CO_2 concentration in the atmosphere due to growing consumption of fossil fuels have invigorated great concerns in the last few decades. Many approaches have been developed for CO_2 utilization, yet artificial photosynthesis for photocatalytic reduction of CO_2 provides alternative prospective for the storage of solar energy into useful chemicals and fuels [1]. Therefore, conversion of CO_2 into useful carbon sources such as CO, CH_4, CH_3OH HCHO and HCOOH using solar energy is one of the ideal way to address both the global warming and energy shortage problems [2–4]. However, the yield and selectivity reported are below the acceptable level of commercialization. Efficient photocatalytic CO_2 reduction requires semiconductor materials that could meet certain stringent criteria [5].

In photocatalytic conversion of CO_2, TiO_2 is one of the well-studied photocatalysts and has been received increasing attentions due to its advantages such as inexpensive, available in excess, nontoxic, photo-stable and strong oxidative potential [6,7]. However, TiO_2 as a photocatalyst has some disadvantages such as the large band gap energy (~3.20 eV for anatase, ~3.0 eV for rutile) which only allows the absorption of ultraviolet (UV) irradiation [8]. Additionally, it has high recombination rate of photo-generated (e^-/h^+) charges and uncontrolled photoreduction selectivity. To improve its photocatalytic performance, many strategies have been developed such as metals-loading, semiconductors coupling and co-catalysts modifications [9–11].

Adding metals to semiconductor to establish metal/semiconductor hetero-junction could enhanced photocatalytic activity under visible light irradiations [12–15]. Recently, metals such as gold (Au), silver (Ag) and copper (Cu) are considered as promising materials for CO_2 reduction applications for the reason that CO

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weakly binds on their surfaces [16,17]. Mainly, Cu produced a mixture of hydrocarbons such as CH_4, CH_3OH, C_2H_4 and HCOOH, however, Au and Ag demonstrated highly selective for CO_2 to CO conversion. Many efforts have been performed in the use of these metals to enhance photocatalytic performance of TiO_2. For example, Au-loaded TiO_2 nanoparticles were investigated for selective photocatalytic CO_2 conversion to CO [18], production of CH_4 in the photocatalytic CO_2 reduction reaction using Cu/TiO_2 photocatalyst [19], the use of Pt-Cu_2O-TiO_2 co-catalysts for the reduction of CO_2 to CH_4 [20], Cu-loaded In_2O_3/TiO_2 photocatalysts for the conversion of CO_2 to CH_4 and CH_3OH [21], modification of MWCNT/TiO_2 by Ag for enhanced photocatalytic CO_2 reduction with H_2O to CH_4 and C_2H_4 [22] and incorporation of Cu into TiO_2 for photocatalytic CO_2 reduction to CH_4 [23].

To date, nanostructured titanium dioxide (TiO_2) is of great interest owing to larger surface area with excellent optical and photocatalytic properties, thus offer direct pathways for effectively collecting photons and/or electrons [24–26]. Many types of nanostructured TiO_2 have been investigated such as nanowires, nanosheets, nanorods and nanotubes. However, in the development of visible light responsive TiO_2 nanostructures, narrowing the band gap energy of TiO_2 will establish a benchmark for the sunlight-driven functional materials. Recently, Cu-NPs deposited onto TiO_2 nano-flowers has been reported for enhanced photocatalytic CO_2 reduction with H_2O to CH_3OH [27]. Similarly, photocatalytic CO_2 reduction to CO over Cu-loaded TiO_2 nanotubes arrays has been investigated [28]. Besides, $ZnFe_2O_4$/TiO_2 nanobelts have been inspected for CO_2 reduction to fuels [29].

On the other hand, plasmonic photocatalysis has been reported as a capable system to improve efficiencies based on their localized surface plasmon resonance (LSPR) effect. More importantly, both Au and Ag have strong plasmonic effects which capable to improve semiconductor efficiency based on their LSPR effect [30,31]. Loading plasmonic Au-NPs over TiO_2 nanowires has been demonstrated as efficient surface modifiers to enhance TiO_2 photoactivity for photocatalytic CO_2 reduction via SPR effect of Au under visible light. Likewise, Au@TiO_2 yolk shell hollow spheres for plasmon-induced photocatalytic reduction of CO_2 to solar fuels has been investigated [32]. Nevertheless, compared to Au, Ag is much cheaper, which can be used appropriately to enhance TiO_2 photoactivity via LSPR effects photocatalytic CO_2 system. In this case, strongly visible light responsive plasmonic AgX (X = Cl, Br) nanoparticles for photocatalytic reduction of CO_2 to CH_3OH has been reported [33]. Liu et al. [34] reported plasmonic Ag/TiO_2 NRs for CO_2 photoreduction using H_2O reductant under visible light. The enhanced photoactivity of TiO_2 NRs for CO_2 reduction to CH_3OH was evidently due to Ag-NPs SPR effect. Besides, insertion of metallic Ag-NPs onto semiconductor structure reduces the recombination rate of photo-generated charges (e^-/h^+) and improves photocatalytic activity [35]. Moreover, size and shape of noble metals show different physical and chemical properties. When metals NPs of different sizes are loaded over the semiconductor surface, they perform different photocatalytic properties [36]. Recently, size dependent effect of Au-loaded in g-C_3N_4/BiOBr/Au system for photocatalytic CO_2 reduction has been reported [37]. It was noticed that different sizes of Au-NPs have synergistic effects to enhance photoactivity under light irradiations. Therefore, it is vital to explore synergistic effects of Ag-NPs co-coated over TiO_2 NWs for selective photocatalytic CO_2 reduction because of its low cost and higher productivity.

In addition of efficient photocatalysts, the reductant choice is of great importance, as it effects the overall CO_2 reduction process efficiency and products selectivity. In order to achieve the reduction of CO_2, H_2O is usually fed as a reducing agent. Thermodynamically, photocatalytic conversion of CO_2 with H_2O over heterogeneous photocatalysis is not a favorable process because reduction of H^+, released from H_2O, usually competes with CO_2 reduction. This is because H_2O reduction potential to genertae H_2 is lower (0 eV) than the CO_2 standard reduction potential (-1.9 eV). Under such conditions, a reduction competition can be developed between CO_2/H_2O, thus photoreactions would be more favourable for conversion of H_2O to H_2 instead of CO_2 reduction. Recently, we investigated H_2 as a potentially viable reductant for CO_2 reduction to CO and CH_4 over different type of photocatalysts

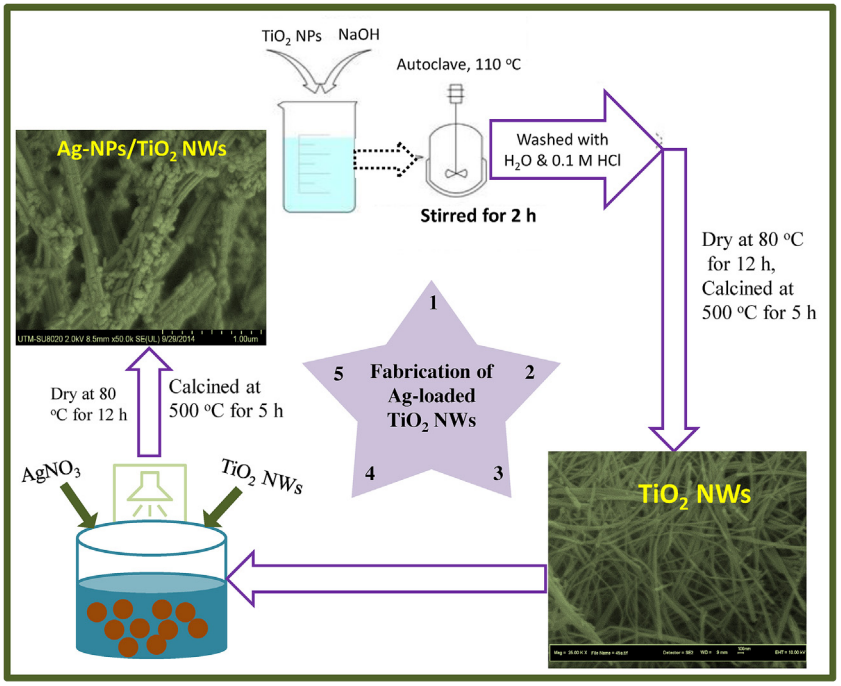

Fig. 1. Schematic presentation for the fabrications of Ag-deposited TiO_2 NWs core-shell hetero-junctions.