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Asymmetric Decoration of Crystalline Graphene with Pt&TiO_2 Nanocrystals as High-Efficient Photocatalyst

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The potential of TiO_2 as a photocatalyst is well recognized and has been studied extensively over many decades. In addition to being photoactive, it is chemically stable and non-toxic, making it very attractive for industrial-scale water treatment [1]. However, there is one major obstacle hampering the advancement of TiO_2, which is the fast recombination rate of photo-generated electron-hole pairs. Recently, surface modification of TiO_2 with Pt nanocrystals (NCs) has been considered as an effective method to increase the photoactivity of TiO_2 [2]. Also, the electronic structure of Pt NCs on graphene [3] has been computed and been found that in the ground state Pt NCs would pull electrons away from graphene. Therefore, hybridizing graphene with both TiO_2 and Pt takes advantage of Pt's high work function (5.1-5.9 eV) by using it as an electron trap center. This composite creates an energetically favorable pathway for photoexcited electrons to transfer from the TiO_2 to the Pt NCs via graphene substrate, encouraging charge separation and thus increasing quantum efficiency.

Highly crystalline graphene supported Pt&TiO_2 composites have been prepared via a two-step deposition process: (1) Hybridize graphene with Pt NCs via a first-step of solvothermal reaction; (2) Afterwards, deposit TiO_2 NCs on the surface of graphene via a second-step procedure where Pt NCs have already been formed by step one. Fig. 1a is a low magnification TEM image revealing that Pt NCs with a high density are formed on the graphene surface. HRTEM image confirmed that the attached Pt NCs are well crystallized, showing face-centered cubic (FCC) Pt with a (111) plane spacing of approximately 0.23 nm (Fig. 1b). The corresponding selected area electron diffraction pattern (SAED) shows the diffraction rings that are coincident with FCC Pt (111), (200), (220), and (311) from inner to outer respectively, as shown in Fig. 1c. Single diffraction spots due to the six equivalent hexagonal graphene planes can also be observed. After the second-step deposition, TiO_2 NCs were deposited on the Pt/graphene surface, as shown in Fig. 1d-1e. TiO_2 and Pt NCs have two different particle sizes, in which the large one is TiO_2 with 10-15 nm while the small one is Pt with only 2-4 nm. Fig. 1f depicts the magnified image of boxed area of Fig. 1e, clearly confirming that both TiO_2 and Pt NCs are well crystallized. Specifically a lattice spacing of 0.35 nm of TiO_2 NCs corresponds to the (101) plane of anatase TiO_2. In addition, based on our observations, most of the TiO_2 NCs have clearly defined shapes including cubes and tetrahedrons.

Fig. 2a shows the powder X-ray diffraction (XRD) pattern of the graphene supported Pt and TiO_2 sample, which clearly shows the peaks for all three compounds, confirming the existence of graphene, Pt and TiO_2. The reflection peaks at $2\theta = 26.4°$ and 54.5° could be assigned to the (002) and (004) planes of hexagonal graphite (JCPDS card no. 41-1487). Another three peaks $2\theta = 39.7°$, 46.2°, 67.5° can be assigned to the (111) (200) and (220) planes of FCC Pt (JCPDS card no. 652868). The remaining seven peaks at $2\theta = 25.2°$, 37.8°, 47.9°, 53.9°, 54.9°, 62.3°, and 69.1° can be indexed to the "▼", (101), (004), (200), (105), (211), (204) and (116) planes of pure anatase TiO_2 (labelled as JCPDS card no. 21-1272). Fig. 2b shows a typical Raman spectrum of graphene supported Pt&TiO_2 sample. EDX spectrum (Fig. 2c) confirms that the sample contains Ti, O, Pt, and C (where Cu signal is from TEM grid).

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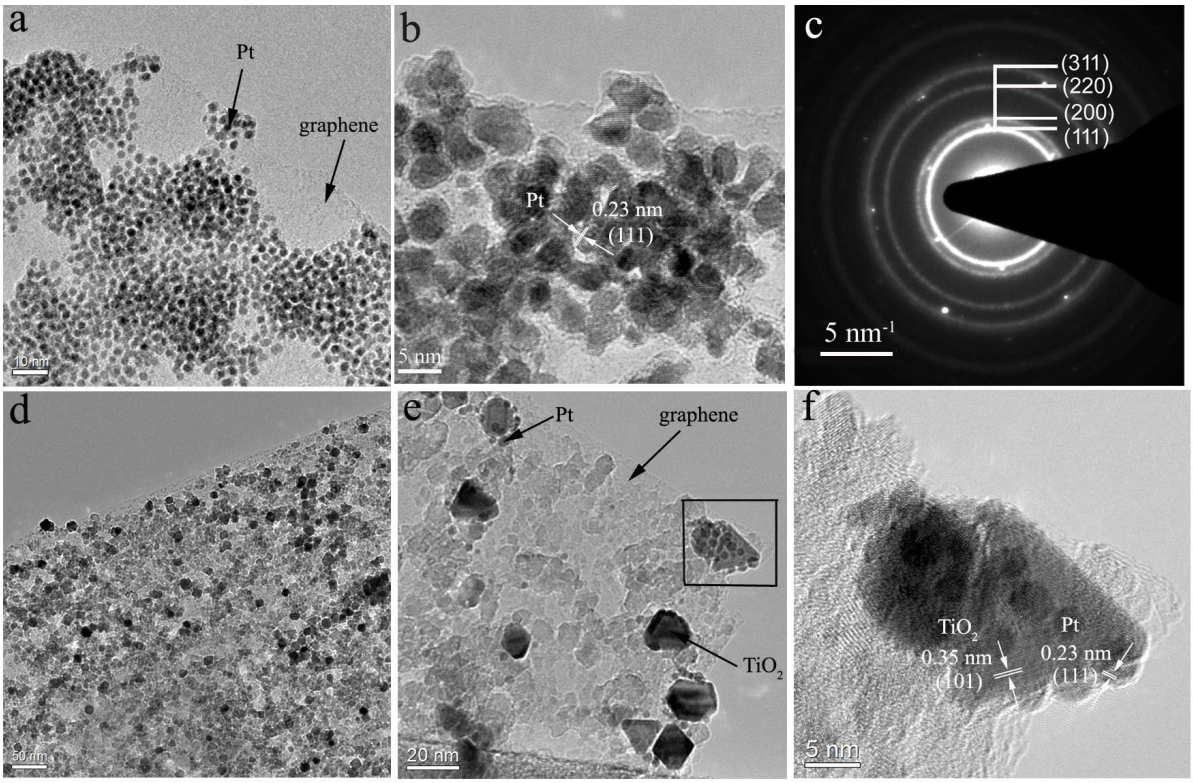

Fig. 1 Two-step deposition to produce graphene supported Pt&TiO_2 composites. (a) TEM image of graphene supported Pt via the first step; (b) HRTEM image of deposited Pt NCs; (c) corresponding SAED pattern; (d-e) TEM images of graphene supported Pt&TiO_2 via the second step; (f) magnified image of boxed area of (e).

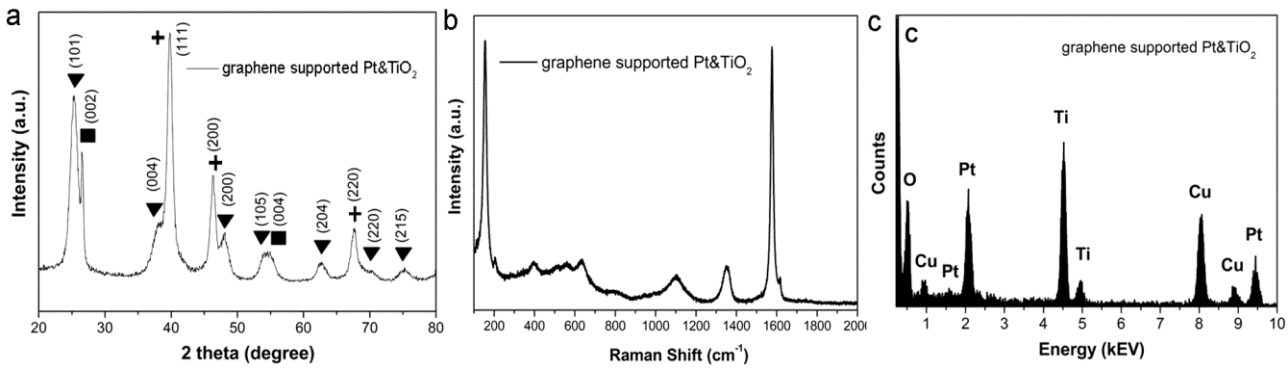

Fig. 2 Comprehensive analysis of graphene supported Pt&TiO_2 composite prepared via two-step deposition. (a) XRD pattern of the sample; (b) Raman spectrum; (c) typical EDX spectrum.

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